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DEVELOPMENT OF BUOY MOUNTED HYDROCARBON VAPOR SENSORS FOR USE IN LOCAL AREA POLLUTION SURVEILLANCE SYSTEMS

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16. Abstract

The feasibility of using hydrocarbon vapor sensors on buoys along watercourses for the signalling of oil spills on a real time basis has been investigated. As a result of laboratory testing of five types of vapor sensors, it was concluded that the Taguchi Semiconductor Gas Sensor (TGS) was promising for this application. Two other vapor sensors selected by the U.S. Coast Guard for further investigation were the Esso oil on water piezoelectric sensor and the Environmental Measurement Systems' Adhistor sensor (WSM-350). These three sensors were evaluated in the laboratory, in the rooftop environment, and in a lake environment. The TGS sensor and the Adhistor sensor were also investigated in the marine environment. Recommendations for further testing and evaluation of the TGS sensor on buoys are made.

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I. INTRODUCTION

Each year a large number of discharges of oil and other hazardous polluting substances from transportation-related processes occur in the navigable waters of the United States. In order to minimize environmental damages from such discharges and to effect prompt containment and cleanup efforts, these pollution events must be detected and reported as quickly as possible. The present study was undertaken to determine if it were feasible to utilize buoy mounted hydrocarbon vapor sensors as a part of a local area pollution surveillance system.

In considering possible requirements for such a pollution sensor system, it was first necessary to consider where and how the sensors would be used and to select those materials which should be detected. Further, consideration of power requirements, cost and period of unattended operation were also matters of prime importance.

At the start of the contract, it was agreed that various forms of oil on water were the pollutants which must be detected quickly. Although the exact kind or quantity of oil spilled was not specified, it was clear that detection of large spills (e.g., 100 barrels or more) was of less importance than smaller spills since the origin of large spills was usually not difficult to trace. Also, large spills were usually reported shortly after they occurred. On the other hand, spills ranging from a gallon to a barrel were to be the primary target of the new oil-on-water detection system. Location of the sensors on buoys along watercourses and subsequent telemetry of the alarm signal triggered by oil vapors was expected to provide information to a shore-based monitoring station on a real time basis.

The use of vapor sensors for the detection of oil spills was proposed on the premise that fresh oil films give off hydrocarbon vapors and the concentration of these vapors often occur in the 1-50 ppm range. A vapor sensor which could produce an electrical response to these quantities of oil would be suitable for use on a buoy and would require less maintenance than a sensor immersed in the water. Also, these sensors were expected to be inexpensive and to operate for 6 months or more on the power supplied by the buoy battery (possibly 12 V with the capacity of 500-1,000 amp-hr). In the early studies on this program, a number of vapor sensors were investigated to determine their suitability for the intended application. The sensor types which were investigated were as follows: (1) experimental thin film resistor sensors (which were to change resistance when oil vapors were present), (2) hot wire

and catalytic hot wire sensors of commercial manufacture, (3) simple PNP transistors, (4) a radioactive ionization sensor, and (5) the Taguchi semiconductor gas sensor, TGS. Later, the Esso piezoelectric oil-on-water sensor and the Environmental Measurement Company's Adhistor or Wesmar WSM-350 were added to the list of sensors investigated.

At first these sensors were evaluated in the laboratory. Those which had promise for use in the marine environment and had the appropriate sensitivity for the pollutant vapors were evaluated for stability and response to pollutant vapors under a variety of environmental conditions including: high and low temperatures, high and low humidities, rapidly changing humidities, wind and salt spray.

The present report provides a brief description of the earlier experiments and rather detailed results on the performance of the TGS sensor system under conditions which can be expected to occur when the sensors are mounted on buoys along watercourses.

II. EXPERIMENTAL INVESTIGATIONS

A total of seven different types of pollutant vapor sensors have been investigated in the laboratory and/or in the field or marine environments. Some of the sensors were eliminated early in the test-and-evaluation phase of this investigation and others have been investigated thoroughly under environmental conditions which could be expected to occur on watercourses. In the interest of brevity, much of the experimental data has been omitted. In many cases, however, typical data are presented to substantiate the conclusions which have been reached.

A. Preliminary Vapor Sensor Evaluation

1. Thin film vapor sensors: Previous studies in these laboratories showed that when thin films of lipophilic materials and/or electrolytes were applied to printed circuit boards, these boards changed their resistances when exposed to a wide variety of gaseous materials. Approximately 40 of the film sensors were fabricated in our laboratories by etching a printed circuit board in such a manner that the resulting

pattern resembled two interlocking combs. The resulting boards (approximately 1/2 in. x 2-1/2 in.) were then coated with thin films of pure materials and mixtures as shown in the following list:

1. Aluminum chlorohydroxide
2. Manganese dioxide + $ZnCl_2$ + NH_4CL + Carbowax 1500 (Union Carbide)
3. Sodium chloride + Carbowax 1500
4. Activated Charcoal + Carbowax 1500
5. Emplex (sodium stearoyl polylactilate, C. J. Patterson, Co.)
6. Aluminum chlorohydroxide + Atlox 1045A (polyoxyethylene sorbitol oleate, laurate HLB, Atlas)
7. Manganese dioxide + Atlox 1045A + NH_4Cl + $ZnCl_2$
8. NaCl + Atlox 1045A
9. Activated Charcoal + Atlox 1045A
10. Emplex + Atlox 1045A
11. Activated Charcoal + NaCl + Atlox 1045A
12. Drene Shampoo (Proctor and Gamble)
13. Hyamine 1622 (p-octylphenoxyethoxyethyl dimethyl benzyl ammonium chloride, Rohm and Haas Co.)
14. Hyamine 1622 + orange shellac

Preliminary experiments on the effect of the pollutant vapors, including hydrocarbons, on the resistance of these thin film sensors were carried out at room temperature and the results were not reproducible. Although changes in resistance were observed on exposure to vapors, humidity effects were excessive and recoveries following exposures were variable. Studies with two of the film sensor boards operated at 65-75°C show that the effect of humidity was reduced and the reproducibility of the responses was greatly improved at the elevated temperature.

Further investigation showed that responses were obtained only at high vapor concentrations; therefore, these sensors were judged to be unsatisfactory for hydrocarbon vapor detection. Preliminary tests of these thin film sensors with coating 12 showed some promise as ammonia vapor sensors.

2. PNP transistor as hydrocarbon vapor sensor: Limited studies have been made with a germanium PNP transistor to determine if it could be used to sense hydrocarbon and other vapors. The transistor selected for this study was a GE top hat No. 2N107. The metal cover was removed with a file so that vapors could reach the active semiconductor element. When the base of this transistor and one other terminal were connected to a multitester, there was a change in resistance on exposure to Skellysolve B. After various experiments with this transistor at room temperature, at 80°C, in the presence of humidity and in the absence of humidity, it was concluded that the transistor was sensitive to water vapor and that dry Skellysolve B seemed to displace the water to cause large changes in meter readings. However, the transistor could not distinguish between water vapor and water vapor plus Skellysolve B at either room temperature or at 80°C. Use of PNP transistors as vapor sensors was eliminated.

3. Hot wire sensors for hydrocarbons: The Mine Safety Appliances Company has developed a portable detection unit for the detection of gas leaks which is called the Explosimeter®. This unit responds to all combustible gases since they burn on the surface of the hot wire sensor resulting in a change of both temperature and resistance of the hot wire. Electrically the hot wire or filament is a part of a Wheatstone bridge circuit and significant electrical signals are produced from very low levels of methane gas. The portable unit is powered by 6 D-cell flashlight batteries which are reported to provide operation of the unit for about 8 hr. Studies were made in which hydrocarbon vapor from gallon jugs possessing 1 part by weight of pollutant per 500 parts of water were aspirated into the MSA Explosimeter. Aspirations were made for either 30 sec or until readings in excess of 50 units were obtained (frequently only a second or two). Operation of the detector so that readings exceed 100 units is likely to cause the filament to fail and require replacement--hence the shorter exposure to vapors giving large responses.

Figure 1 provides the responses obtained with the hot wire sensor when it is exposed to the hydrocarbon test vapors. Responses above the dotted line (i.e., above the 50-unit mark) were the result of

Vapors

1. H_2O	11. Acrylonitrile	21. Acrolein
2. JP-4	12. Ammonia	22. Isoprene
3. #1 Fuel Oil	13. Acetone	23. Xylene
4. #2 Fuel Oil	14. Chlorine	24. Toluene
5. #5 Fuel Oil	15. Styrene	25. Vinyl Acetate
6. #6 Fuel Oil	16. Benzene	26. HCl
7. Sweet Crude B	17. Natural Gas	27. Phenol
8. Sour Crude C	18. Epichlorohydrin	28. Skelly B
9. 4-Nitrophenol	19. Methanol	
10. Nitric Acid	20. Carbon Tetrachloride	( ) Denotes the sample was not tested

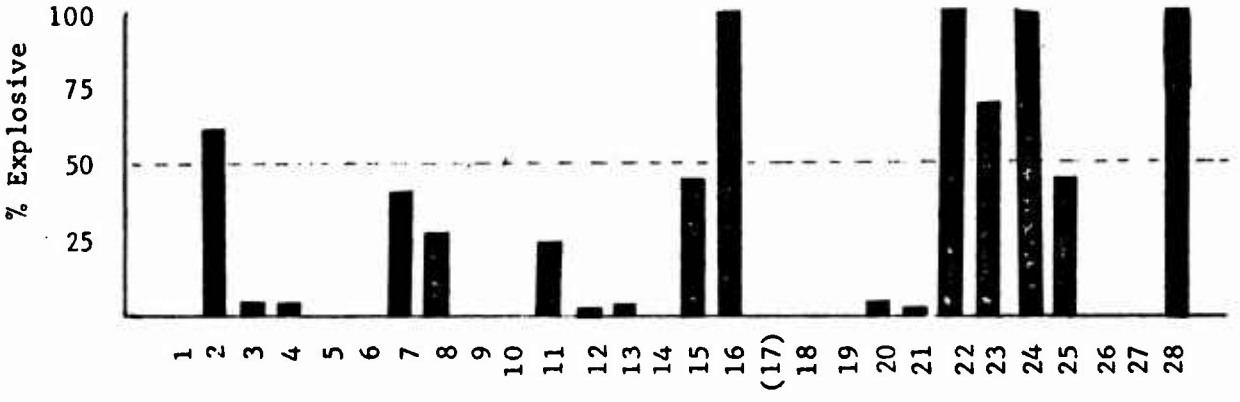


Figure 1. Response of the hot wire sensor to pollutant vapors over water. (Values in upper half of graph may exceed values shown.)

short exposures and maximum responses may actually exceed the responses shown. We were particularly pleased to note that this unit gave no response to air at 100% RH. This means that amplification of the signal might easily increase the sensitivity of the unit without encountering too much noise from humidity changes.

During field tests with the MSA Explosimeter, there was insufficient sensitivity to permit detection of the test vapors after they were diluted by the 4-8 mph breezes. Some experiments were conducted to see if the sensitivity of the MSA Explosimeter could be increased without unduly increasing the background noise. In Figure 2, the response of the MSA system (operated with an external amplifier, an AC power supply, and a 1 liter/min Brailsford blower) to Nos. 1, 2, and 5 fuel oils is shown. As may be observed, the pen displacement on the recorder (3 mV full scale) was markedly enhanced through the use of the amplifier (20 x gain) but the amplified baseline may present problems. It is probable that the baseline could be flattened electronically if a decision to use this type of sensor in the buoys should be made. One problem with this amplified sensor is that its response to natural gas and certain other volatile hydrocarbons is so much larger than the response to the fuel oils that it might be difficult to keep responses to methane and to fuel oil on the same scale. Since the amplified MSA Explosimeter provides enhanced responses to the less volatile hydrocarbons and no signals to most of the nonorganic types of vapors, the possibility of using this sensing system together with other sensors to obtain information relative to the type of hazardous spill which may have occurred is a possibility. It was concluded that the hot wire sensor was less suited for hydrocarbon monitoring than was the Taguchi sensor described below.

4. Suitability of an ionization sensor for pollution detection: An ionization detector was investigated to determine its possible response to a variety of pollutant vapors. The preliminary studies reported here were conducted with a Model No. FT-200 Ionization Smoke Detector manufactured by the Fire Alert Company of Denver, Colorado. This detection unit used a radioactive probe (radium 226) to detect smoke and other particulate matter in the air. A proportional response to pollutants could be obtained with this ionization sensor. A Tetronix Oscilloscope (with memory) was used with it to allow visualization of the sensor output. This combination permitted direct observation of voltage at the sensor both before and after exposure of the sensor to pollutant test vapors. The following response measurements were made to see what kinds of responses could be obtained. In these tests, concentrated pollutant vapors were generated close to the ionization sensor.

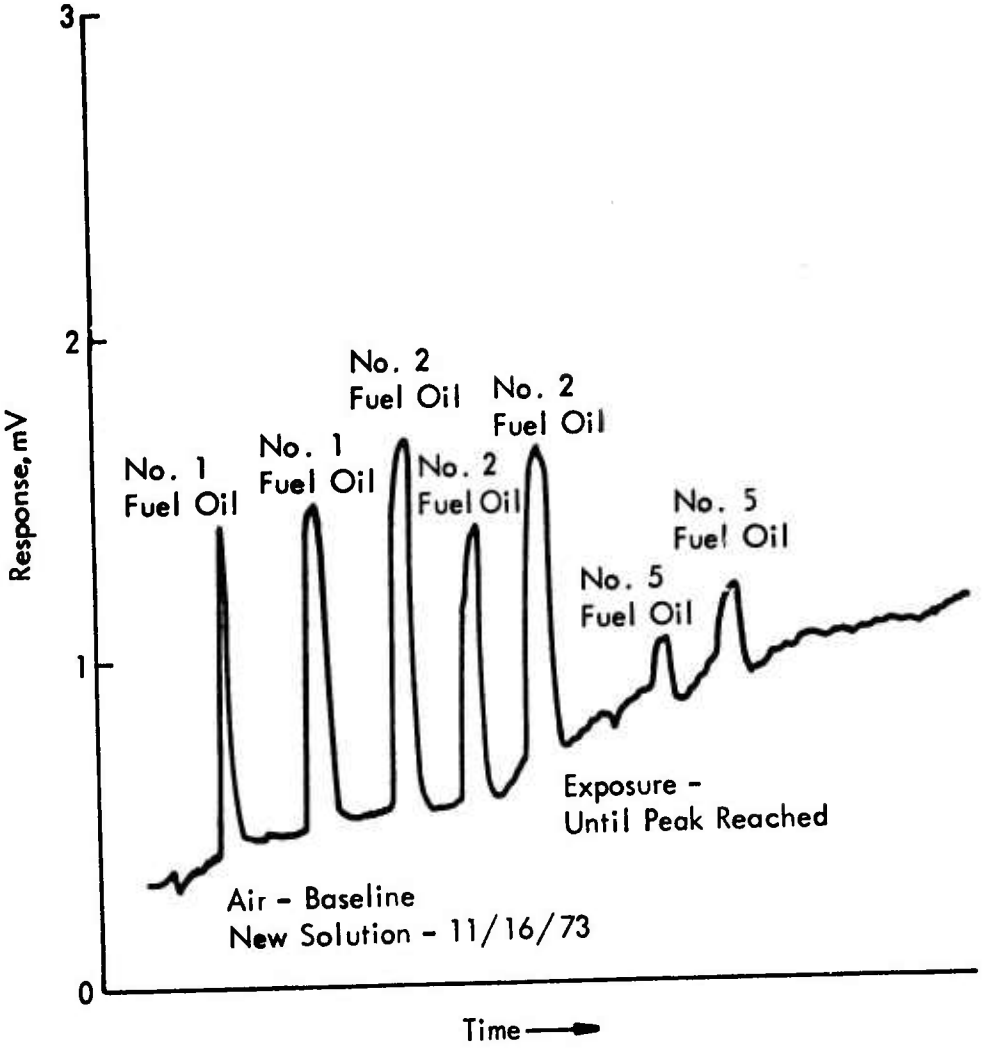


Figure 2. MSA explosimeter (with external amplifier, AC power supply and Brailsford blower) response to fuel oil vapors showing baseline drift and signal-to-noise ratio.

Response	Little or No Response
Burning string	Skellysolve B (hexane fraction)
NH_4Cl smoke	Ethyl alcohol
Water vapor over dry ice	Dioxane
Bunsen burner (flame close to ionization detector)	Carbon dioxide
Fuming hydrochloric acid	Ammonium hydroxide
	Water vapor
	Chloroform
	Chlorobenzene
	Tetranitromethane
	2,4-Dinitrotoluene

Since the basic detection principle of the electron capture detectors (used extensively in gas chromatographs) is similar to that used in the present ionization detector, it was expected that large responses would be obtained with the organochlorine and nitro compounds. From these preliminary experiments it was concluded that, since the sensitivity to smoke and particulate materials was so high and the response to potential pollutants was so low, further experimentation for intended usage was not justified.

B. Taguchi Semiconductor Gas Sensors

Descriptive information about some of the Taguchi Gas Sensors (TGS), as supplied by Figaro Engineering, Inc., is reproduced in Appendix II of this report. So far as we are aware, Figaro Engineering, Inc. was the first company to make available commercial sensors of this type. However, thin film semiconductor sensors were described in the literature previously.(1,2) As shown in these papers, thin films of many metal oxides, including specifically ZnO and SnO_2, show the phenomena of changing their electrical resistance on the sorption and desorption of gaseous materials such as hydrogen, hydrocarbons, alcohols, aldehydes, ethers, amines, etc. Much of the present investigation is concerned with a determination of the suitability of the TGS sensors for use on buoys for the rapid detection of oil spills on water. The following paragraphs provide additional information on the TGS sensors.

1. Description of the TGS sensors: A diagram of the TGS sensor is provided in Appendix II. Also shown is a simple wiring diagram for sensors of this type. It will be noted that underneath the stainless steel screen is a small ceramic bead which incorporates two noble metal

heaters and the semiconductor chip; only one wire coil is used to heat the chip, the other coil is used as a connector to the other side of the semiconductor chip. Heat is needed to desorb the vapors on the semiconductor chip; the manufacturer suggests that 2 min should be adequate for this desorbtion. After the chip has been heat cleaned, it is possible to cool the sensor to room temperature and still obtain one response to a hydrocarbon vapor; a second response is not possible until the sensor is heat cleaned again. Although the operating temperature of the sensors is reported by the manufacturer to be in the 200-400°C range, we think that there is no need to operate the sensors above 200°C since good responses and recoveries are obtained when the sensors are operated in the 100-200°C range. Although the TGS literature hints at the oxidation of gaseous materials at the sensor surface, we conclude that such oxidation is not usually observed and is not a necessary part of the detection process.

A property of the TGS sensors which is important to their possible use for oil detection is that they give a continuous signal so long as the test vapor is present and then recover quickly after the vapor is gone. This mode of response is far superior to some types of sensors which respond only to a rate-of-change of vapor concentration and are blind to the level of material being sensed.

2. Operating principle: The operation of transistors and semiconductor gas sensors is very similar. In a transistor, the conductivity of the semiconductor material is controlled by the application of a control voltage; in the semiconductor vapor sensors, the adsorption of a gas on the surface of the semiconductor causes a charge transfer phenomena which increases its conductivity. The amount of change in conductivity is related to the amount of energy causing the charge transfer from the semiconductor surface and differs for different materials. Also, the quantity of material adsorbed affects the conductivity change or the magnitude of response obtained.

3. TGS sensor response profile measurements: Before a sensor can be chosen for a particular application, it is important to know how it responds to substances commonly found in the proposed environment.

Various standard test methods were considered for contacting sensors with the pollutant vapors. Since the sensors were to be used in a marine-type environment where the humidity is usually very high, it was important that the tests be done in the presence of water vapor to eliminate the possibility that the sensors respond to water vapor instead

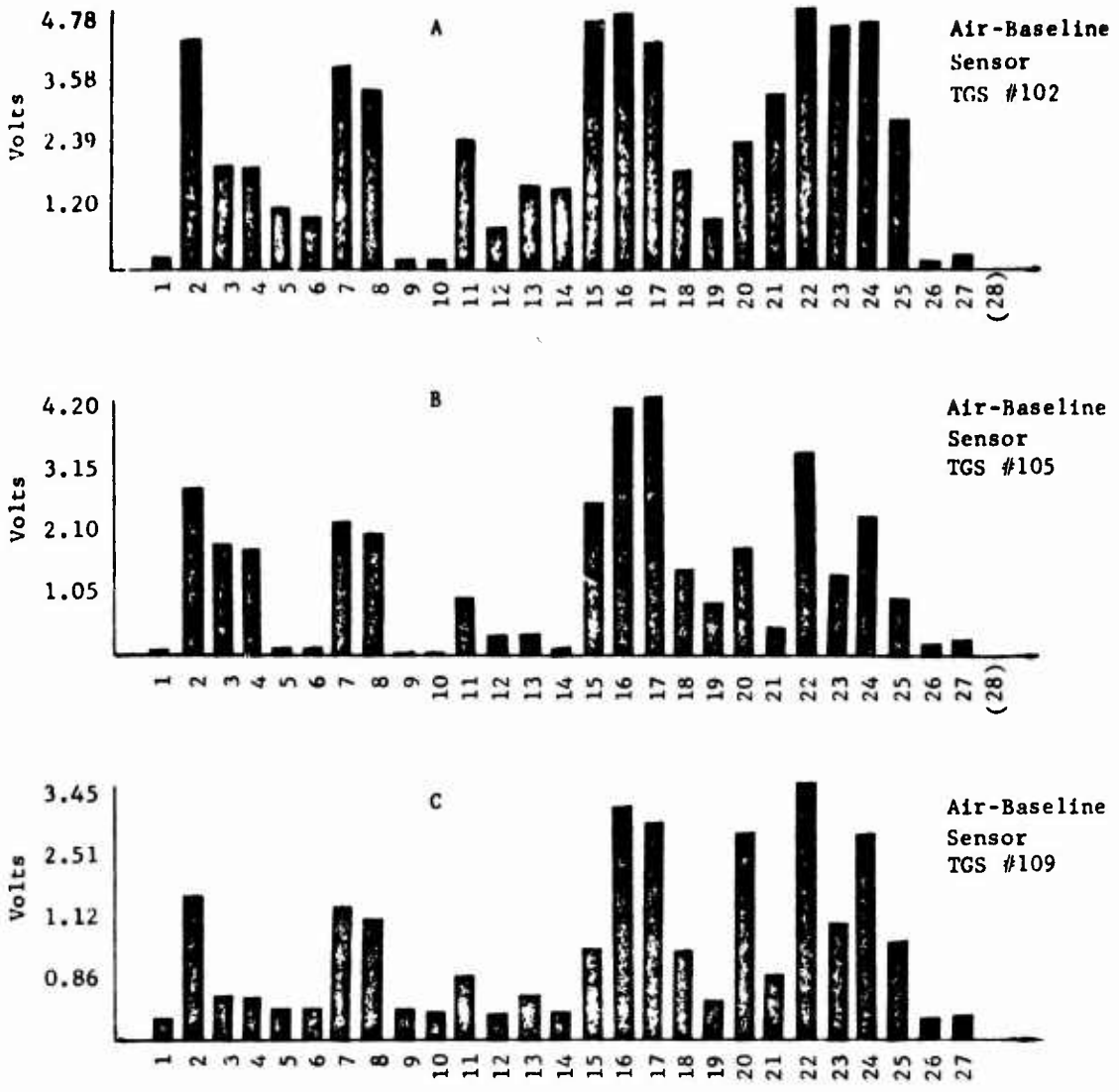
of to the pollutant vapors. The standard test procedure called for exposing the sensor first to water vapor in a closed container and then to the vapor above a mixture of water and the test pollutant. In this manner, the effect of the pollutant vapor alone on the sensor could be measured; also, since the vapors were in a closed system, it was possible to measure the reproducibility of response from a single sensor and also to compare responses from different sensors of the same or different types.

Figure 3 presents in bar-graph form the relative sensitivities of three different TGS sensor types to water vapor and 26 pollutant vapors which were chosen so as to present a profile of the types of responses which might be obtained with a wide variety of gaseous materials. Attention is called to the fact that different vertical scales are used in the charts; this was done to emphasize the relative responses of the different pollutants. It will be noted that isoprene gave the largest response for each of the three sensors and that we chose to make its bar the same length in the three graphs. The actual voltage response with each pollutant with each sensor is shown in the figure.

Figaro Engineering, Inc. has reported that TGS No. 102 is a smoke and CO detector, TGS No. 105 is a smoke and isobutane detector, TGS No. 109 is a general purpose detector with response to isobutane equal to that of the TGS No. 105. Based upon the data presented here, the TGS No. 102 sensor gave the largest responses to the different vapors from fuel oils and crude petroleum products. Therefore, it was investigated more extensively than the other TGS sensors.

4. Analysis of TGS semiconductor chip: An X-ray fluorescence analysis of the semiconductor portion of a TGS sensor was conducted to determine whether it was a stannic oxide sensor as the manufacturer's brochure hinted or whether it was a combination of oxides. The analysis shows that the TGS sensor is really made with pure stannic oxide on a support, and that no other element above atomic number 21 is present. This X-ray fluorescence analysis was conducted with a spectrophotometer using a LiF crystal and is limited to wavelengths less than about 3.5 Å.

Powder diffraction analysis showed that the tin was present as SnO_2; also identified in the sample was alpha Al_2O_3 in the ratio somewhere between 3:1 and 5:1. Significant quantities of other materials were not detected although silicon may be present. Carbon (either amorphous or graphitic) was definitely not present in significant amounts. The quantities of tin, aluminum, and silicon present could be determined



Vapors

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7. Sweet Crude B	17. Natural Gas	27. Phenol
8. Sour Crude C	18. Epichlorohydrin	
9. 4-Nitrophenol	19. Methanol	
10. Nitric Acid	20. Carbon Tetrachloride	

Figure 3. Comparison of three types of Taguchi gas sensors with pollutant vapors.

accurately by adsorption spectroscopy after dissolving the semiconductor material with HF in a bomb; however, it was not shown how the chip was made. Further analytical studies were not conducted. We suspected, however, that tin was deposited on the alundum support in high vacuum after which it was oxidized in a controlled atmosphere to give the film of stannic oxide. It has not yet been determined whether the use of different metal oxides could yield semiconductor chips with selectivity for different gaseous materials.

5. Six-month performance test of TGS sensors: The 30-week endurance test of five TGS gas sensors was completed during this contract and the results are presented in Table 1. Only the response of these sensors to isoprene vapors is reported since this is adequate to show that the sensors can perform for extended periods of time without losing sensitivity. Response of these same sensors to some 25 other vapors has been measured at each of the seven time periods indicatd in the table. These studies show that the response profile of the individual sensors is essentially unchanged during the 30-week period. As shown in the footnote to the table, the one sensor which failed probably had a defective heater at the start of the test which caused it to draw more current and to overheat. In the future, it would be advisable to check the heater currents on individual TGS sensors prior to their selection for use in environmental monitoring. Sensors should also be tested for their response to standard vapors before being used in environmental monitoring. From this endurance test, it is concluded that the TGS sensors are stable and can easily meet the requirement for functioning for 6 months without servicing or replacement.

6. Effect of salt spray on TGS performance: Since it is intended that the sensors be used in a marine environment where salt water is present, studies were made with a TGS sensor to determine the effect of salt spray on performance. In this test, a Type 1 TGS sensor was placed inside of a glass cylinder (1-1/4 in. diameter by 6 in. long) and turned on while salt spray was blown gently through the cylinder. The salt spray was generated from a 3% salt solution through the use of a nebulizer operated with compressed air. The aerosol particle size was estimated to be mainly in the 1-5 size range. As may be seen from Figure 4, there was no loss in the response of this TGS sensor to benzene vapors (i.e., over water) during the 400-min exposure to the salt test. The exterior of the sensor possessed a light frosting of salt at the end of the test. From these data, it is concluded that the TGS sensors can tolerate salt spray for extended periods provided that they are turned on during their exposure. It is presumed that most of the salt particles

TABLE 1. ENDURANCE TESTING OF TGS SENSORS

Coating (a)	Response to Isoprene Vapors, V						
	Weeks						
	0	3	6	11	17	24	30
Aluminum Monostearate	3.32	3.95	3.88	4.12	--(b)	--	--
Dimethyldi-chlorosilane	3.58	3.95	3.95	4.08	3.75	3.88	4.22
Potassium Ferrocyanide	3.55	3.90	4.00	3.95	3.80	3.85	4.18
Sodium Cyanide	3.35	3.80	4.00	3.30	3.93	4.40	4.22
None	3.85	4.02	4.18	4.40	4.10	4.12	4.45

(a) Four of these sensors had previously been dipped in solutions of substances shown to measure possible changes in selectivity.

(b) This sensor failed between the 11th and 17th week due to cracks which formed between the semiconductor material and the heater. It was observed that this sensor was much hotter than the others; a faulty heater probably explains its early failure.

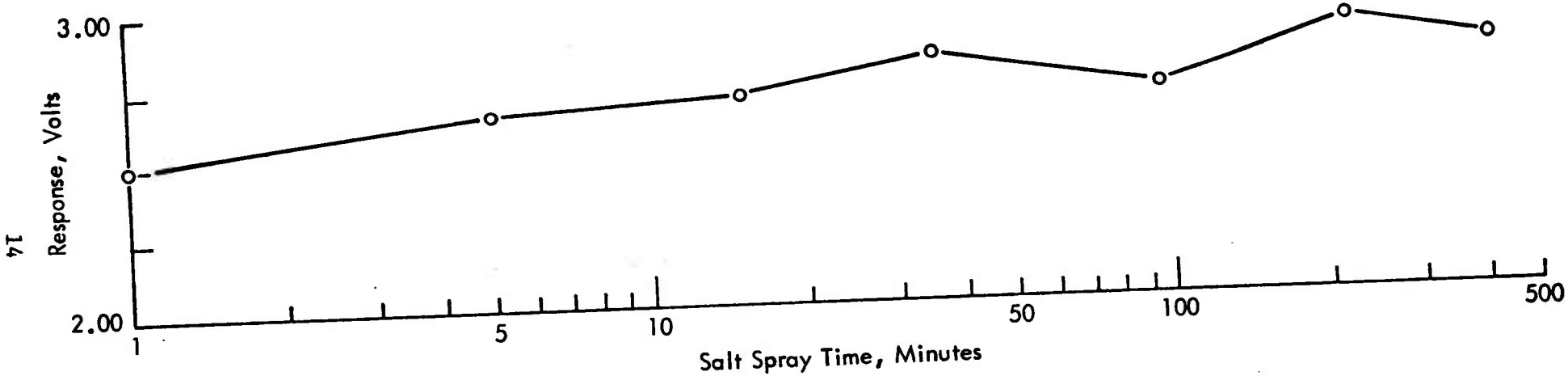


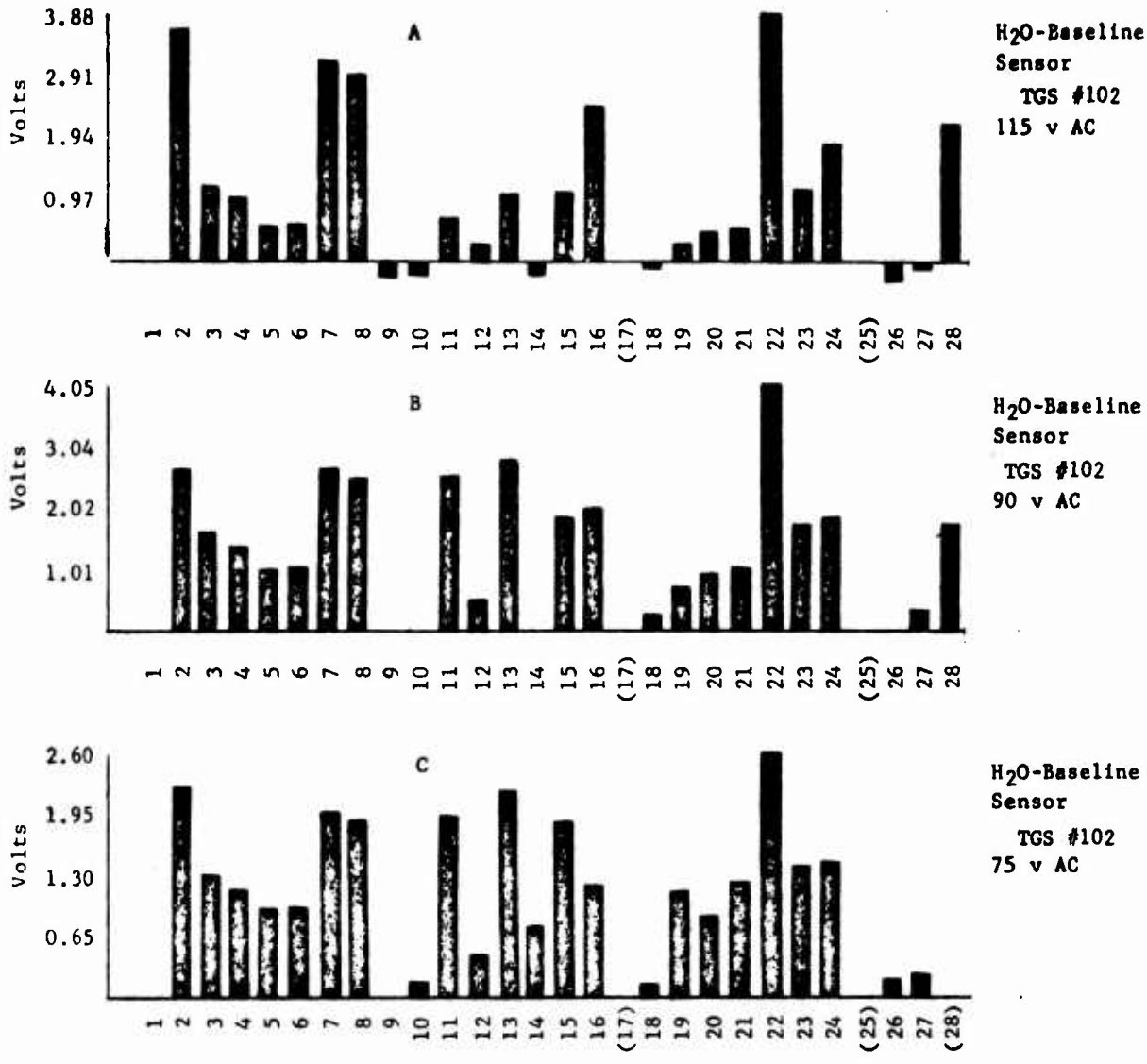
Figure 4. Effect of aerosolized 3% salt solution on response of TGS sensor to benzene vapors.

are deposited on the cool portions of the sensors rather than on the heated semiconductor surface; this conclusion is based upon the construction of the Thermopositor aerosol precipitator which uses heat to accelerate the precipitation of aerosol particles on nearby cold surfaces.

7. Effect of fluctuations in power supply on TGS sensitivity: It is obvious that fluctuation in voltage supplied to a buoy-mounted sensor may occur due to changes in the battery temperature or during the discharge of the battery. It was therefore important to determine how changes in the battery supply voltages might affect the baseline voltages and the sensitivity to the various pollutants.

For the present experiment, the TGS sensor type 102 was operated from line power using the circuitry illustrated in Figure 5. This sensor has a rated heater voltage of 1.0 V and a circuit voltage of 100 V; however, with the circuit chosen, the heater was 1.0 V and the circuit voltage was 115 V when the line voltage was 115 V. The performance of this TGS sensor was determined at three different line voltages, namely: 115, 90, and 75 V AC. The results of this experiment are shown in Figure 5. The TGS sensor heater voltages were 1.0 V, 0.78 V, and 0.65 V, respectively. It should be noted that in the bar graph, the responses have been normalized so that the height of the isoprene response is the same in each experiment even though the responses were 3.88 V, 4.05 V, and 2.60 V, respectively. Thus, the response to isoprene was significantly reduced at the lower voltage. When the TGS sensor was operated at 75 V, the major difference observed was the slow recovery from the pollutant after exposure; in the case of isoprene, the recovery time increased from 1 min at 115 V to 25 min at 75 V. At the lower voltage, more time was needed to establish the normal baseline voltage. In summary, the TGS sensors work best at their rated voltages, but they still respond well to hydrocarbon vapors and maintain stable baseline voltages even though the voltage to the sensor may fall as much as 20-30%.

8. Intermittent duty cycle to reduce power consumption: Since the pollution sensors are to be mounted on buoys using storage batteries for power, the feasibility of operating the sensors intermittently was considered as a means to conserve energy. In an experiment, the objective was to determine how long it would take a TGS sensor to reach its equilibrium reading after being turned off for 5, 10, or 15 min. The sensor was exposed to water vapor both during the on and off parts of the cycle. In each case, approximately 30 sec were required for the sensor to stabilize itself. With the sensor operating on a 5-min



Vapors

1.	H_2O	11.	Acrylonitrile	21.	Acrolein
2.	JP-4	12.	Ammonia	22.	Isoprene
3.	No. 1 Fuel Oil	13.	Acetone	23.	Xylene
4.	No. 2 Fuel Oil	14.	Chlorine	24.	Toluene
5.	No. 5 Fuel Oil	15.	Styrene	25.	Vinyl Acetate
6.	No. 6 Fuel Oil	16.	Benzene	26.	HCl
7.	Sweet Crude B	17.	Natural Gas	27.	Phenol
8.	Sour Crude C	18.	Epichlorohydrin	28.	Skelly B
9.	4-Nitrophenol	19.	Methanol		
10.	Nitric Acid	20.	Carbon Tetrachloride	( )	Denotes the sample was not tested

Figure 5. Effect of line voltage changes on performance of a TGS sensor.

cycle, it would be possible to keep the electricity turned off as much as 90% of the time. On the other hand, if power is available, it would be far more satisfactory to operate the sensors continuously.

9. Baseline stability out-of-doors: Previous studies with the TGS sensors have been particularly concerned with their response to a wide variety of pollutant vapors and their recoveries after exposure. Experiments were conducted for determining the stability of the TGS baseline voltages when the sensors were operated out-of-doors for extended periods of time. For these experiments, we used TGS sensors (one at a time) mounted in a 2-ft section of galvanized 3-in. flue pipe. The flue pipe with its TGS sensor was hung vertically outside of a second floor laboratory window on the south side of the building and the signal from the sensor was monitored continuously for several days in order to determine the effect of various environmental parameters such as wind, humidity, dust, ambient air pollutants, light, dark, temperature, etc. Figure 6 presents a 24-hr portion of this tracing which was selected because of the baseline variation observed when the gusty wind developed.

To read this chart, start in the lower left-hand corner and read up; the time of day is typed on the chart so that it is possible to compare daylight with dark hours. At midnight (24:00 hr) it may be noted that the baseline is stable and a little lower (perhaps 25-30 mV) than at 12 noon on a clear day. Between 7:00 and 10:30 a.m., a wind came up and it was gusty and humid; as a result of these wind gusts and resultant cooling, the baseline voltage fluctuated some but mostly to the left (i.e., lower voltages)--this is just the opposite direction of responses which are produced by hydrocarbon vapors. As a part of this experiment, the sensor was exposed to weak hydrocarbon vapors before and after the test to be sure that the sensor was operational; but this part of the curve was not included in this figure. Tracings for other 24-hr periods have been made and the baseline voltages have been very stable also.

10. Test of chimney-mounted TGS sensor: Testing of the TGS sensors was conducted at MRI's Deramus Field Station where it was possible to mount the TGS sensor in a 3-in. flue pipe and place it on the spillway of the 7-acre lake there. Figure 7 shows the apparatus used for these tests and the location of the chimney on the spillway; it may be noted that the bottom of the flue pipe was only a couple of inches above the water, which was flowing from the lake. Small oil slicks on the lake were produced with the help of a small graduated cylinder tied to the

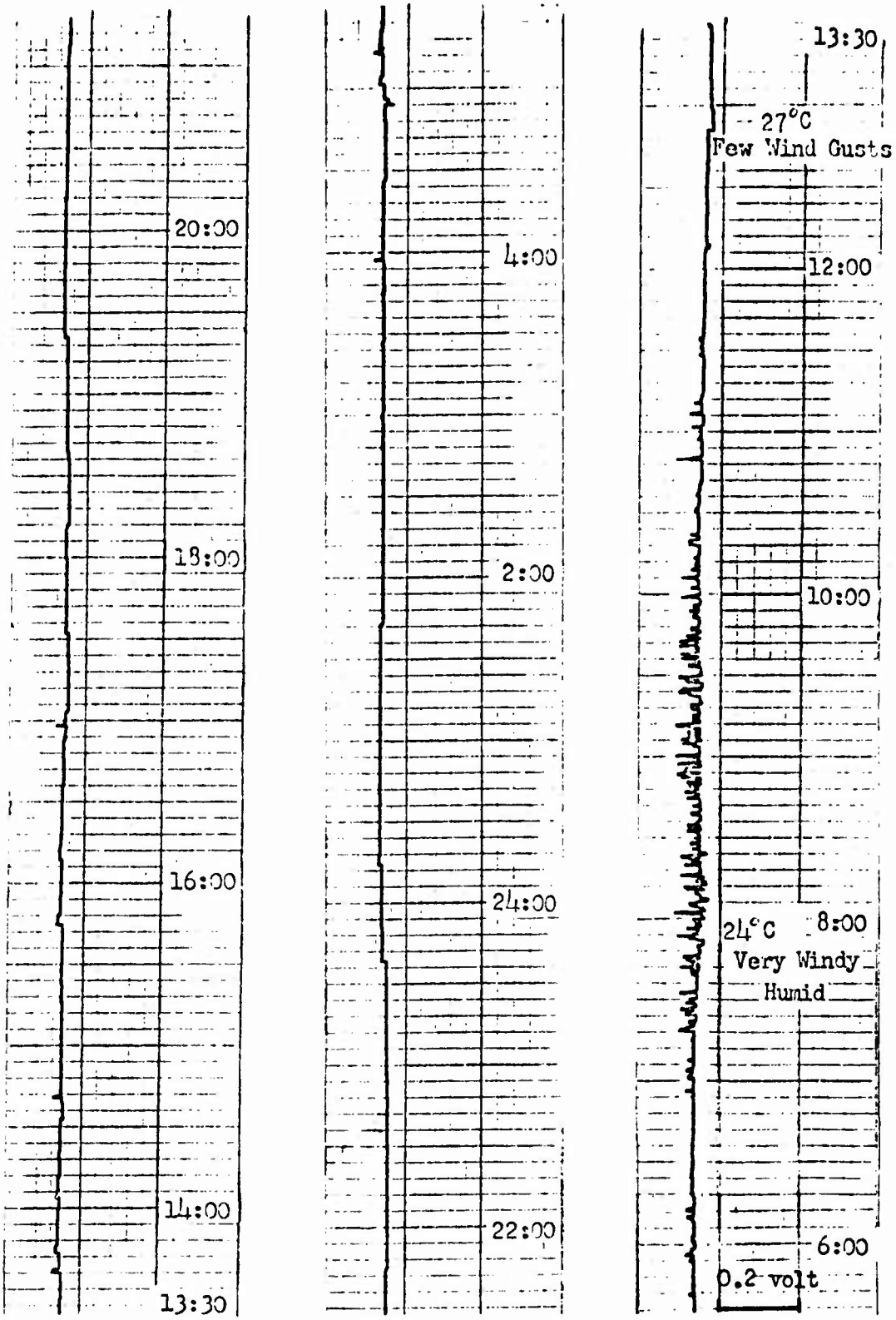


Figure 6. Twenty-four hour strip-chart recording of TGS sensor No. 102 performance outside second floor window.

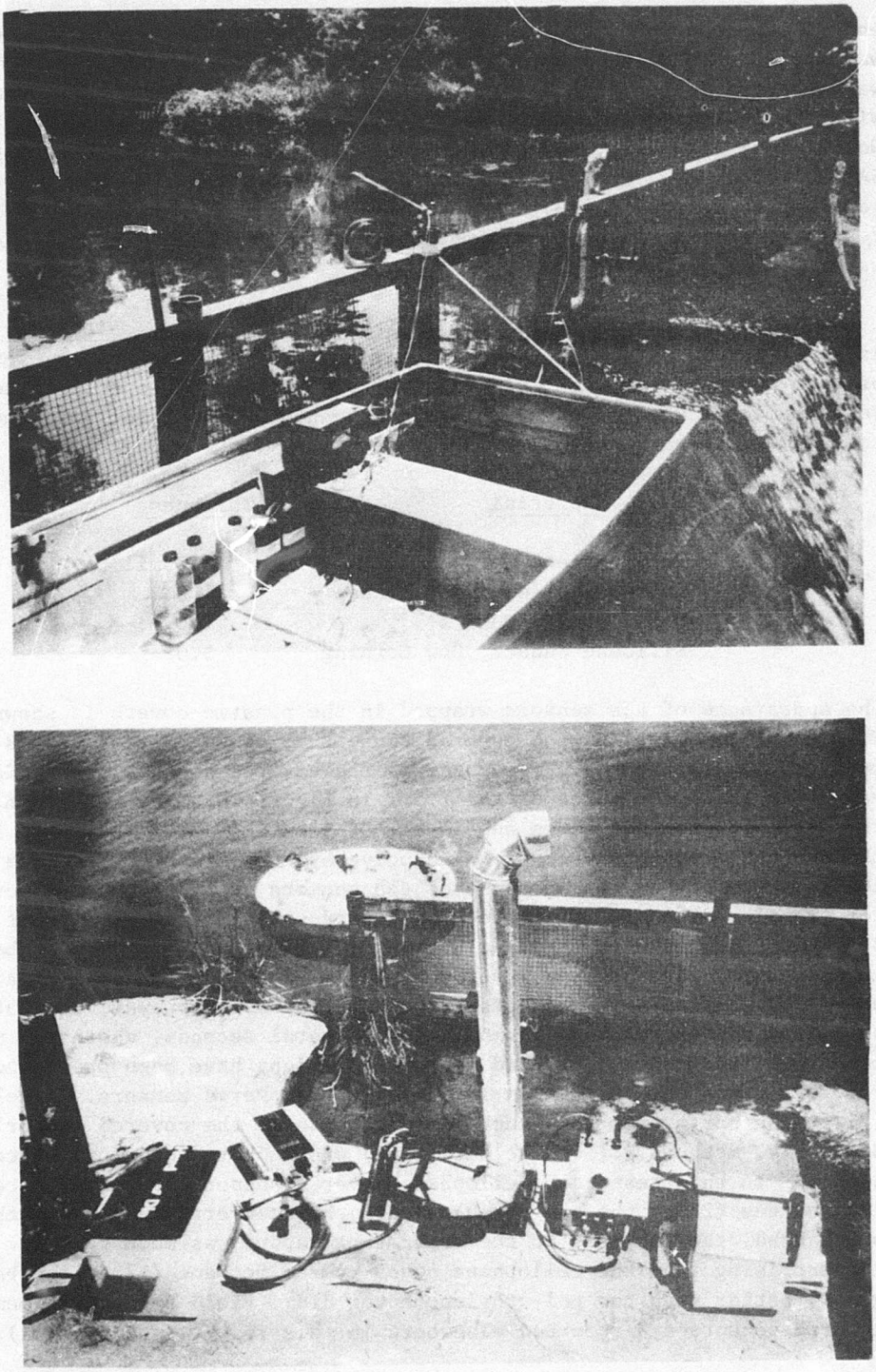


Figure 7. View of test site and experimental oil slick detection equipment.

end of a bamboo pole. Either 5 or 10 ml of the test petroleum product was poured on the lake, after which it moved to the TGS chimney where it was detected (see Figure 8). In this manner, good signals were obtained with the following petroleum vapors: JP-4, fuel oil No. 1, fuel oil No. 2, fuel oil No. 5, and sweet crude C; no response was obtained with SAE 30 motor oil. From the chart, it may be seen that the noise level was low; in several cases, the recovery of the sensors was slow as a result of the time needed to completely remove the oil film from the water.

11. Membrane covers for TGS sensors to change selectivity: In an effort to obtain greater selectivity with the TGS sensors, several of them were covered with thin films of plastic in the hope that the less permeable vapors would not produce responses. The following membrane covers were investigated:

Material	Thickness
Polyethylene	1.3 mil
Cellophane (dialysis grade)	1.0
Saran Wrap®, Dow	1.0
Silicone Rubber, Dow Corning	5.0

The appearance of the sensors wrapped in the plastic covers is shown in Figure 9. Responses of the covered sensors to standard test vapors were measured and the relative responses of the covered sensors to standard vapors is shown for three of the films in Figure 10. The bar graph for the Saran film is not shown but is almost identical with the graph for the cellophane-covered sensor. The polyethylene film seems to have had the least effect on the response of the sensors to hydrocarbon vapors; for example, JP-4 (bar 2 in the graph) produced a response of about 325 mV for both the covered and uncovered sensor, while isoprene (bar 22 in the graph) gave responses of about 380 mV for both the covered and uncovered sensors. The big difference in response, however, is that the uncovered sensor reached its maximum in several seconds, whereas 2 min were required with the covered sensor. As might have been predicted, recovery times were also much longer for the covered sensors. Acrolein (21 on the bar graph) gave much less response to the covered sensor. Similarly, methane (17 on the bar graph) was much reduced for the covered sensor. In this test, the cellophane-covered sensor gave as much response to isoprene (22 on the bar graph) as did the uncovered sensor; on the other hand, the response to the other test vapors was much reduced. It is surprising that the cellophane cover passed methane (17 on the bar graph) better than the polyethylene cover did. Field tests with membrane covered sensors are reported elsewhere in this report (see page 51).

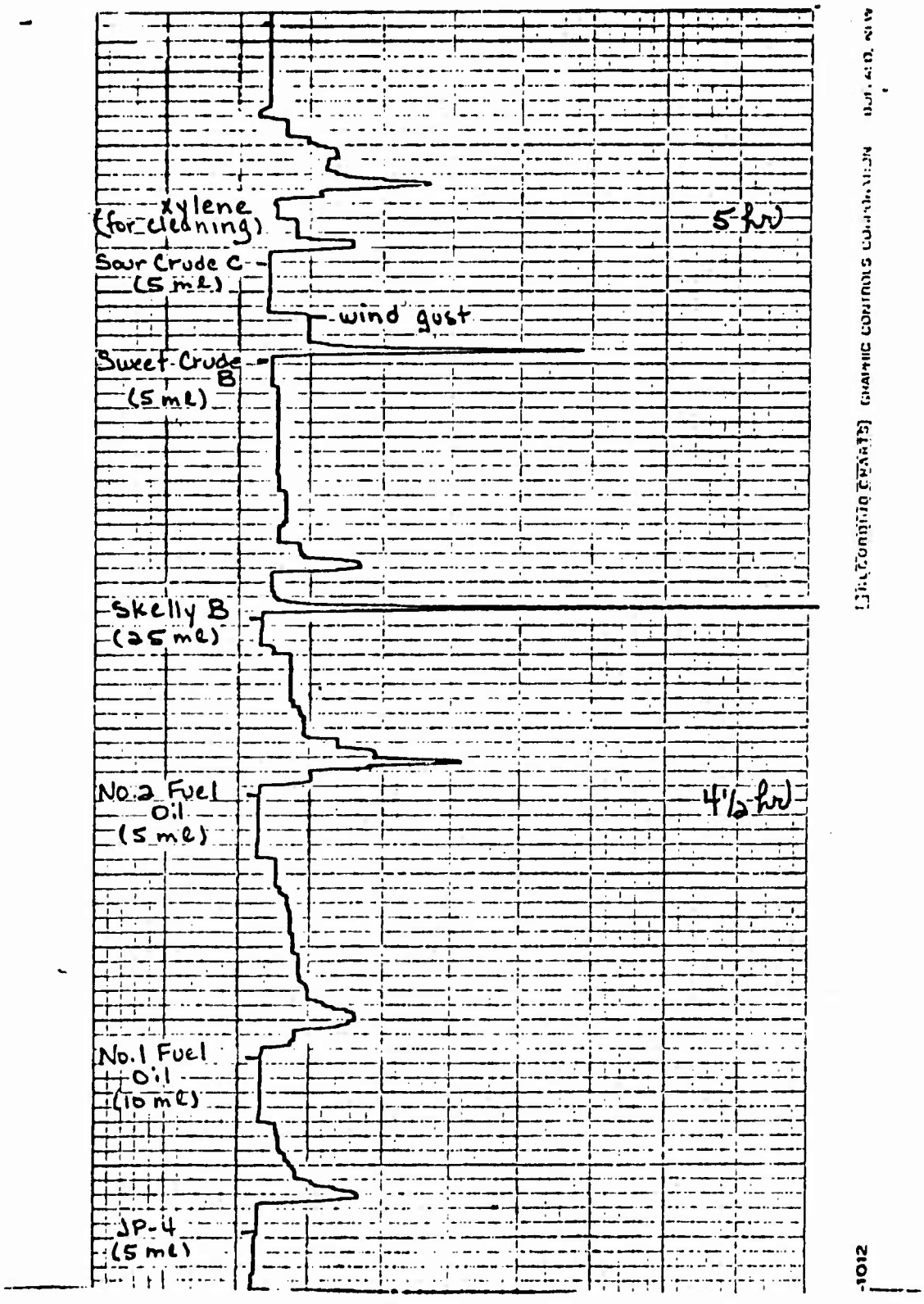


Figure 8. Strip-chart recording showing typical performance of TGS No. 102 in chimney as slicks resulting from 5 to 10 ml oil pass under chimney.

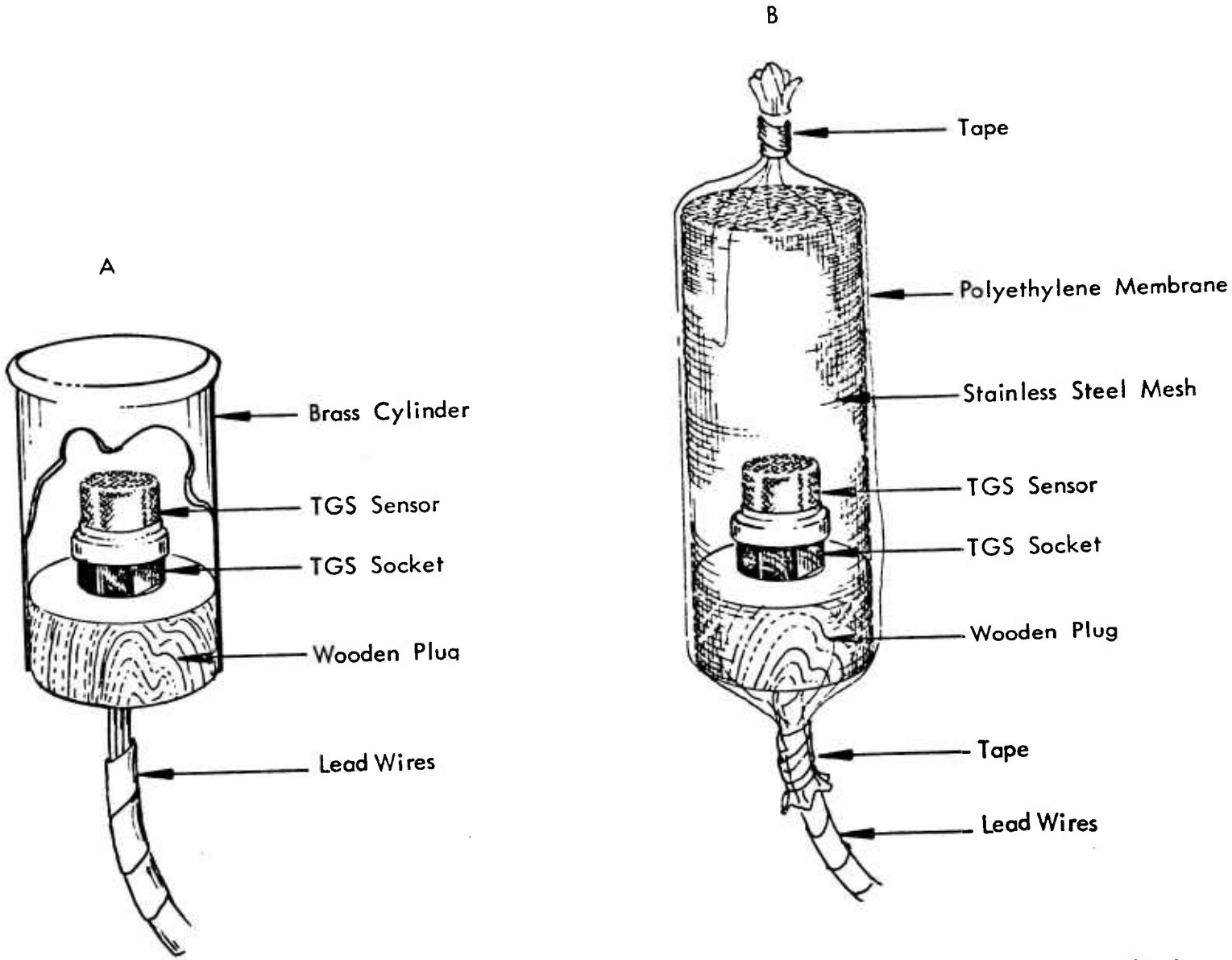


Figure 9. TGS probes for field use. A - TGS sensor mounted in brass cylinder. B - TGS sensor mounted in wire mesh framework with membrane cover.

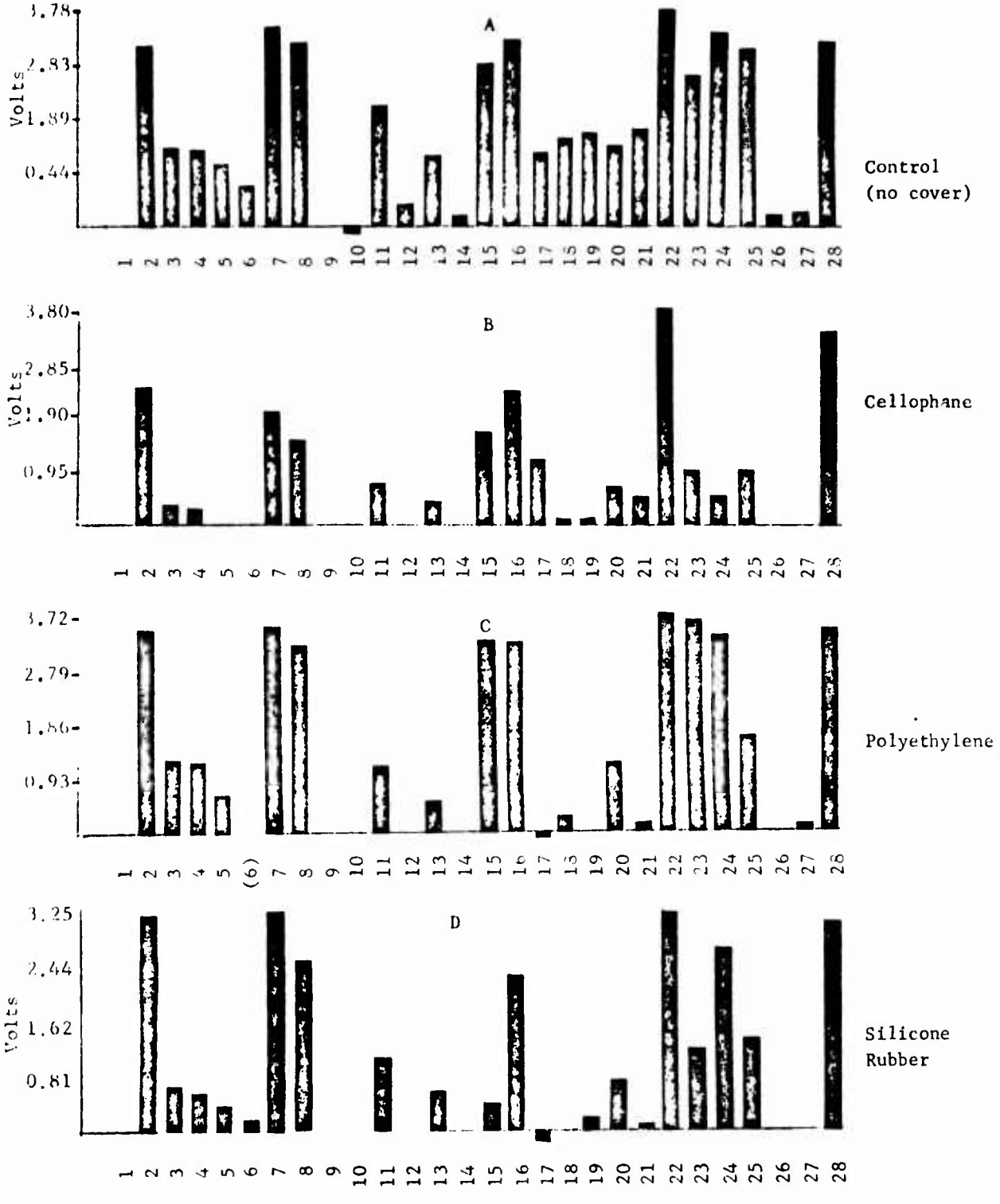


Figure 10. Response to TGS No. 102 sensor to standard pollutant vapors (see Figure 1 for pollutant code) showing effect of semipermeable membrane covers.

12. Chemical treatments of TGS sensors to change selectivity: In the early part of this investigation, the objective was to detect and identify spills on water. Later this objective was changed to detect oil spills on water. Therefore, some preliminary experiments were conducted for the purpose of changing the response profiles of the TGS sensors. The semiconductor chip inside of the TGS sensor was chemically changed or coated with various chemicals including specifically:

$CuSO_4$	Aluminum monostearate
$CoCl_2$	$(CH_3)_2\ SiCl_2$
CrO_3	H_3PO_4
$K_4Fe(CN)_6$	NaOH
HCl	NaCN

Following the application of the chemicals, the sensors were again tested for their response to the battery of standard test vapors. Copper sulfate gave an immediate decrease in response to everything except to isoprene; after 9 days it responded only to isoprene and after 7 days more it did not respond to anything. A similar effect was noted with cobaltous chloride-coated TGS sensors.

Aluminum monostearate was applied to the crystal from a benzene solution; after drying, it was found that the response of the sensor was unaffected and there was no observable effect after using the coated sensor for a month. Similarly, phosphoric acid, dimethyl dichlorosilane, and potassium ferrocyanide were without effect.

In summary, the coating of the sensors with chemicals did not achieve the change in sensitivity anticipated. Coating of the sensor with catalysts such as palladium chloride might provide a method to modify the response of the sensor to carbon monoxide which could be a potential interferent in some environments.

13. Sensor power requirements and alarm logic: In order to operate the TGS sensors, it is required that two voltages be supplied. The heater voltage requirements vary from 1.0 V for the TGS No. 102 to 5.0 V for the TGS No. 812. (Figaro agreed to supply us with sensors with 12-V heaters, but they have not yet done so.) The circuit voltage can be varied over wide limits provided suitable load resistances are provided; usually these circuit voltages applied across the semiconductor chip range from 10-120 V. In order to keep the sensor at the appropriate temperature so that it will respond and recover quickly, it is necessary to spend about 0.4 W. The power would be reduced a little if the sensor were placed in a plastic bag and insulated from the wind.

The TGS No. 711 sensor is meant to be operated at lower temperatures and, therefore, requires less power. Unless the voltage is increased momentarily after it has been exposed to vapors, it will recover very slowly; and this performance is not recommended for the present application.

Operating a 1.0-V heater from a 12-V power supply can be an inefficient process if the power is supplied with a dropping resistor, since 11/12 of the power would be wasted. Studies with a 12-DC to 1.0- and 1.2-V inverter showed that it was a more efficient method of supplying the power. In this case, the inverter consumed approximately 0.45 W, while the sensor consumed 0.4 W to make a total power drain of 0.85 W which was considered to be quite wasteful.

In the tests with the TGS No. 812, the 5-V heater voltage was supplied with a dropping resistor. In this case, the apparatus was much simpler than the inverter but the efficiency was still less than 50%. Two improvements have been considered. In one option, two of the 5-V sensors could be operated in series and the efficiency would be excellent. In the other option, the sensors could be operated with a 6-V battery or from sections of the 12-V buoy battery with automatic switching as one half of the battery became nearly discharged.

The power requirements of the alarm circuitry are very small when compared to the heater power. The semiconductor maintains a high resistance until the hydrocarbon is adsorbed to its surface. At this time, the resistance falls rapidly and a bell or other alarm can be made to ring without the use of a relay or other current switching circuitry.

Alarm logic can often provide a method of improving the discrimination of an alarm for the signal of interest and minimization of response to signals of little or no interest. The simple alarm threshold logic has been investigated; with this type of logic there is no alarm signalled until the sensor voltage rises to a preset threshold. Another alarm logic of potential interest with the TGS sensors inserts a delay into the response so that only signals which persist for a period of perhaps 30 sec or more are signalled. Time delay logic may enable the TGS sensors to distinguish between oil spills or response to airborne interferences.

14. Laboratory and preliminary field evaluation of TGS sensors: In the laboratory and preliminary field evaluation, the TGS sensors described above were shown to be sensitive to hydrocarbon vapors in the concentration range expected to be encountered in the marine environment.

Their reliability and reproducibility were proven in a 6-month stability test. After many hours of monitoring out-of-doors, it was concluded that baseline stability was not a problem and that temperature and humidity changes were small enough so that compensating electronic circuitry was not necessary to separate the response signals from the noise. Although the TGS sensors do require a moderate amount of power, it seems likely that it will be possible to operate them on buoy batteries for periods of about 6 months. These sensors respond quickly to pollutant vapors and recover within seconds after the pollutant vapors are removed. For many possible applications, the alarm logic is likely to be quite simple and very little electronic hardware will be needed to complete the detector package for use on the buoys. The sensors are relatively inexpensive and are easily replaced. Additional data on the performance of these sensors in the marine environment are presented later in this report.

C. Esso Piezoelectric Oil-On-Water System

Under contract to the Coast Guard, Esso Research and Engineering Company, Linden, New Jersey, had developed, tested and delivered an experimental prototype piezoelectric vapor sensor system for the detection of oil spills on water. This system was subsequently delivered to MRI by the Coast Guard for further testing and comparative evaluation with the other vapor sensors being investigated. This section summarizes the test procedures used in the evaluation, the data collected and the basis for the conclusions and recommendations which have been made.

1. Description of Esso oil-on-water detection system: The Esso oil-on-water piezoelectric sensor used three quartz crystals; one hermetically sealed, one coated with a silicone rubber, and another uncoated, for the detection of oil on water. This system measures the change of frequencies of these crystals when exposed to fumes from oil on water. The complete sensor is composed of many parts; for convenience they may be grouped on the basis of the area in which they are to be used. Figure 11 shows those parts of the Esso sensor which are to be mounted on a buoy along a watercourse. Many of the specific parts are identified in the call-outs affixed to the photograph. The output, D3, and data are then remotely linked via coaxial cables (not shown) to the data receiver shown in Figure 12. These component parts are intended to be located inside where an operator can observe the strip-chart tracings of the frequency difference between the uncoated and the coated crystal oscillators (Difference-3 or D3).

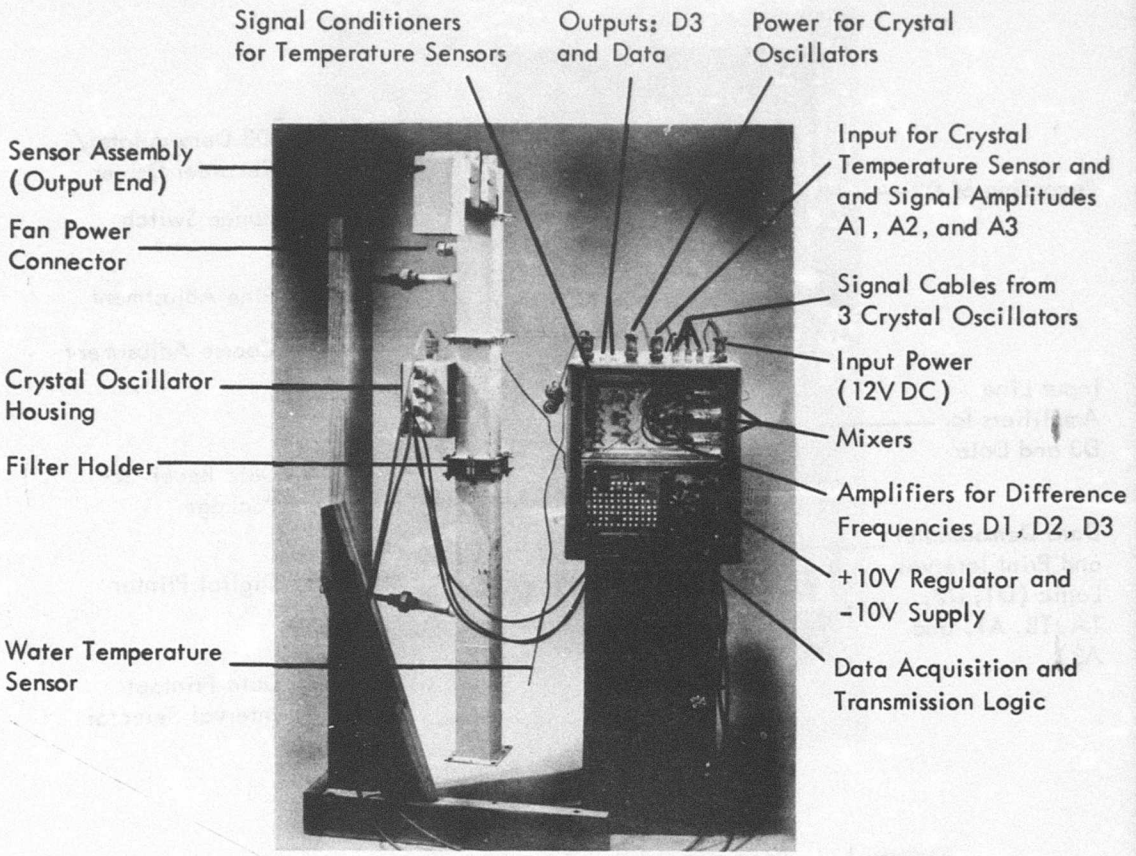


Figure 11. Sensor assembly and electronics cabinet part of Esso piezoelectric oil-on-water detector for buoy mounting.

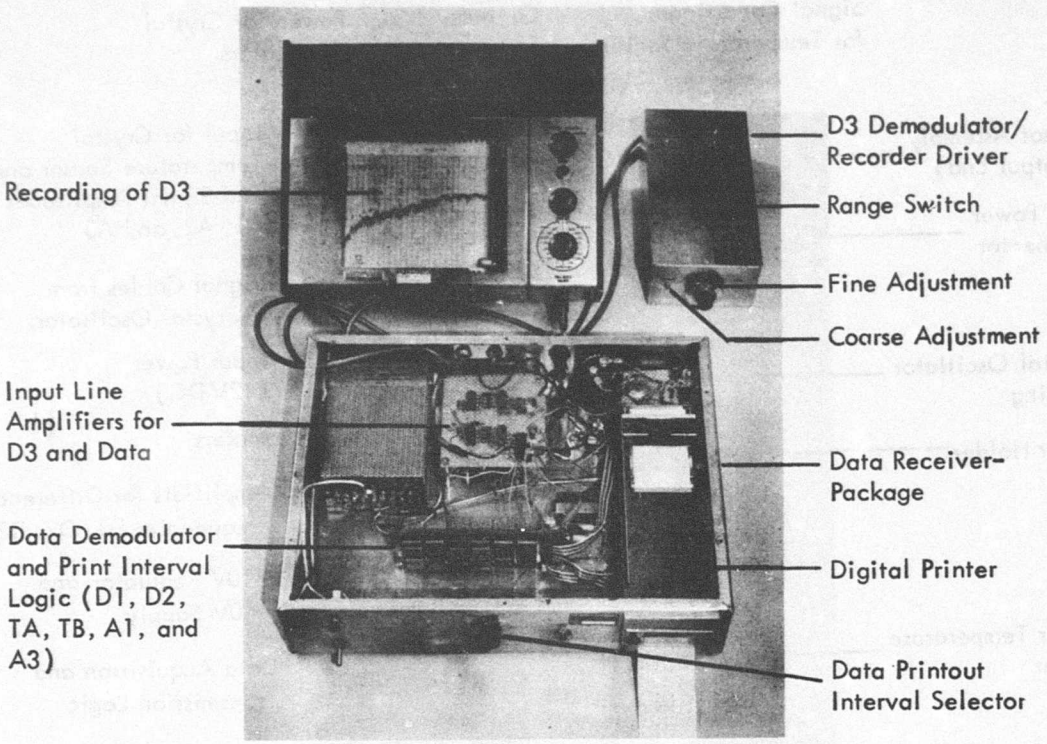


Figure 12. Data receiver (with printer and recorder) part of Esso piezoelectric oil-on-water detector system

Every 2 min the remote sensor transmits six pieces of information describing sensor operation and environment via cables to the data receiver. These are:

1. D1 - Frequency difference between oscillator 1 (coated crystal) and oscillator 2 (sealed reference crystal).

2. D2 - Frequency difference between oscillator 2 and oscillator 3 (uncoated crystal).

3. Temperature of air (TA) in °C + 30.

4. Temperature of water (TB) in °C + 30.

5. A1 - Relative amplitude of oscillator signal for coated crystal.

6. A2 - Relative amplitude of oscillator signal for uncoated crystal.

This entire set of data is printed at intervals of 2, 4, 6, or 10 min as selected by the operator and set by the selector switch on the front of the receiver cabinet. Changes in this setting should be made shortly after a data printout.

The difference between D1 and D2, items 1 and 2 in the printout, is D3, the difference between the frequencies of oscillators 1 and 3. This signal is also transmitted over one of the coaxial cables and provides a continuous indication of the sensor's response to hydrocarbons. This signal is coupled through amplifiers in the receiver-printer cabinet and then out to the demodulator/recorder driver and then to the strip-chart recorder. The demodulator/recorder unit has three sets of controls, a range selector, and coarse and fine adjustments. These settings determine the linear region of frequency to voltage conversion produced by this unit. It is important to operate in a linear region so that maximum response is indicated on the strip-chart recorder.

There is no alarm logic in the system. As a consequence, it would be necessary for the operator to observe the recording and also the digital information printed out at frequent intervals to judge whether D3 changes were due to oil spills or to temperature or humidity changes.

2. Environmental testing and evaluation

a. Test conditions: Three environmental test conditions were used in the evaluation of the Esso sensor. The first was a 2.5-cu ft chamber, the second was a 195-cu ft incubator, and the third was the rooftop environment. Testing was initiated after a preliminary but thorough electronic examination of the complete detection system.

The Esso sensor and its chimney were connected to a 2.5-cu ft environmental chamber, in which temperature and humidity were regulated. Air was recirculated through the chimney and the box in the same manner used in wind tunnels. The chimney was insulated and the temperature thermostatically regulated. A 50-cfm fan in the box was adequate to circulate the air. Both temperature and humidity were varied, and a series of oil samples (vapors) were exposed to the sensor.

The Esso sensor was transferred to a walk-in incubator with a 195-cu ft capacity. The temperature was thermostatically regulated at 50°C, and humidity levels were varied. The effect of humidity on the Esso sensor is reported elsewhere (see page 33). The sensor was exposed to various fuel oil vapors; however, levels were too low for detection. Other oil sensors were evaluated simultaneously with the Esso sensor. These other sensors were able to detect low level samples; consequently, larger samples were not used.

The Esso sensor was transferred to the rooftop to determine environmental effects, if any. The word "environment" includes temperature, humidity, wind speed and direction, sky conditions, rain, snow, sunshine, and other possible interferences. The sensor was mounted on the south side of a wind shield but at a distance great enough to allow wind circulation around the sensor. While the sensor was exposed to fuel oils, a record of the environmental conditions was made.

b. Response profiles to vapors from fresh oil films: The Esso sensor is capable of responding to a variety of oil vapors. Typical D3 values for 0.25 ml oil on water in a 2.5-cu ft chamber (19.0-21.5°C, 38.0-38.5% RH) exposed for 60 sec are as follows:

JP-4	2.0-6.5 Hz
No. 1 Fuel Oil	1.3-3.1 Hz
No. 2 Fuel Oil	1.0-1.4 Hz
No. 5 Fuel Oil	0.4 Hz
No. 6 Fuel Oil	0
Sweet Crude B	2.7 Hz
Sour Crude C	2.7 Hz
Motor Oil	0
H_2O Blank	0

This is shown in Figure 13.

The small response values of D3 are due to the small sample size. When a larger sample is used, the response levels are increased. An exposure to 0.25 ml JP-4 showed a response of D3 = 3.4 Hz; but an exposure to 1.0 ml JP-4 showed a response of D3 = 17 Hz. (This was reproducible.) This insensitivity to low levels of oil may be beneficial to the Coast Guard. Generally, it is the fresh spills of considerable size that are of concern and need to be detected quickly.

c. Response profiles to vapors from aged oil films: The Esso sensor performs well in the detection of aged oils. The oils were aged over water under a hood with the hood operating. The following are typical responses to 2.0 ml samples exposed to the sensor for 10 min:

(1) No. 2 Fuel Oil

Fresh	10.2 Hz
Aged 22 hr	6.5

(2) No. 5 Fuel Oil

Fresh	6.8 Hz
Aged 25 hr	0.8

(3) No. 6 Fuel Oil

Fresh	2.3 Hz
Aged 25 hr	0

(4) Sweet Crude B

Fresh	10.0 Hz
Aged 24 hr	2.1

(5) Sour Crude C

Fresh	5.2 Hz
Aged 20-1/2 hr	1.3

This ability of the piezoelectric crystals to detect samples 24-hr old is an asset. Spills older than 24 hr may be of less interest to the Coast Guard since by that time they would have already been reported; repeated detection of these older spills would not be necessary.

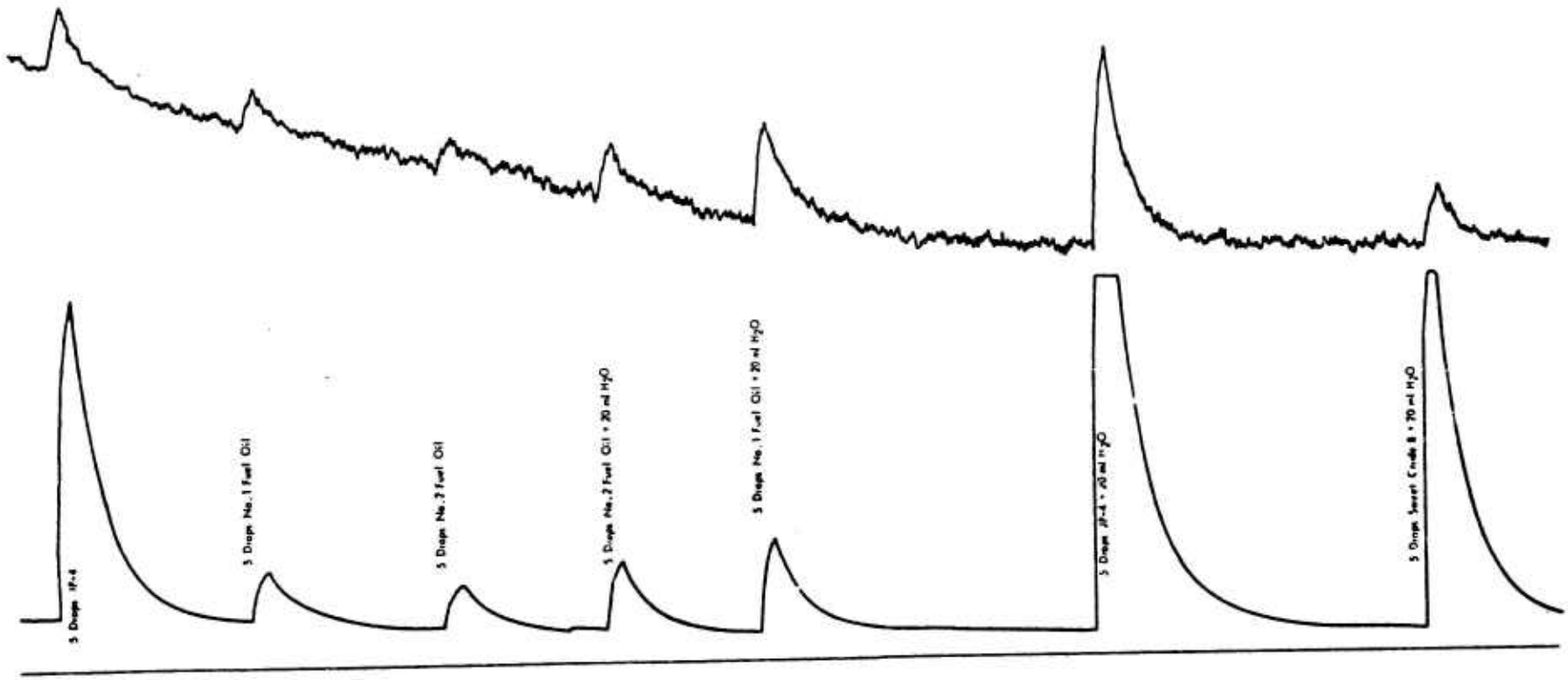


Figure 13. Response of the Esso oil-on-water piezoelectric sensor (upper curve) and the Taguchi semiconductor gas sensor (lower curve) in an environmental chamber (19.0 to 21.5°C and 38.0 to 38.5% RH) to petroleum product vapors.

d. Effects of wind: In some sensor systems, wind gusts increase the noise level of the baseline recorder tracing. However, there has been no change in the performance of the Esso sensor in the presence of winds up to 28 mph, with or without the 2-W Hico vaneaxial blower (14 cfm) operating (Figure 14):

28-mph wind, 2-W fan on; T = 27°, RH = 50%, D3 = 393 Hz
28-mph wind, 2-W fan off; T = 28°, RH = 50%, D3 = 394 Hz

It can be concluded that the responses of the Esso sensor are larger and more reproducible when the fan is operating. However, in a marine environment, we suspect that natural air currents produced by movement of the buoy or differences between water temperature and air temperature would tend to move air containing the pollutants to the sensor with the result that the blower would be less important under a marine environment than in a laboratory environment.

e. Temperature effects: Temperature changes do affect the value of D3. The most dramatic change was that observed when the Esso sensor was moved from a 50°C environment to a 0°C environment. The frequency D3 decreased from 400 Hz to 160 Hz. A typical environmental temperature effect is that observed at 5% RH when the temperature rises from 37°C to 48°C and D3 increases from 381 Hz to 406 Hz in 2-1/2 hr total time. The temperature effect on D3 is reversible, as temperature drops, D3 drops. It might be possible to minimize the temperature effect by a choice of precision or matched crystals. Other forms of electronic compensation may also be available, if we can determine the frequency characteristics of the crystals being used. This problem is compounded by yet-to-be-determined aging characteristics of the three different crystals, coated, uncoated, and sealed.

It is important to realize that weather conditions do affect the sensor's performance. The presence or absence of sunshine and/or clouds create a very obvious temperature effect which shows in the D3 tracing. The rooftop experiments show that environmental effects can occur quite rapidly and that alarm circuitry based on detection of rates of change of signal must take this into account.

f. Humidity effects. Humidity changes also affect the frequency readings of the crystals. At a constant temperature of 49°C, when the humidity rises 24% (i.e., 12% to 36%) the frequency of D3 rises from 415 Hz to 436 Hz, or a change of 21 Hz in 2 hr. This effect is reversible; when the humidity drops, D3 also drops (at a constant temperature). It is probable that this humidity effect can be compensated for electronically.

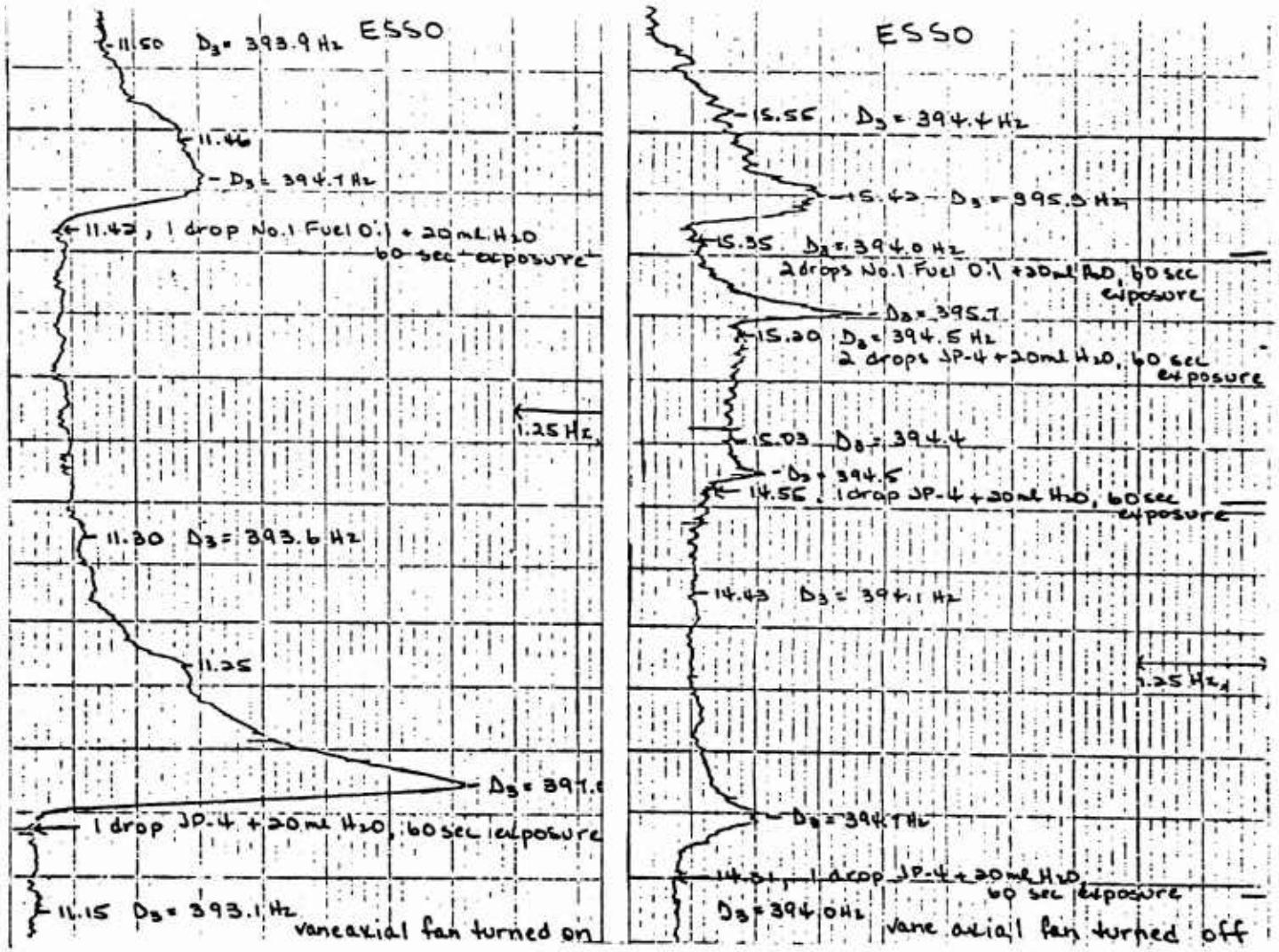


Figure 14. Strip-chart recording showing response of Esso sensor to petroleum vapors with 2-W fan turned on (left curve) and with 2-W fan turned off (right curve).

g. Combined humidity and temperature changes: There are instances when humidity and temperature increase together and decrease together. This combined effect results in a more rapidly changing D3 than when only one variable changes. When both humidity and temperature increase, D3 increases; when both humidity and temperature decrease, D3 decreases. A strip-chart recording of this effect is shown in Figure 15.

h. Interferences: Only three interferences were observed with the Esso sensor; they were dust particles, and high concentrations of carbon dioxide and carbon monoxide. It is probable that other interferences exist; however, they were not observed in our tests.

(1) Dust particles: When a dust particle lands on a crystal, the frequency of D3 is altered as much as 20 Hz. This might be remedied by placing a material such as cheesecloth around the crystals. This would allow penetration of vapors but not particles.

(2) CO_2: Exposure to CO_2, from dry ice or a bunsen burner (soft flame) results in an interference signal. Prolonged exposure to CO_2 creates a very erratic D3 tracing and an overall severe decrease in D3 value.

(3) CO: Exposure to CO from a bunsen burner hard flame results in production of a signal.

i. Reliability and durability: The Esso sensor is reliable in its responses to the oil vapors and the frequency changes at constant temperature are reproducible.

Most of the difficulties encountered during the evaluation of the system were concerned with the digital printer and the remote recording system. This is not considered serious since these components are not likely to be included in proposed modifications in which the alarm logic is mounted on buoys. The stepwise change in frequency of one oscillator which occurred when the temperature of the system was below freezing may have been due to condensate or ice on the quartz crystals. In one other case, dust on a crystal disrupted the normal oscillator frequency; this probably occurred because the air filter in the sensor chimney was removed to speed up air flow through the chimney. Probably a thimble-shaped filter over the crystals would have protected the crystals without impeding the air flow through the chimney. The 2-W Hico vaneaxial blower failed and was replaced and the replacement failed. The manufacturer said that the life expectancy of these fans is 1,000-3,000 hr (40-125 days).

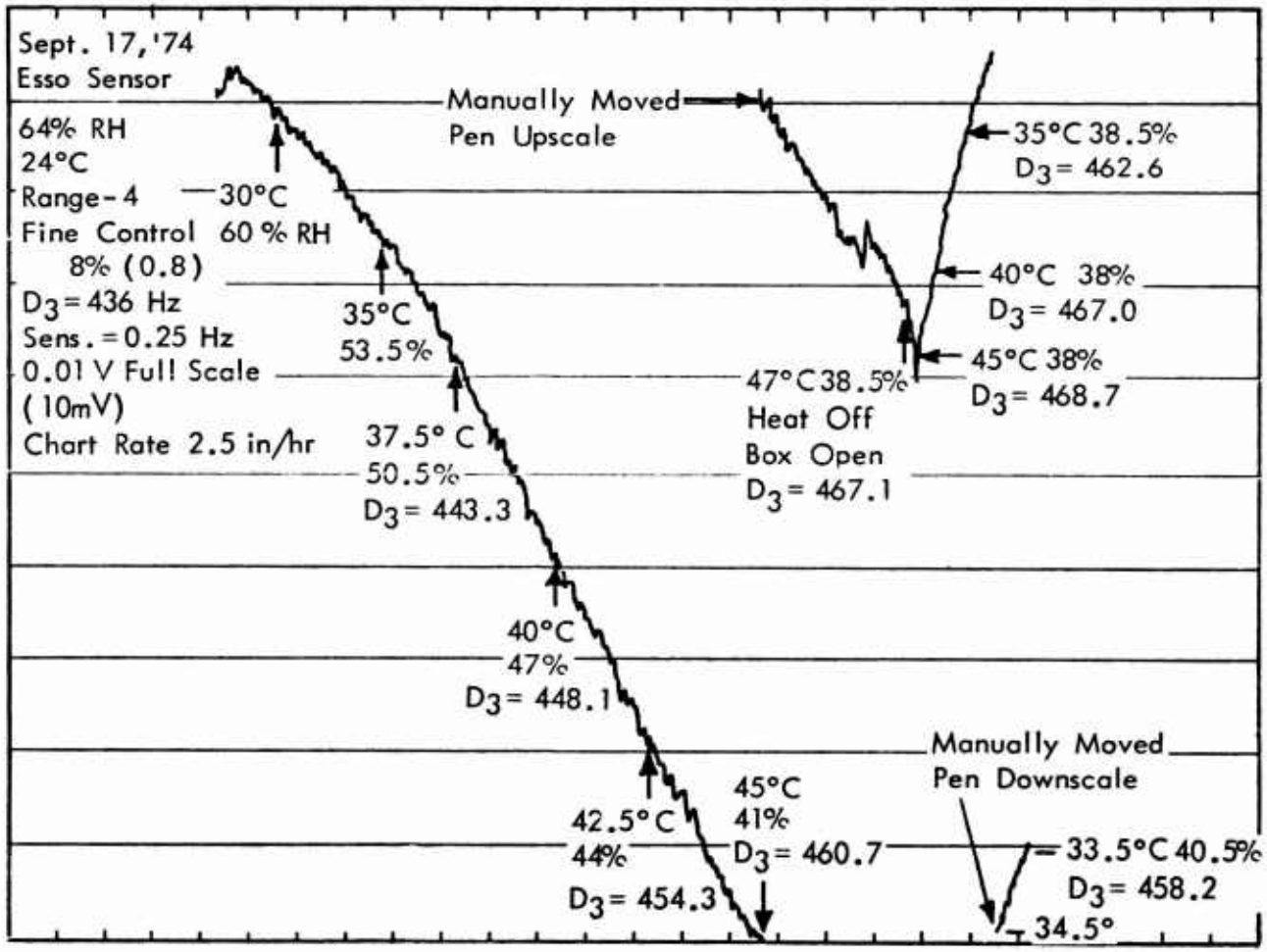


Figure 15. Effect of temperature and humidity on the difference in frequency (D3) of the coated and uncoated quartz crystals.

j. Sensitivity of the Esso sensor system: The sensitivity of the Esso sensor to hydrocarbon vapors is difficult to quantitate because tests have been run with crude mixtures which have varying effects on the silicone-coated crystal. Based upon observations of the aged oil films, it is concluded that the Esso system is more sensitive to the higher molecular weight (less volatile) fractions of oil than it is to the low-boiling fractions. By weighing films before and after their use in the environmental chamber and by assuming that the portion of fuel oil No. 2 lost by evaporation was equally distributed in the air (i.e., not adsorbed to surfaces, etc.), it is estimated that 50-100 ppm of the volatiles from fuel oil is the minimum needed to produce a satisfactory response with the piezoelectric sensors. This estimate agrees with the reported sensitivity value.(3)

3. Potential usefulness of Esso system: The concept of using piezoelectric crystals for detection of oil vapors is basically sound. The Esso sensor, as now constructed, responds to vapors from gasoline, JP-4, fuel oils Nos. 1-6, sweet crude B, and sour crude C at levels which can be expected in the air over a spill. It does not respond to motor oil (motor oil is not volatile enough to be detected by any vapor sensor known to us). Small oil slicks or exhausts from boats passing by the sensor are not expected to cause false alarms. The Esso sensor responds to oils aged up to 24 hr. This enables detection of a slick for an extended period of time compared to the TGS sensor. The sensor is not affected by wind or wind gusts.

The Esso sensor has several possible disadvantages. The air filter in the chimney blocks air circulation past the crystals. Removal of the filter exposes the crystals to fog, dust, salt spray, etc. Engineering design changes are needed to improve air flow and protect the crystals. Temperature and humidity changes cause frequency drift to an extent that requires compensation. False alarms could be triggered by high levels of CO_2 and CO; but this is not anticipated to be a problem.

The Esso oil-on-water piezoelectric sensor system, as now constructed, is unsuited for use on a buoy because of its lack of alarm logic and the use of coaxial cables to transmit data. The power used to actuate the oscillators and transmit seven pieces of data every 2 min to a revote location via cables is about 40 mA at 11.7 V or 0.468 W; this power consumption, except for the fan, is acceptable.

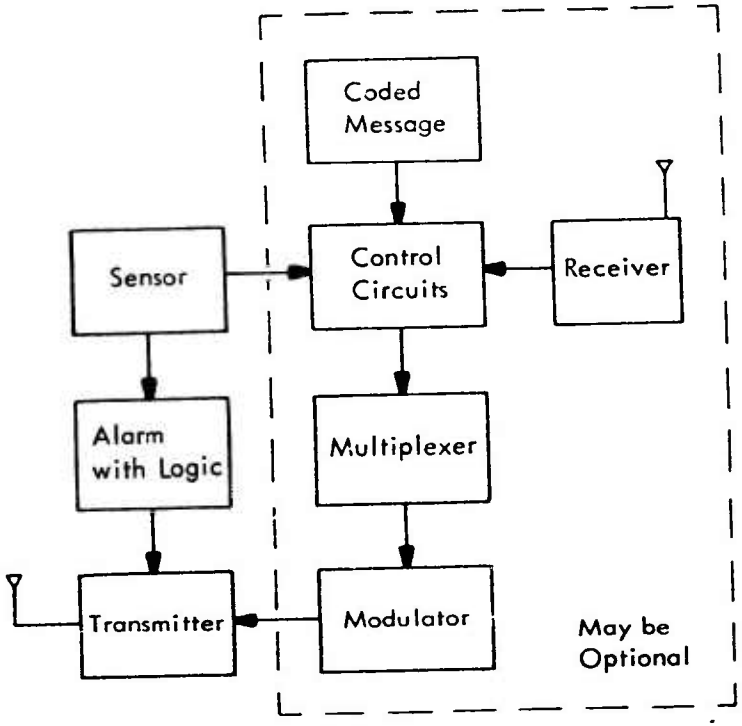
Considerable improvement in the system is needed to achieve the development of buoy-mounted alarm logic which would signal an alarm when D3 changed abruptly. Modifications to make the system usable are described below.

As presently envisioned, each buoy would transmit a coded identifying signal as an alarm. The shore-based receivers, which are capable of picking up signals from a number of channel-based buoys, would automatically relay the information to a central location. If needed, personnel could then interrogate the buoy, requesting a transmission of the data being monitored so that false alarms could be ruled out. Block diagrams of proposed buoy and shore systems are shown on page 39.

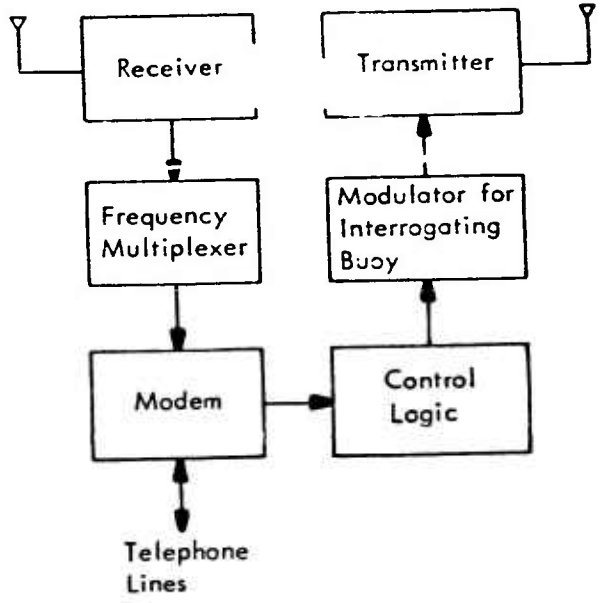
The proposed piezoelectric sensor system may consist of crystal sensors in one package, alarm circuits in one or more packages, and transmitter and receiver in separate packages. Test points would permit a maintenance technician to isolate problems. Working in conjunction with a partner at the shore-based installation would probably be required. The entire alarm package may have to be made removable so that it can be taken aboard the service vessel for maintenance.

4. Recommendations related to piezoelectric sensor system: The adaption of the piezoelectric sensor system for the Coast Guard's use would have required more time and money than was available on the contract. Therefore, it was our recommendation that work with the Esso sensor be discontinued to enable concentrated effort on more promising sensor systems.

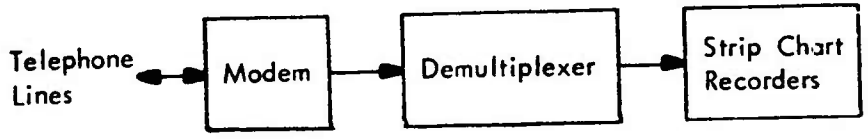
If work should be resumed on the piezoelectric sensor system for oil spill monitoring, the following actions are recommended: (1) select precision-matched crystals which will not require temperature compensation; (2) apply a silastic coating to one crystal (as done by Esso); (3) devise temperature and/or humidity compensating circuitry to be added to the sensor if necessary; (4) redesign packaging of the crystals to protect them from particulates and allow access of the vapors to the crystals; (5) devise self-contained buoy-mounted alarm logic which can activate telemetry equipment when spills are present; (6) decide whether information about air temperature, water temperature, and oscillator amplitudes are needed to distinguish spills from noise; (7) devise a telemetry system using digital signals to notify a monitoring station of a spill and its location; and (8) field test the unit in an area where spills are present.



BUOY



SHORE BASED ROBOT STATION



CENTRAL LOCATION - DISPATCHER

D. Wesmar Adhistor Sensor System

A new and relatively untried vapor monitoring system using an Adhistor sensor for monitoring oil on water was purchased by the Coast Guard from the Environmental Measurement Systems Division of Wesmar (905 Dexter Avenue North, Seattle, Washington 98109). The initial unit supplied was identified as Water Surveillance Monitor (WSM-350) which had a strip-chart recorder on the front of the cabinet. Later the company loaned MRI a second unit which was essentially the same as the first but which was identified as the Vapor Monitor (VM-400). This instrument did not possess the recorder and possessed slight differences in the electronic circuitry which permitted more stable operation at high sensitivity without the "dead band" observed at the low hydrocarbon vapor concentrations with the WSM-350.

The Adhistor sensor used with the WSM-350 and VM-400 systems is reported to consist of resistors made of silicone rubber impregnated with various conductive particulate materials. Adsorption of hydrocarbon vapors causes their resistance to change.

Examination of the wiring diagram revealed that each Wesmar air sensor was packaged with two identical hydrocarbon detection devices, one of which was wrapped in a protective coating. In the electronic circuitry the covered and uncovered hydrocarbon sensors were wired into separate legs of a Wheatstone bridge circuit which fed a differential amplifier. This dual sensor arrangement provided compensation for temperature changes; however, during out tests, temperature compensation was not too good. Apparently the covered sensor did not change temperature as quickly as the uncovered sensor, with the result that the output of the WSM-350 changed markedly with the temperature.

Examination of the WMS-350 system has revealed that the Van der Waal's switch provides minor changes in the voltage supplied to the sensor. For example, a Van der Waal's setting of 10 applies the least current to the sensor and is, therefore the least sensitive position. On the other hand, a Van der Waal's setting of 60 applies the most current to the sensor and is its most sensitive position. The difference between the 10 and 60 settings are small and are used to compensate for differences in affinity of vapors for the hydrocarbon sensor and to permit at least an approximate calibration of the instrument in ppm for specific vapors or gases. For our studies, the Van der Waal's switch was left in the most sensitive position for all tests (i.e., 60). At this setting the sensitivity of the instrument was controlled adequately

with the meter multiplier switch which connects the sensor voltage to amplifiers with different gains. With the sensitivity switch in the "A" position, the scale registered 0-10 ppm; in some of the early tests, the Wesmar sensors were exposed to hydrocarbon vapors for only 30-60 sec. Since the response to high levels of JP-4 took about 2 min (see Figure 16), exposure times of 2-10 min were used in studies with the Wesmar sensors to maximize the responses.

The sensitivity of the sensors to a variety of materials varied from compound to compound and was reported to parallel Van der Waal's Constants for gases. That is, the sensitivity of the Adhistor was greater for those pollutant molecules with greater adhesion to the sensor surface. The Adhistor sensor responds to those materials with Van der Waal's "a" (attractive force) greater than 9.00; therefore gases such as oxygen, nitrogen, methane, ethane, and propane will not react. Higher molecular weight hydrocarbons, ethers, alcohols, ketones, chlorinated hydrocarbons, etc., are reported to respond. "Operational Instructions for WSM-350," "Facts Regarding the WSM-350 Sensor," and some test results supplied by Environmental Measurement Systems are reproduced in Appendix I of this report.

Two things which made the WSM-350 system potentially attractive for Coast Guard use were: (1) the report that the sensor could be used either above or below the surface of the water for sensing the presence of oil spills; and (2) the unit (excluding the recorder) required very little power to operate.

Preliminary experiments were conducted with the ceramic-encased Wesmar sensors under water. In these tests, the change in baseline due to the use of cool water were excessive and several minutes were needed to equilibration. Addition of JP-4 on top of the water and swirling the mixture for 2 min failed to produce a response. It was claimed by the manufacturer that the ceramic-encased sensor was particularly valuable as a vapor sensor since the ceramic case permitted occasional dunking of the sensor without injuring its sensitivity. Aside from temperature effects, this claim was substantiated.

As shown earlier, the response of the WSM-350 system to high levels of JP-4 was satisfactory; however, response of this system to the standard hydrocarbon test vapors in the 25-100 ppm range were small or nonexistent. Examination of the 10 sensors supplied with the instrument revealed wide variations in their electrical resistances and also their responsiveness to the hydrocarbon vapors. In subsequent studies, only the most sensitive individual sensors were used.

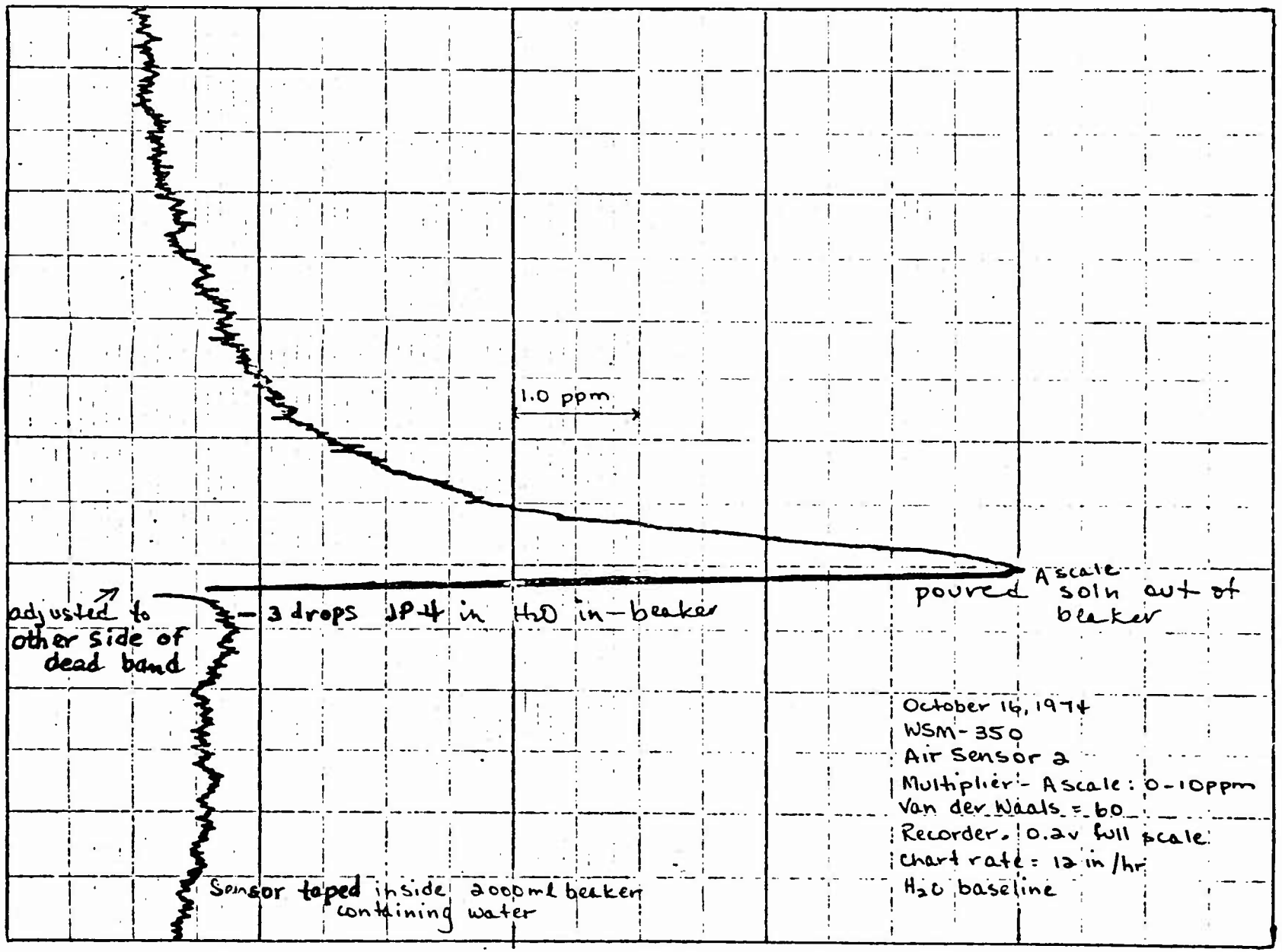


Figure 16. Response of Wesmar Air Sensor (Adhistor) to JP-4.

During the course of the studies, the Environmental Measurement systems supplied us with two additional types of "new and improved" Adhistor sensors. One was called "the platinum sensor" and the other was designated as the "2.75 K Ω sensor." Of the three types received, the last gave the fastest response and the greatest sensitivity; however, the differences in sensitivity of these sensors was not large.

Figure 17 shows a strip-chart recording of the output from the WSM-350 system with the 2.75 K sensor inside a small environmental chamber and exposed to changes in temperature and also exposed to 1 ml of fuel oil No. 2 in a beaker with 100 ml of water for two 15-min periods. The output voltage change resulting from the 4°C temperature change was about twice the change which was obtained from the exposure to the fuel oil. This figure shows that the response begins to level off at 15 min and that recovery of the original baseline voltage is about three-fourths complete in 50 min. Other tracings not reproduced here show that the sensor recovery is complete in 1-8 hr, depending upon the selection and concentration of vapors to which it has been exposed. Perhaps the most important observation is that a subsequent exposure gave approximately the same response as the original exposure. Figure 18 provides information showing the response of this same sensor system to sweet crude B. The lesser response to sweet crude B on its second exposure is probably due to reduced volatility due to lower water temperature for the second exposure.

For the determination of baseline stability and response of the WSM-350 system under a noncontrolled environment, the 2.75 K sensor was placed in the chimney with the Esso and TGS sensors; and the assembly was placed on the roof of the laboratory with cables long enough to permit the sensors to be monitored by recorders beneath them inside the laboratory. Figure 19 shows what happens to the baseline voltage when the sun rises on a cool morning and warms up for about 5 hr. After about 2 hr, the pen would have gone off the chart if the zero adjust knob on the recorder had not been manually reset. After another 3-1/2 hr, the pen did go off the chart. On this basis, we concluded that there was little or no temperature compensation in the sensor.

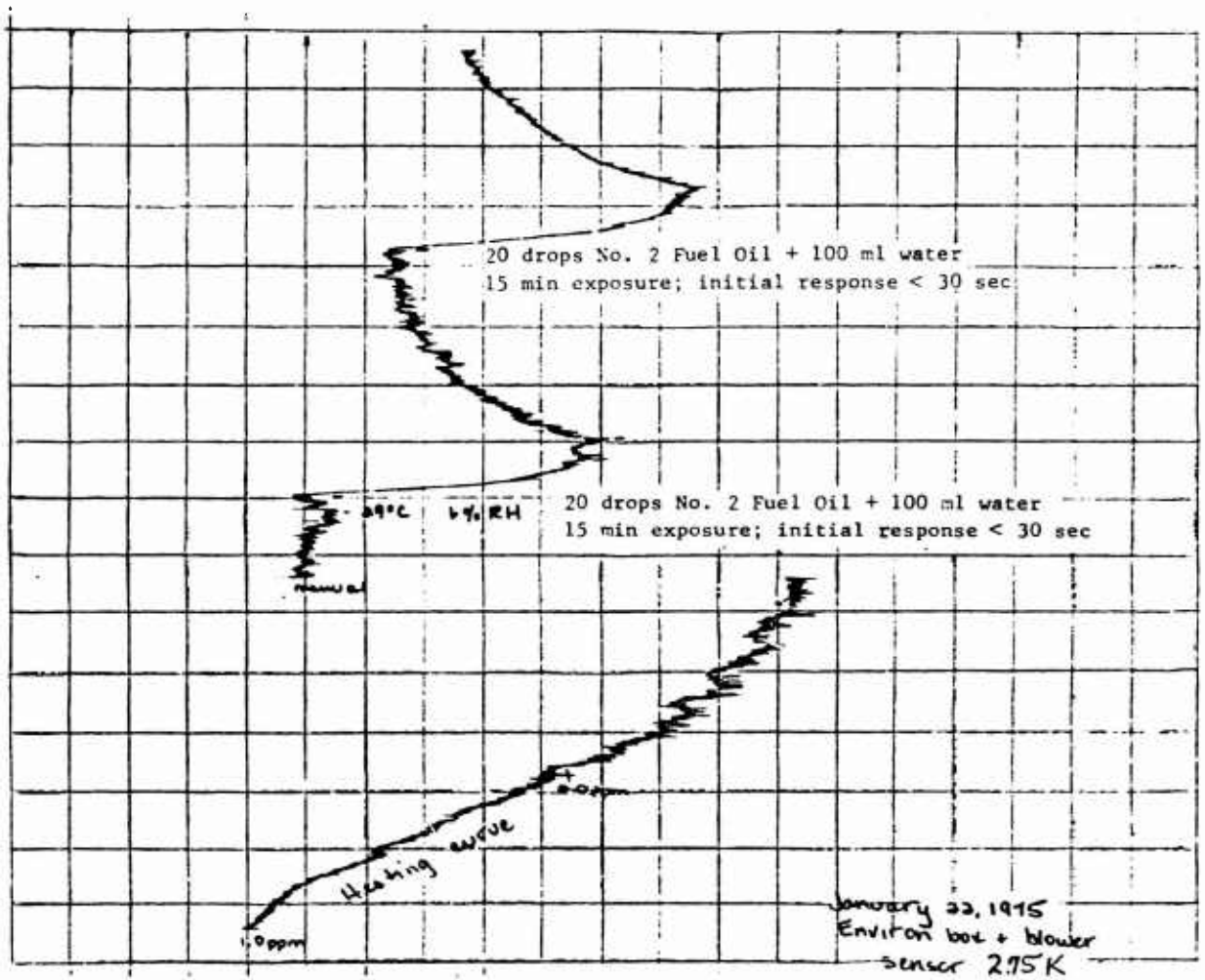


Figure 17. Response of WSM-350 oil monitor with 2.75 K sensor to temperature change and to fuel oil No. 2. (Tests were conducted in 1.68 cu ft environmental test chamber with mechanical air circulation. The strip chart moved down at 2 in/hr; the temperature started at 24°C and rose to 29°C as shown by the "heating curve." The recorder scale was arbitrary but was equal to 3.7 ppm divisions on the WSM-350 meter.)

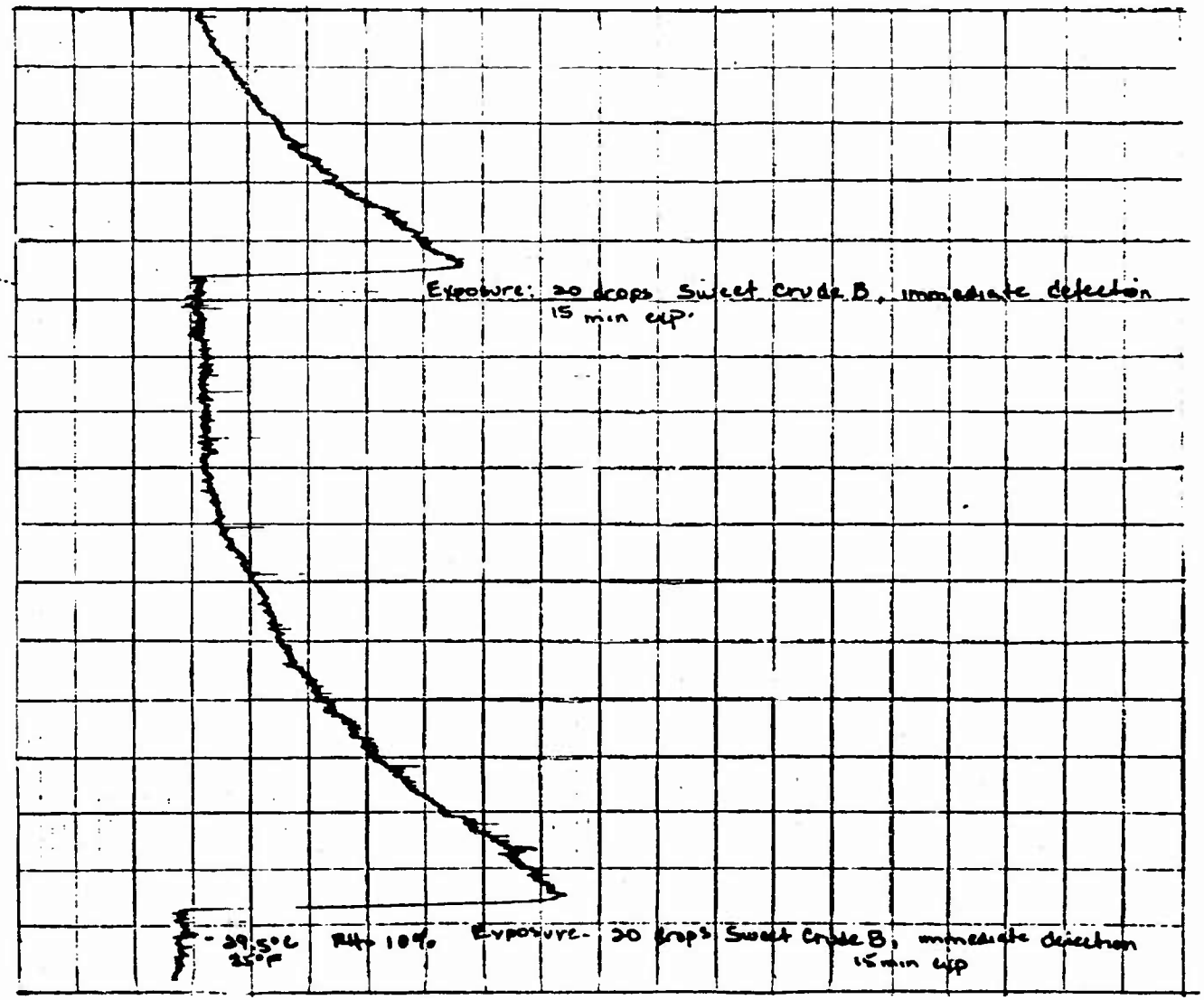


Figure 18. Response of WSM-350 oil monitor with 2.75 K sensor to sweet crude B (see Figure 17 for additional test information).

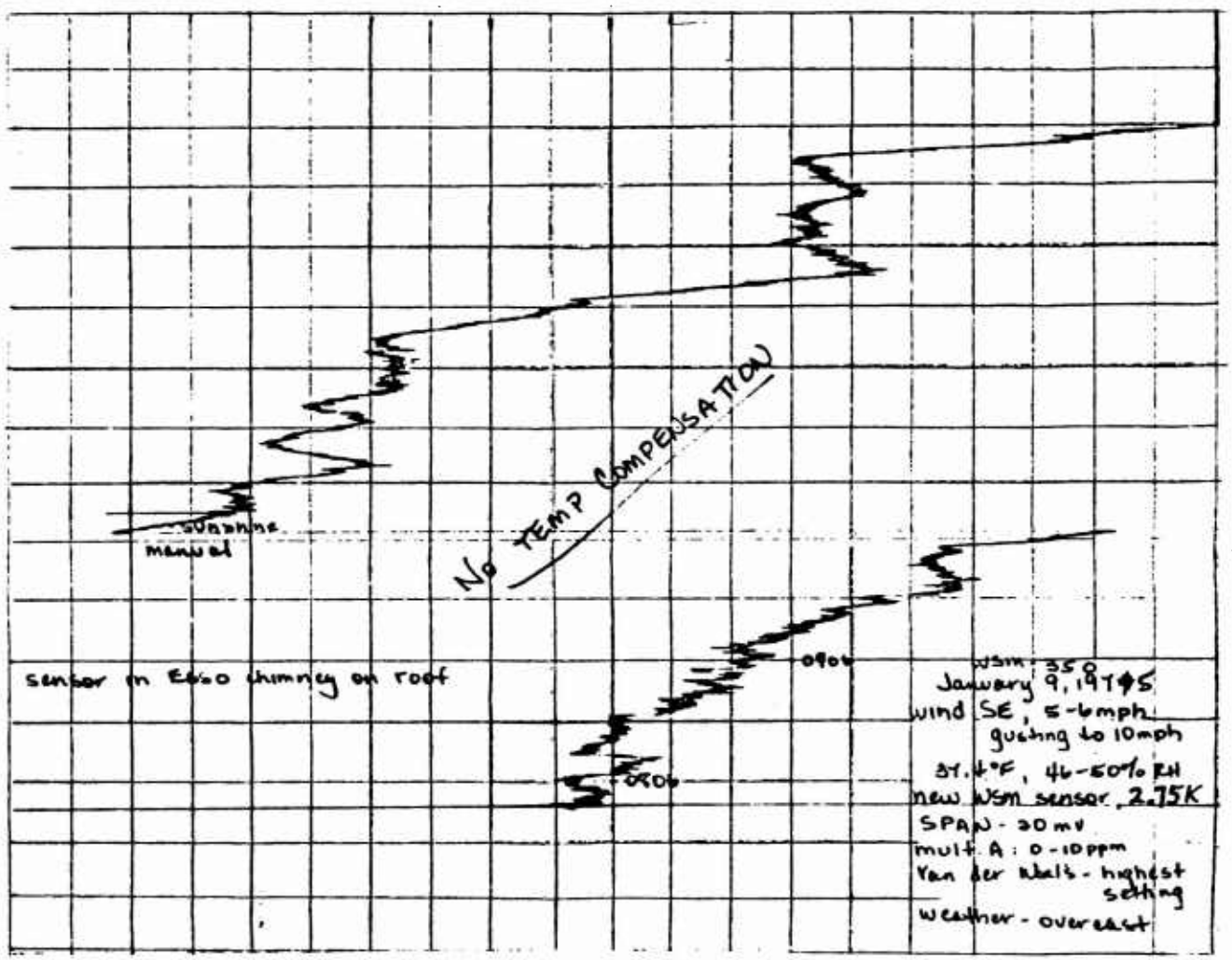


Figure 19. Effect of environmental changes on the WSM-350 oil monitor with the 2.75 K sensor.

Figure 20 shows a tracing made as a part of the continuation of the experiment described in Figure 19; at this later time, the temperature and baselines were more stable. In this experiment, the three types of sensors were exposed simultaneously in the chimney (with the Esso fan running) for 5 min to vapors from 1.5 ml of sour crude C in a beaker with 100 ml of water. The response was so low as to be indistinguishable from the noise. Although not shown on this chart, both the Esso and the TGS sensors provided responses well above the baselines and noise levels. It is concluded that the 2.75 K sensor is less responsive than the TGS sensors, but more responsive than the original WSM-350 air sensors or the improved platinum sensor which had been evaluated earlier.

The 2.75 K sensor for the WSM-350 unit has been compared with a TGS No. 202 sensor in a 1.68-cu ft environmental chamber. Testing in this chamber was done at 29°C, 5-12% RH, Van der Waals = 70 (470 K Ω resistor added), Multiplier - A scale: 0-10 ppm, zero adjusted to 1.0 ppm (to avoid dead-band problem), and the air blower running. A series of exposures to 1.0-ml samples of fuel oils on 100 ml of water gave the results as follows:

Hydrocarbon Vapor	WSM-350 Response, ppm	TGS No. 202 Response, volts
No. 1 Fuel Oil	0.4-2.6	4.1
No. 2 Fuel Oil	0.3-0.5	3.2
No. 5 Fuel Oil	0.1	1.7
No. 6 Fuel Oil	0.0-0.2	0.5
Sweet Crude B	0.3-0.7	5.8
Sour Crude C	0.3	2.8
40 SAE Motor Oil	0.0	0.0

Further laboratory testing of the WSM-350 sensor system was not done because (1) its response was slow, (2) its signal to noise ratio was poor, and (3) its recovery after exposure was slow.

A new temperature compensated vapor monitor (VM-400) was loaned to MRI to replace the WSM-350 with the 2.75 K Ω sensor. Some limited data (see Appendix I) was supplied with this instrument which suggested that the new unit had improved sensitivity; also we had been assured that the response of the new unit would be faster and that the "dead band," which had been troublesome with the earlier model, had been removed. This apparatus was taken to the Houston Ship Channel and the results are shown in the section describing the second field trip (see page 57). No correlation of the peaks with pollutant vapors seen by the

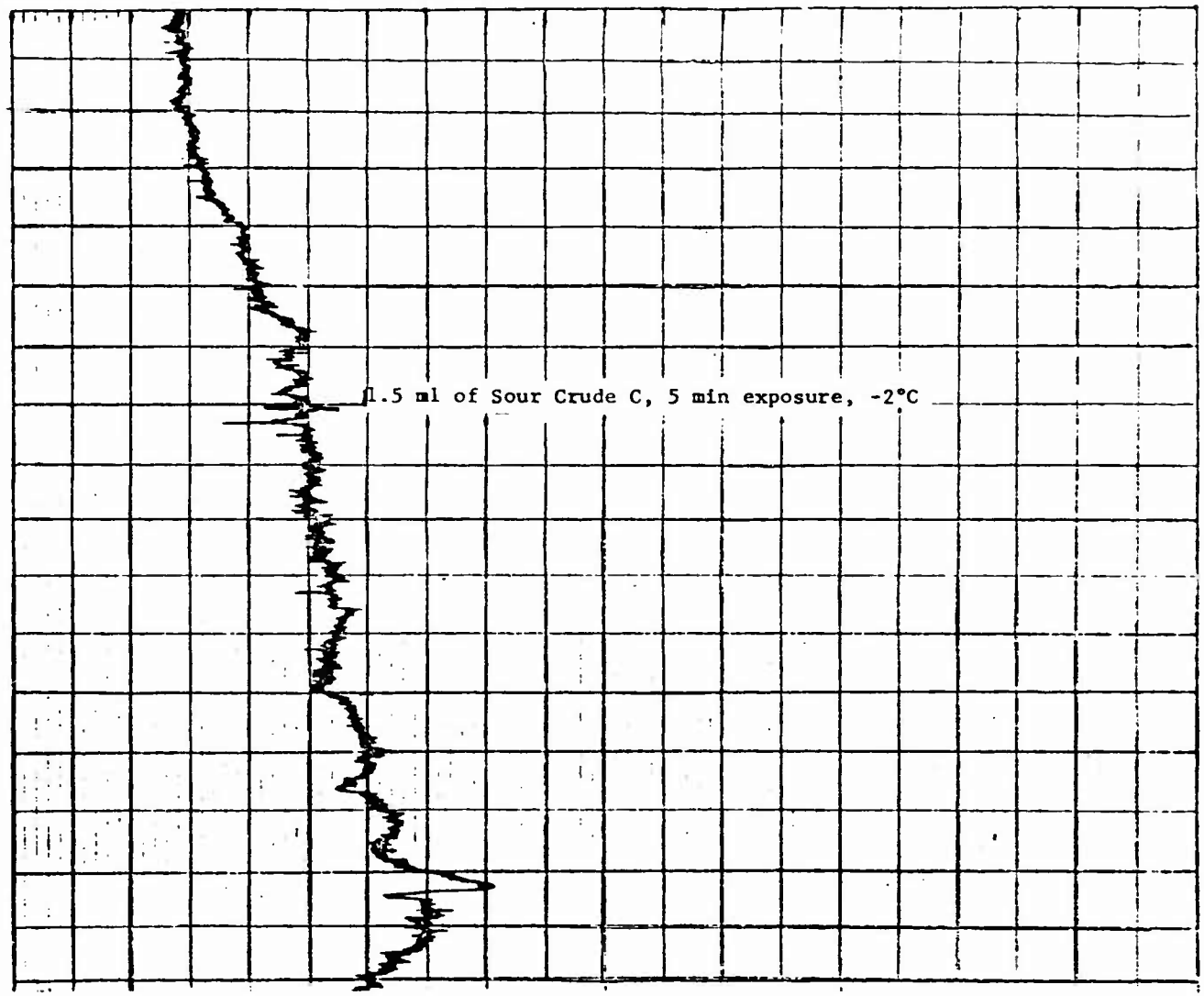


Figure 20. Response of the 2.75 K sensor to sour crude C. Test conducted on roof-top with sensor in chimney with TGS and Esso sensors.

other sensors at the same time could be made. Further, the response to oil on water was so small that it could not be differentiated from the noise. Undoubtedly, a good share of the problem was due to inadequate temperature compensation.

On the basis of studies conducted, it was concluded that the Wesmar Adhistor sensors, in their present state of development, were unsuited for Coast Guard use on buoys.

E. Selection of Sensors for Field Tests

In the rooftop experiments with the three sensor systems, it was found that only the TGS system gave stable baseline voltages, which remained below the response levels attained when challenged with small quantities of hydrocarbon vapors. In these studies, the two TGS sensors which were investigated were the TGS No. 202 and the TGS No. 308 (12 V battery operated) and they were operated out-of-doors for 70 days without turning them off; that is, each sensor operated for 1,680 hr to make a total running time of 3,760 hr. Although small changes in baseline voltages did occur during strong or gusting winds or severe changes in temperature and humidity, these changes were small and probably not sufficient to necessitate the use of temperature compensation to make them functional for Coast Guard use. As a result of the favorable results obtained in these experiments, a decision to test these sensors in the marine environment was made by an agreement of the project personnel with the technical monitor. Table 2 summarizes the performance criteria used in selecting the TGS sensor for immediate testing in the marine environment.

During the testing with the Esso sensor system, several failures were observed: (1) at low temperatures there were abrupt changes in oscillator frequencies which made the system nonoperational; (2) large changes in baseline voltages accompanied changes in temperature and humidity; and (3) no simple alarm logic was available which would permit signalling the presence of an oil spill without a large number of false alarms. As a consequence of the problems encountered, a decision was made to set aside the piezoelectric sensor system for the present. Elsewhere in this report, a summary of the test and evaluation of this sensor system is given along with an enumeration of the strong as well as the weak points for this sensor system.

TABLE 2. COMPARISON OF THREE OIL-ON-WATER VAPOR SENSORS FOR COAST GUARD USE

Evaluation Parameters	TGS	Esso	Wesmar 2.75 K
Sensitivity to Vapors (est.)	25 ppm	50 ppm	200 ppm
Power to Operate	0.4-0.9 W	0.48 W	< 0.4 W
Response Time	1-5 sec	1-5 sec	1-80 sec
95% Recovery Time	10-20 sec	5-15 min	1-8 hr
Humidity Effect	Slight	Slight	Slight
Temperature Effect	Small	Large	Large
Baseline Stability	Good	Very Poor	Poor
Signal/Noise Ratio	Good	Poor	Poor
Reliability	Good	Fair	--
Response to Vapors from Aged (24 hr) Films	Poor	Fair	None
Alarm Logic	Simple	Complex	Complex
Cost of System with Alarm Logic (approx.)	$500-2,000	$3,000-8,000	$2,500
Wind	Slight	No Effect	--
Smoke	Responds	Slight	--

F. Field Testing of Various Sensors

Testing of the TGS and Wesmar sensors in the marine environment was undertaken to prove their ability to detect fresh oil spills on water and their ability to reject interferences in an environment approximating that of buoys located along watercourses. Testing in the marine environment was expected to reveal the magnitude of possible interference problems and help in their resolution.

In the following sections of this report, testing and evaluation of oil spill detectors on three separate field trips to the Houston Ship Channel are described.

1. Field trip No. 1: A boat was chartered from Boat Town in Clear Lake, Texas. There is a direct water route from Clear Lake to the Turning Basin in downtown Houston via Galveston Bay and the Houston Ship Channel (Figure 21). It was expected that more small spills (usually 10 gal. or less) on water would be observed if the sensors were taken to the oil spills rather than by putting the sensors in a stationary location and waiting for the spills to come by. For this first test, the sensors were hung from the side of the boat; the electronic equipment was placed in the cabin and powered by the boat generator or by shore power while tied up at Boat Town (Figure 22). The sensors were operated continuously during the test and data from each sensor was recorded on strip-chart recorders.

Two types of TGS sensors were used, each with a different alarm logic. The TGS No. 202 sensor had threshold alarm logic. This logic was set to trigger an alarm when a preset threshold (variable from 1.3-2.7 V) voltage was exceeded. The TGS No. 308 sensor used a rate-of-change logic which would alarm when a voltage increase of 60 mV/sec was exceeded. Two strip-chart recordings were made for each sensor, one for the response profile and the other for the logic tracing.

Figures 23 and 24 show the response profiles of the TGS sensors while operating in the Houston Ship Channel. Various industries are located along the channel from one end to the other. Air pollutants from these industries were detected by the TGS No. 202 and No. 308 sensors. The alarm threshold logic with the TGS No. 202 sensor did alarm. To prevent these false alarms, the threshold level of the alarm was raised and could be raised even more. The rate-of-change logic with the TGS No. 308 sensor showed fewer alarms, even though the response profile showed detection of the natural gas odorizing plant. These figures also show that turning the boat around exposed the sensors to the boat's exhaust. This, in turn, triggered alarms in both sensors.

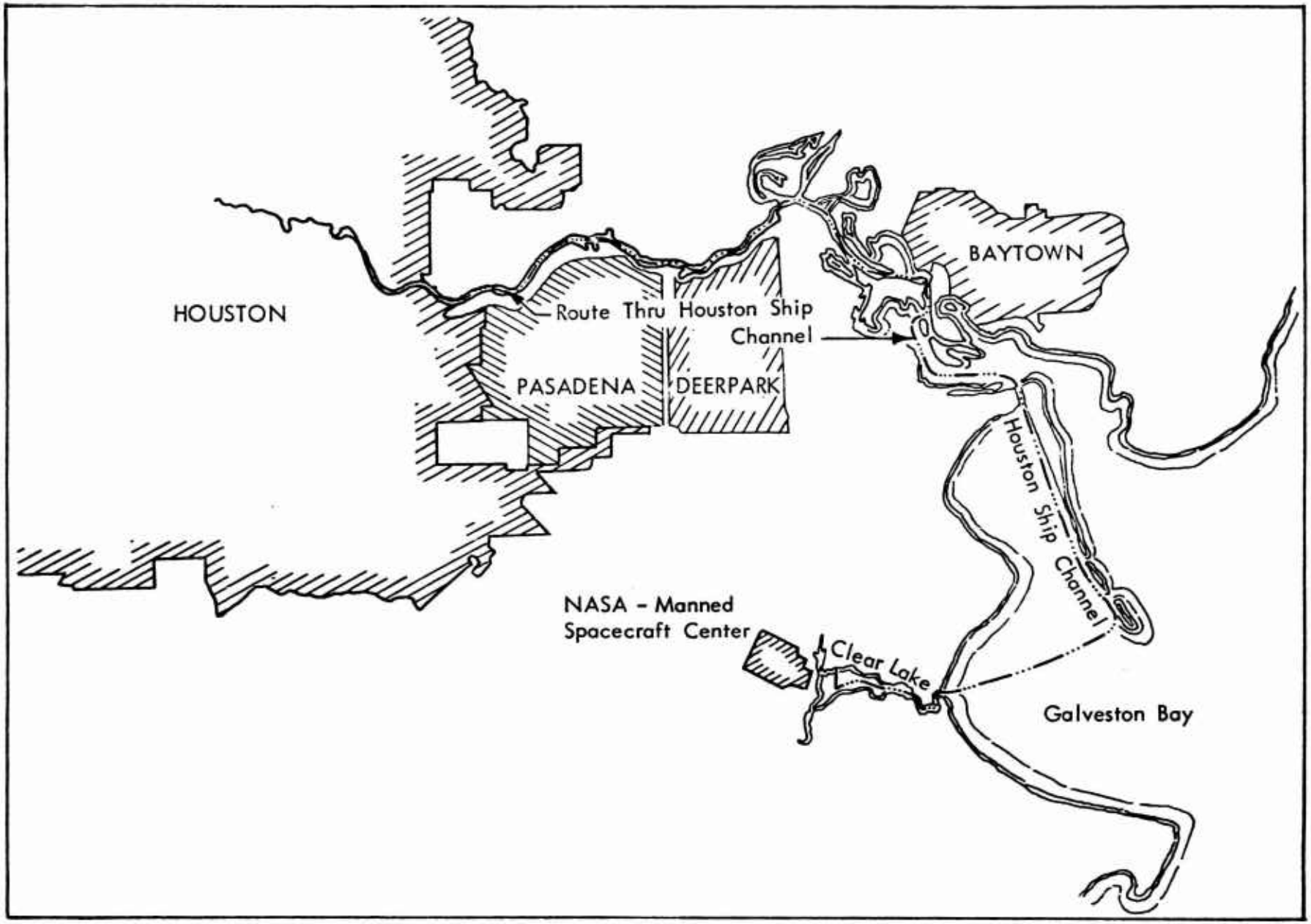


Figure 21. Map showing route taken in TGS sensor test.

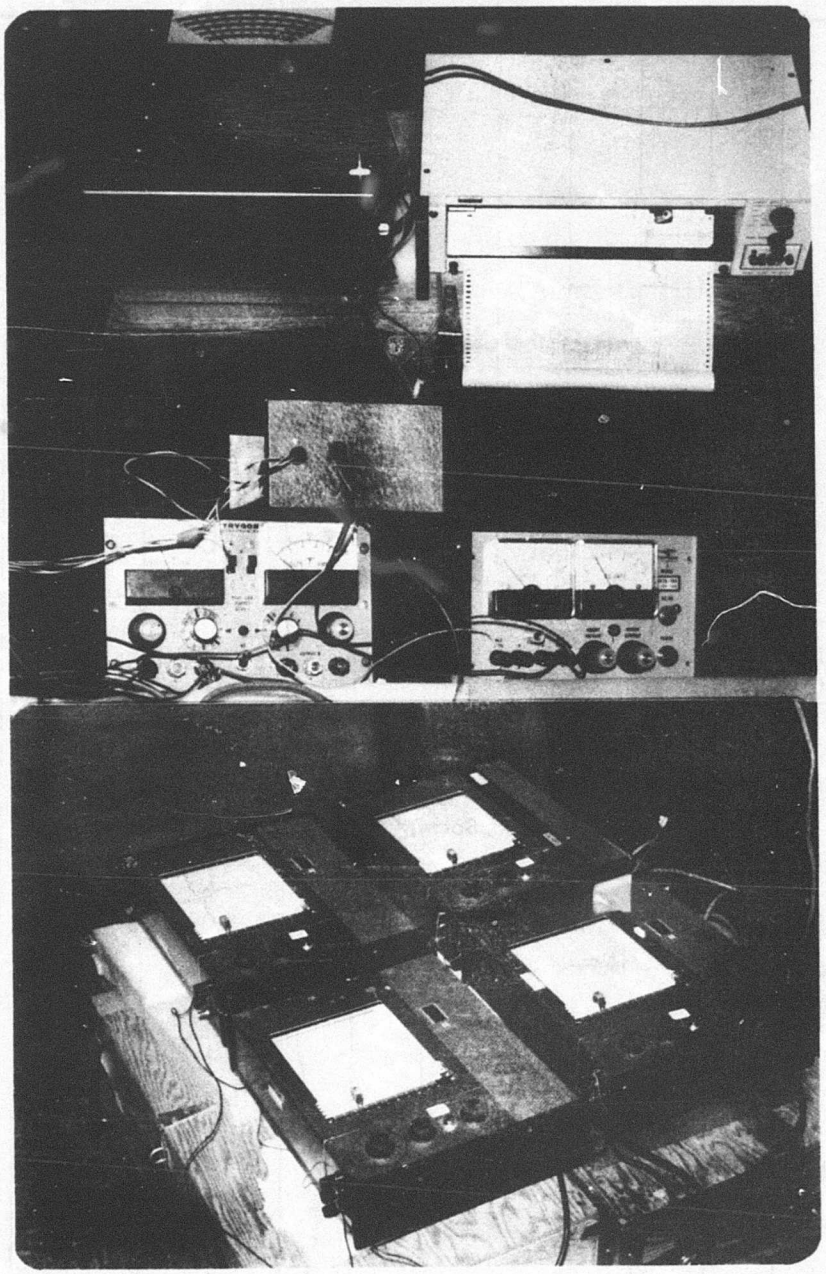


Figure 22. Apparatuś aboard boat in Houston Ship Channel. Wesmar sensor and recorder (upper); AC to DC regulated power supplies (center); strip-chart recorders (lower).

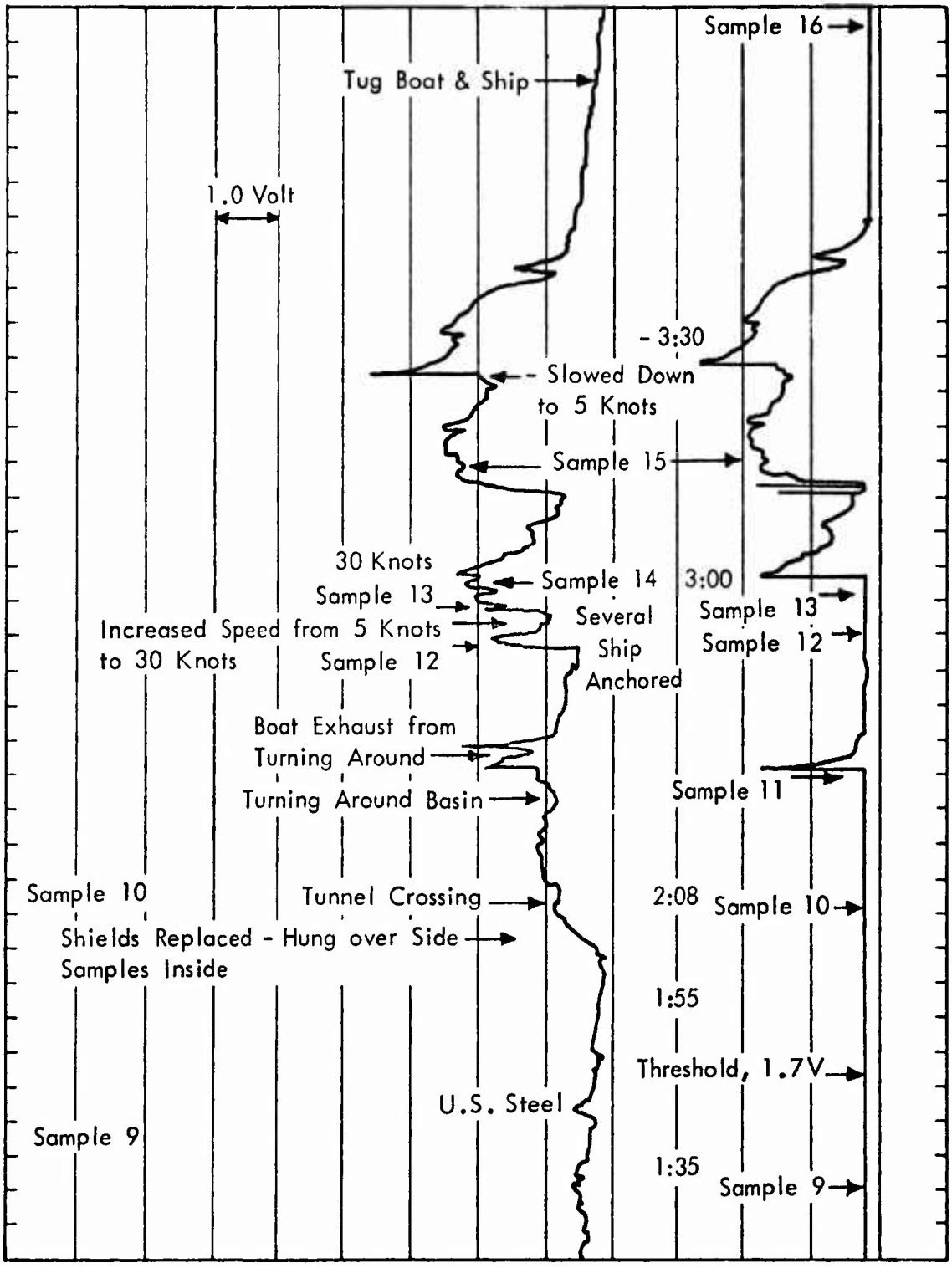


Figure 23. Response profile of TGS sensor No. 202 (left curve) and alarm threshold logic tracing (right curve) to various petroleum or industrial vapors along the Houston Ship Channel.

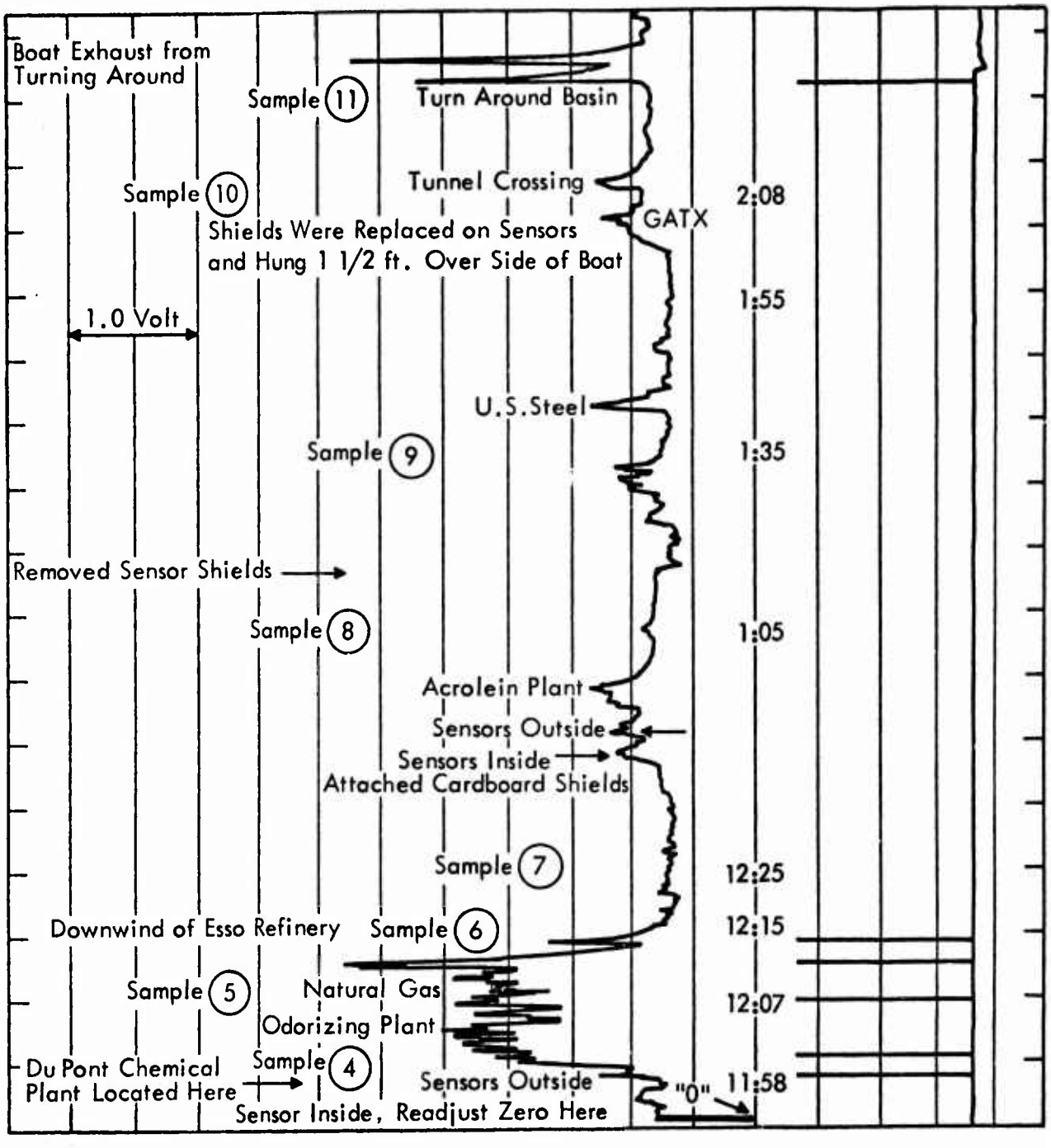


Figure 24. Response profile of TGS sensor No. 308 (left curve) and rate of change logic tracing (right curve) to petroleum vapors or effluents from various industries along the Houston Ship Channel.

During the 3 days of testing, no oil was observed in the Houston Ship Channel, Galveston Bay, or Clear Lake. The only slick encountered was the one accidentally made when the boat tanks were overfilled at the Boat Town fuel pumps (estimated volume of spill was 25 ml). Both the TGS No. 202 and the No. 308 sensors detected the gasoline. The TGS system with the rate-of-change logic gave an alarm, but the TGS sensor with the alarm threshold logic did not. The alarm threshold was set at 2.3 V at this time. This voltage was higher than the response to the gasoline, hence no alarm.

Since oil was not observed on the surface of the water on this first trip, it was not possible to move the sensors to it to see if or how long they responded. Some of the things learned on this trip, however, were the following:

1. When the boat turned around, the sensors responded to the boat's own exhaust.

2. A natural gas odorizing plant and an acrolein plant along the ship channel produced responses and, in one case, an alarm.

3. Both TGS sensors responded to the small spill of gasoline (around 25 ml) although only the rate-of-change logic signalled an alarm.

4. Operation of the TGS sensors for a 24-hr period on Clear Lake (except for one alarm) gave baseline data closely resembling the rooftop monitoring done in Kansas City.

5. No sensors failed during this 3-day test, although it was concluded that the sensors should be protected with a porous, thimble-shaped cover of ceramic material, an organic film such as silastic, or other material permeable to petroleum vapors.

The sensors were tested in the field with metal cylinder shields and cardboard extentions on the cylinders. However, testing showed that the sensors needed to be totally enclosed in a protective covering. Figure 9 shows two TGS probes which have been tested in the laboratory in a 1.68-cu ft environmental chamber. One probe possessed a stainless steel mesh cylinder attached to a wooden plug on which the TGS sensor was mounted. This framework was covered with a polyethylene membrane 0.001 in. thick. These were tested during subsequent field trips.

2. Field trip No. 2: A larger boat (this time 40 ft) was chartered for the second field test in the hope that it would be more resistant to wakes and rough water. As before, the electronic equipment was powered by the boat generator and the sensors were hung about 6 ft from the water along the side of the boat. The recorders and electronic packages were placed inside of the cabin.

Sensors tested were: (1) the TGS No. 202 and No. 308 with the inverter breadboards used in the previous field test, (2) two No. 202 and two No. 308 sensors operating from the dropping resistor breadboard, and (3) the VM-400 ceramic-coated sensor from Environmental Measurement Systems, Inc. In this test, no alarm logic was used; instead, continuous recordings were made with each sensor with the intention of fitting an alarm logic to the data after returning to the laboratory. Frequent standard exposures were performed throughout the 3 days of testing to show that the systems were functioning and responsive to hydrocarbon vapors. The standards, prepared in advance of the trip, were a mixture of 1.0 ml No. 1 fuel oil and 20 ml water in a tightly-capped plastic bottle. Response of each TGS sensor (10-sec exposure) and the VM-400 sensor (30-sec exposure) to the standard was recorded on the strip-chart recorders.

Initially, only one TGS No. 202 sensor was enclosed in a polyethylene membrane. The baselines for the uncovered sensors proved to be noisier than desired. As a result, these sensors were covered with the same type membrane used for the covered No. 202 sensor (see Figure 9). With the sensors totally enclosed, the noise level was diminished and the response level to the standard hydrocarbon exposure was decreased to 0.3 V from a previous level of 6 V. Because of this, the ends of the polyethylene covers were cut off so the cylinders were open to the air and the open end pointed down. Thus resulted in a better response to the standard, but still allowed the sensors some protective shielding.

While monitoring the water in the ship channel, the wind was usually from the south. This was unfortunate because most of the refineries and industries were also located on the south side of the channel. This resulted in our sensors responding to the air pollutants from the refineries. The sensors were hung on the port side of the boat which provided some shielding from the air pollutants when the boat was headed towards the bay.

The first small patch of oil seen was located across from the Coast Guard facility. The initial response to the oil was much larger than after the boat had turned around and passed through the oil a second time (see Figure 25). This lesser response may be due to spreading of the oil slick by the boat and by the decreasing concentration of oil present when the second pass through the oil was made. Figure 25 also shows the large responses of the TGS sensors to the boat exhaust, this was a problem when turning the boat around to pass through the oil again. Later, another patch of oil by the Crown Refinery was detected, but no return pass was made. Even though the TGS sensors are capable of detecting air pollutants from the refineries and industries, the response to them was lower than the response levels to oil patches in the channel.

The Vapor Monitor VM-400 sensor unit and data obtained from tests conducted at Environmental Measurement Systems at a temperature range of 32-48°F, were received the afternoon before our sensor equipment was to be shipped to Houston. Recorder tracings showing response and noise levels were not received with these data. Their test results are summarized in Appendix I and show that the sensor responds well to crude oil and diesel fuel. Because the data looked promising, the unit was included in the field test.

Only brief laboratory tests had been performed to assure that the sensor was working before it was packed and sent to Houston. The VM-400 ceramic sensor was operated at its most sensitive settings (Van der Waals = 5, Multiplier = A, 0-10 ppm) for almost all of the testing in the Houston Ship Channel. During this testing, the operating temperatures were from 50-80°F. A few tests were done with a Multiplier setting B, 0-100 ppm. This appeared to be too insensitive a level for monitoring because the baseline was flat and did not respond to oil or anything else. As can be seen in Figure 26, the noise level of the VM-400 sensor is very high and the sensor also had to be manually readjusted frequently throughout the field test to keep it on scale. Inadequate temperature compensation and slow response to oil were problems. It was our decision to discontinue further testing of this unit.

In general, it may be concluded that the two types of TGS sensors performed equally well during the second field trip. However, there were some equipment failures which should be mentioned. The inverter breadboards operating one TGS No. 202 and one TGS No. 308 sensors failed. In one system, there was a short and in the other system, there was a failure which resulted in loss of sensor sensitivity. However, none of the TGS sensors themselves failed during the field test (as shown by sensor test after return to the laboratory). Failure of the inverters is not considered to be a serious problem since these will not be used in the buoy systems.

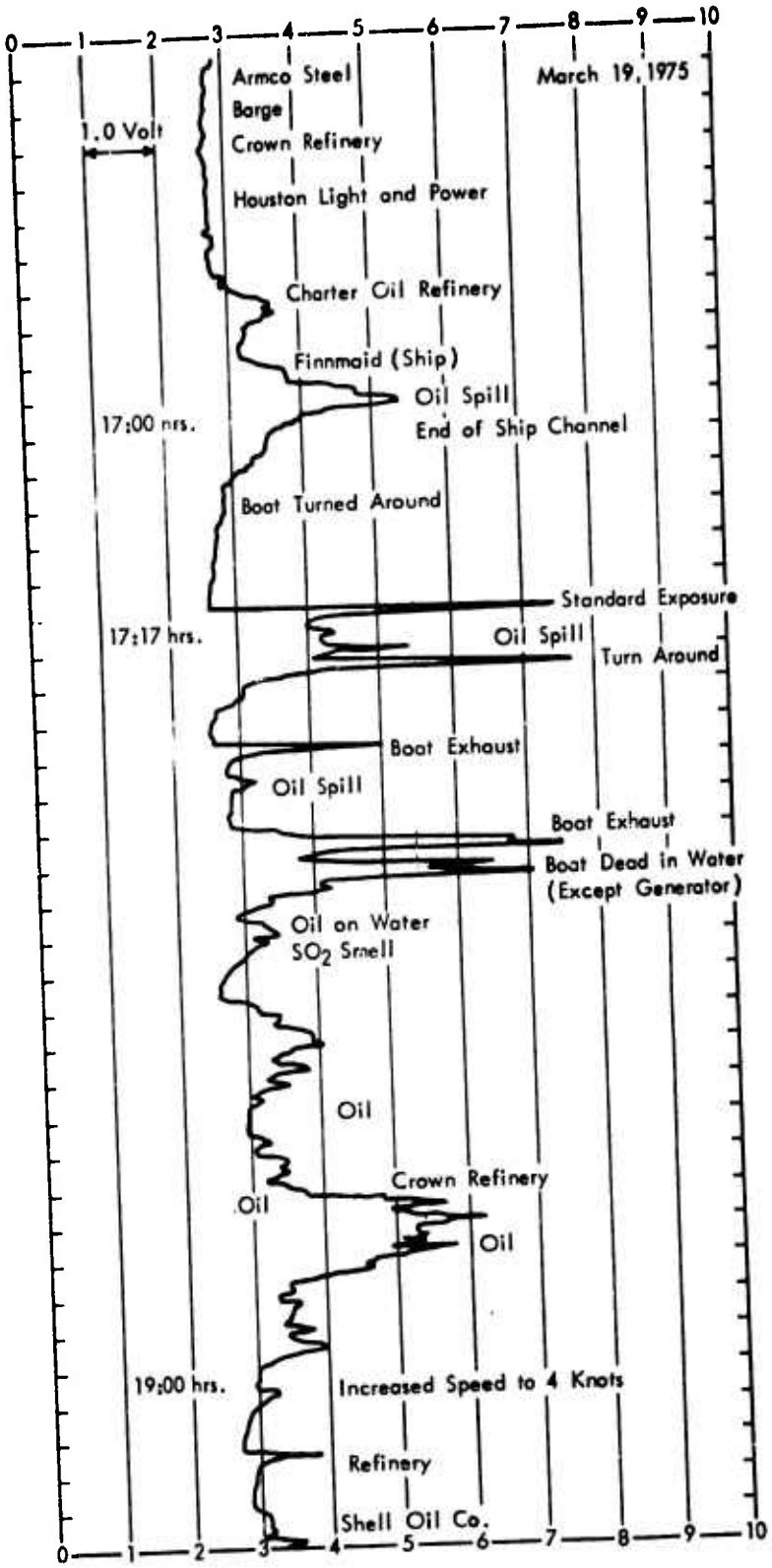


Figure 25. Response profile of TGS sensor No. 202 to oil and air pollutants in Houston Ship Channel.

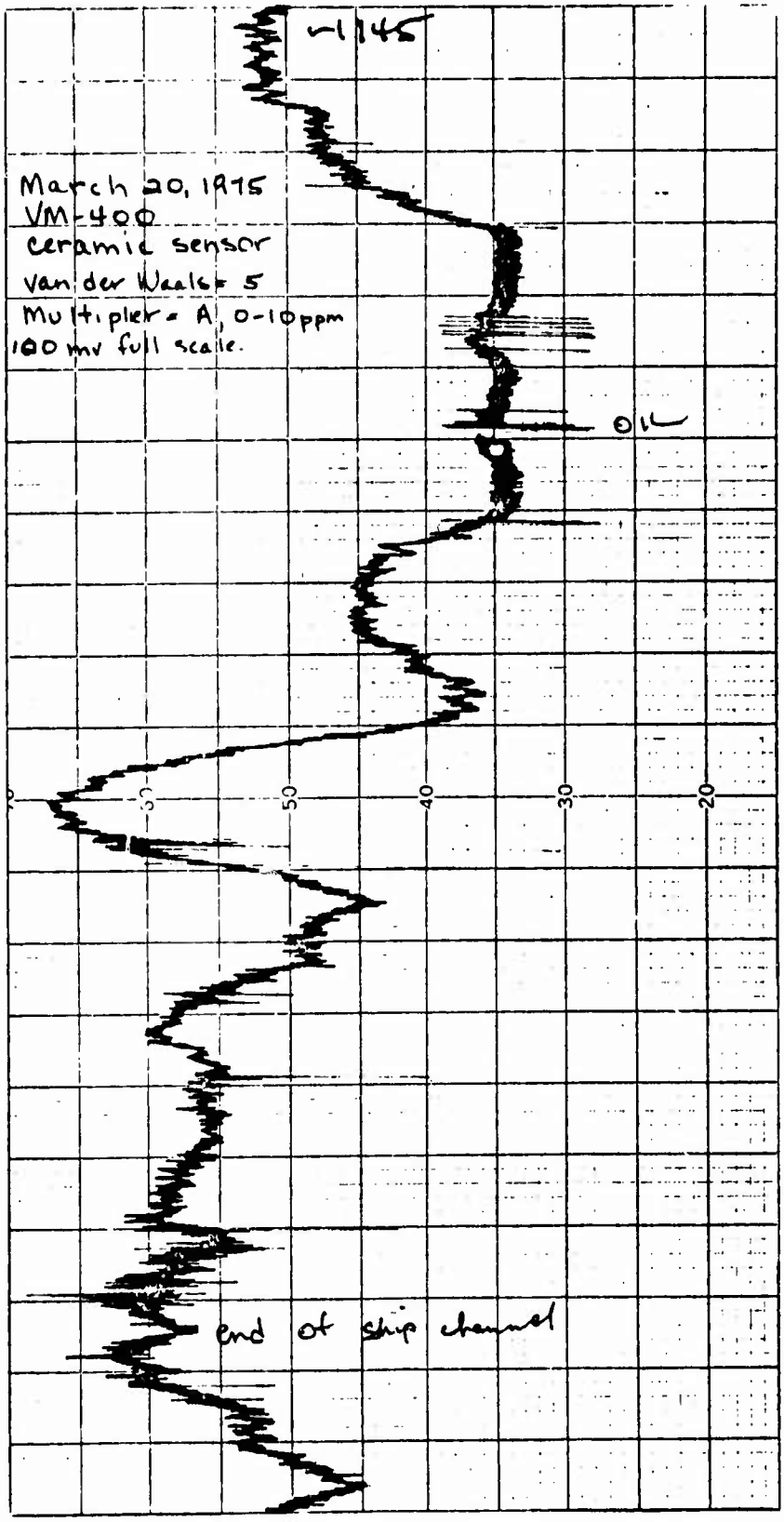


Figure 26. Response profile of ceramic enclosed VM-400 sensor to oil in Houston Ship Channel.

From the test, it was concluded that alarm logic can probably be chosen which will eliminate response to most of the airborne pollutants at the concentrations experienced during the field test. However, ship and boat exhausts are a problem and investigation of methods of reducing response to these interferences without eliminating response to the hydrocarbons is needed.

3. Field test No. 3: A third field test was conducted with the sensor equipment mounted on a boat; it started at Clear Lake and moved to the Houston Ship Channel as in the two previous field trips. Severe weather was encountered with the result that the large waves passing over the boat shorted out the test equipment and the test was temporarily halted. After a return to MRI to repair the equipment, the test was resumed. The various objectives of this field test No. 3 were as follows:

1. Evaluate alternate methods for packaging the sensors so that they would be protected from water and still respond to vapors.

2. Determine the best elevation of the sensors above the water so as to maximize the response to oil vapors and minimize the response to air pollutants.

3. Compare the two new 5-V TGS sensors with TGS sensors which had been investigated previously (i.e., TGS No. 202 and No. 308) under the marine environment.

4. Find out if membrane covered sensors give improved discrimination between oil vapors and diesel exhaust.

5. Gain more information about the relative magnitude of responses to interferences and to exhaust which could be used in selecting alarm logic for use with sensors on buoys.

a. Apparatus for test: Figure 27 shows a diagram of a sensor support containing 12 sockets at 2, 4, and 6 ft above the surface of the water after it was mounted to the front of the boat. In Figure 28 an enlargement of one of the sockets fitted with a sensor and with a 4-in. length of PVC pipe (1 in. ID) arranged to provide a windshield and splash protection is shown. A 1/4-in. hole was drilled in the side of the PVC pipe to speed the movement of the vapors to the sensor.

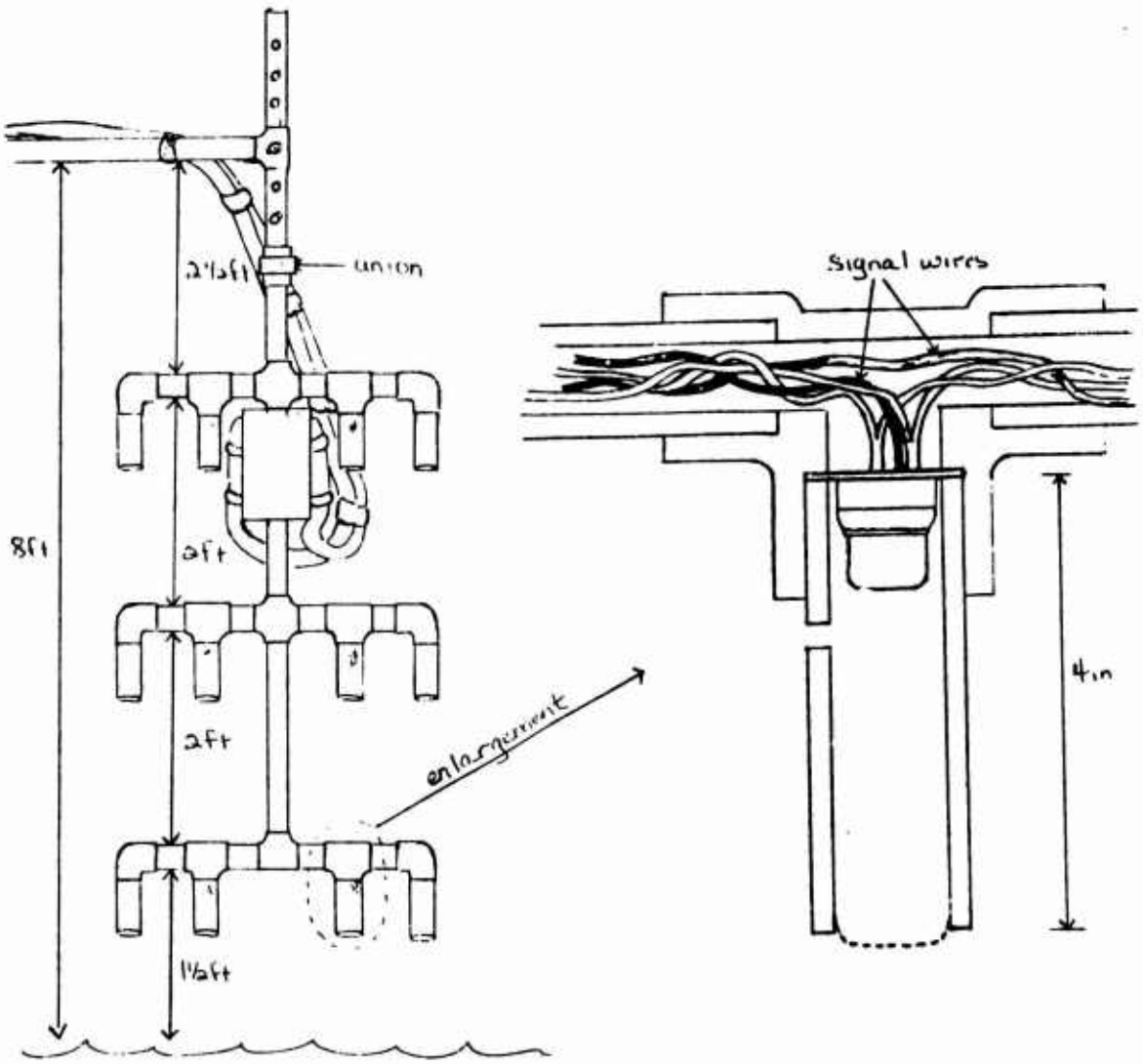


Figure 27. Diagram of sensor tree and detail of PVC-cylinder covered sensor socket.

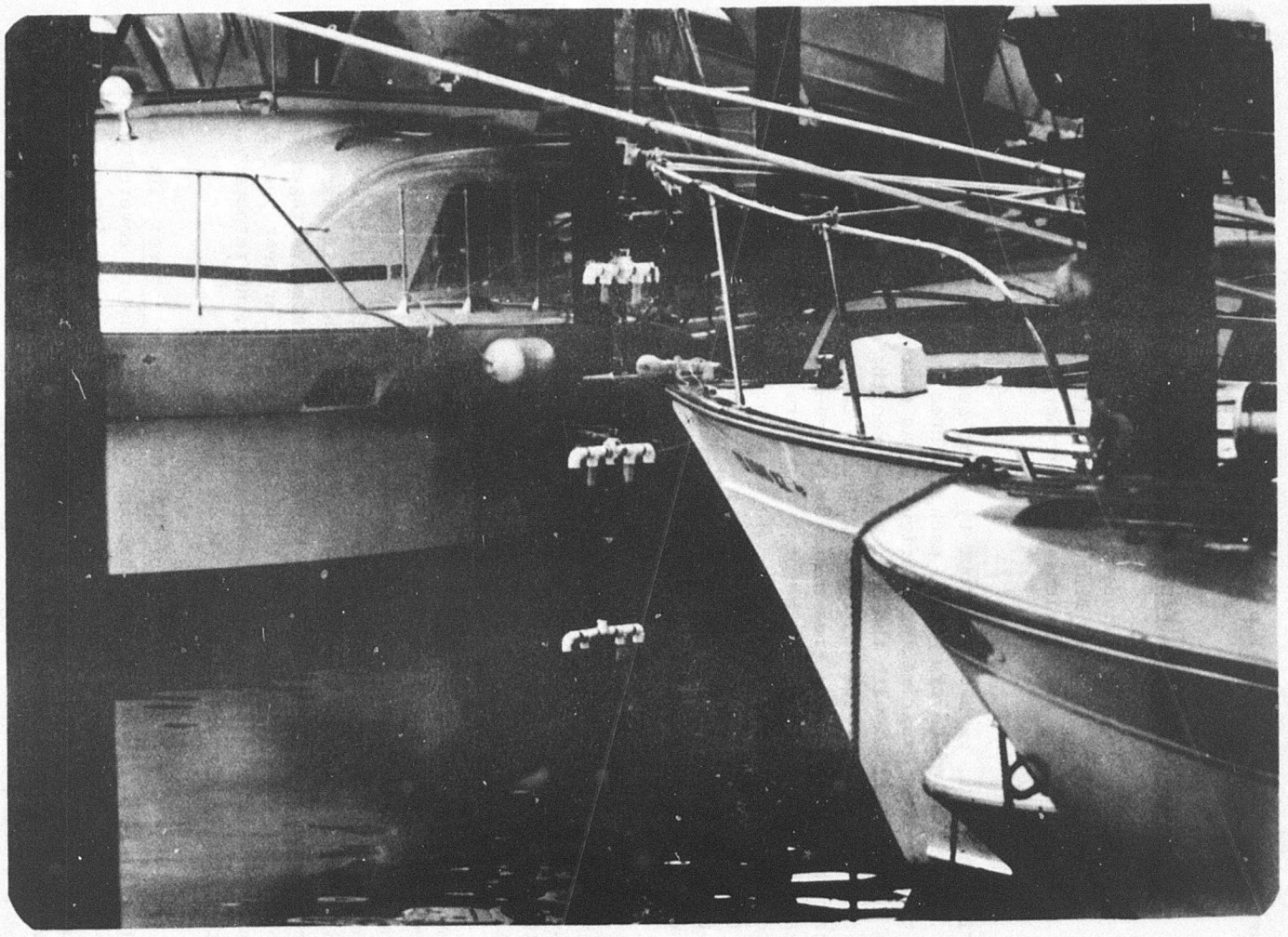


Figure 28. Bow of boat with sensor tree positioning the sensors at 2, 4, and 6 ft above the water.

During the week-long test period, the variables investigated included:

TGS Sensors	Kinds of Covers	Height Above Water
No. 202	PVC Cylinder (with screen in end)	2 ft
No. 308	50 Mesh Brass Screen Cylinder	4 ft
No. 711	Polyethylene Bag over Screen Wire	6 ft
No. 812		

During the test, each of the four types of sensor was tested with each of three kinds of covers and at each of three heights above the water. In the previous experiments, difficulty was encountered in maintaining the heater voltages with the long wires from the cabin to the sensors. In this experiment, the voltage regulation components were located in a metal box on the sensor tree close to the sensors; the recorders were located inside the cabin as before. No alarm logic was incorporated into any of the sensor circuits. In an effort to improve the precision of the recorded data, a standard bias voltage was introduced from time to time to calibrate the system and to assist in calculation of the actual voltages generated by the sensors.

b. Performance of TGS No. 711 with screen cover at Clear Lake: Figures 29a and 29b show a 9.5-hr baseline tracing obtained at Boat Town Dock. At 23:30 hr, when the tests were begun, the baseline voltage was around 3.8 V; at the conclusion of the test, the voltage had fallen to approximately 2.3 V. The gradual drop in baseline voltage may be attributed to the lower heater current on this sensor and the longer time period necessary to establish the minimum baseline voltage. As shown in the Technical Data Sheet for this sensor (see Appendix II), the manufacturer recommends the use of a higher voltage to clean the semiconductor chip after which the lower voltage provides good sensitivity and probably extended operating life. This conclusion is based on the observation that use of voltages higher than the rated voltages tend to shorten the life of the sensors. During the 9-1/2 hr test period, there was very little voltage fluctuation and, obviously, no response to either oil or air pollutants.

c. Performance of the three sensor covers: The largest and most rapid responses were obtained with the sensors covered with the 50-mesh brass screen wire cylinder. However, the protection of the sensor from drowning was poor as shown in Figure 30. In this case, the covered sensor was mounted about 1-1/2 ft above the water; but the wake from a passing boat was large enough so that it hit the boat with sufficient force to splash on the sensors and soak them.

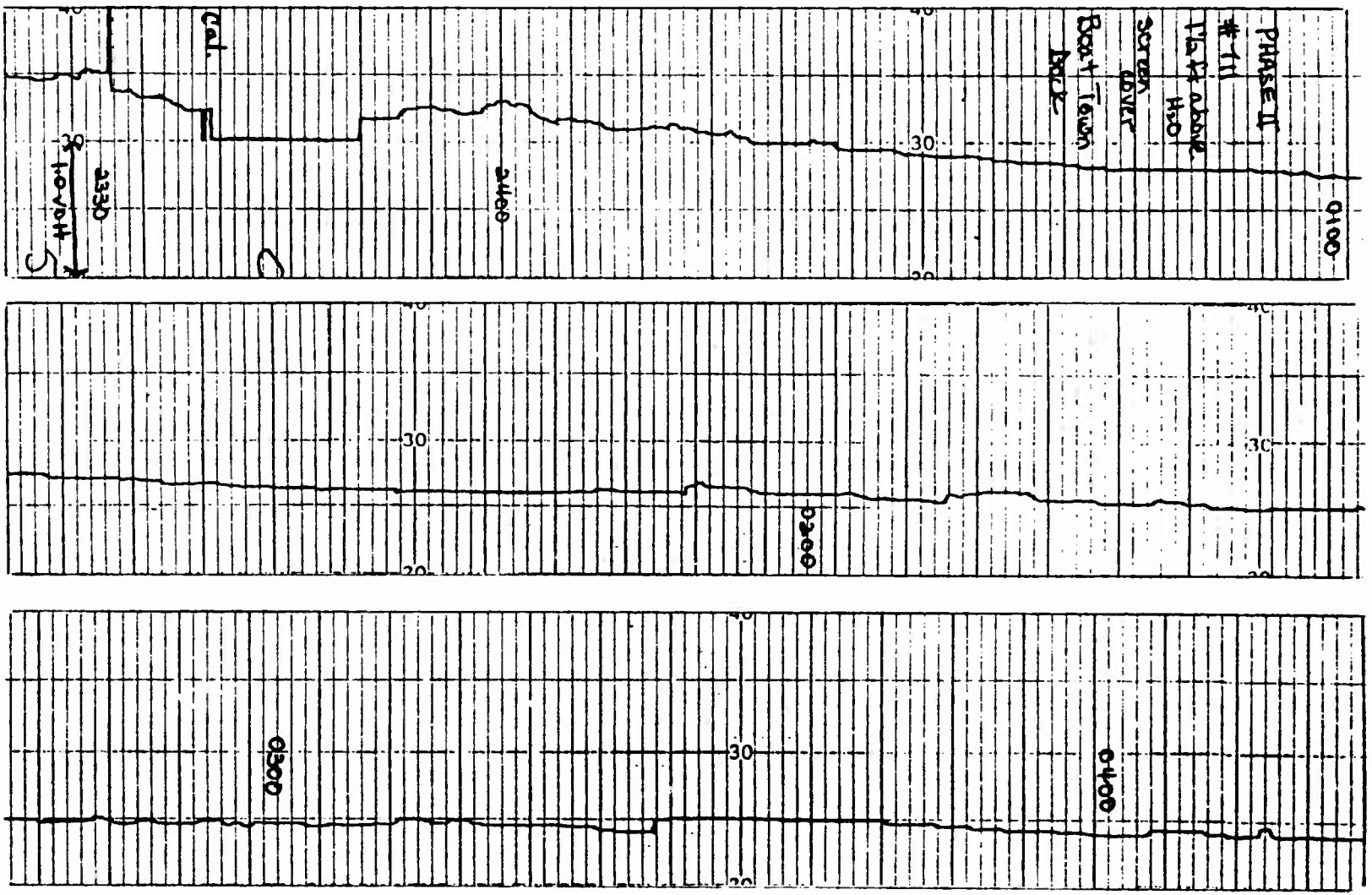


Figure 29a. Nine and a half-hour strip-chart tracing of TGS sensor No. 711 operating in Boat Town Dock (continued in Figure 29b).

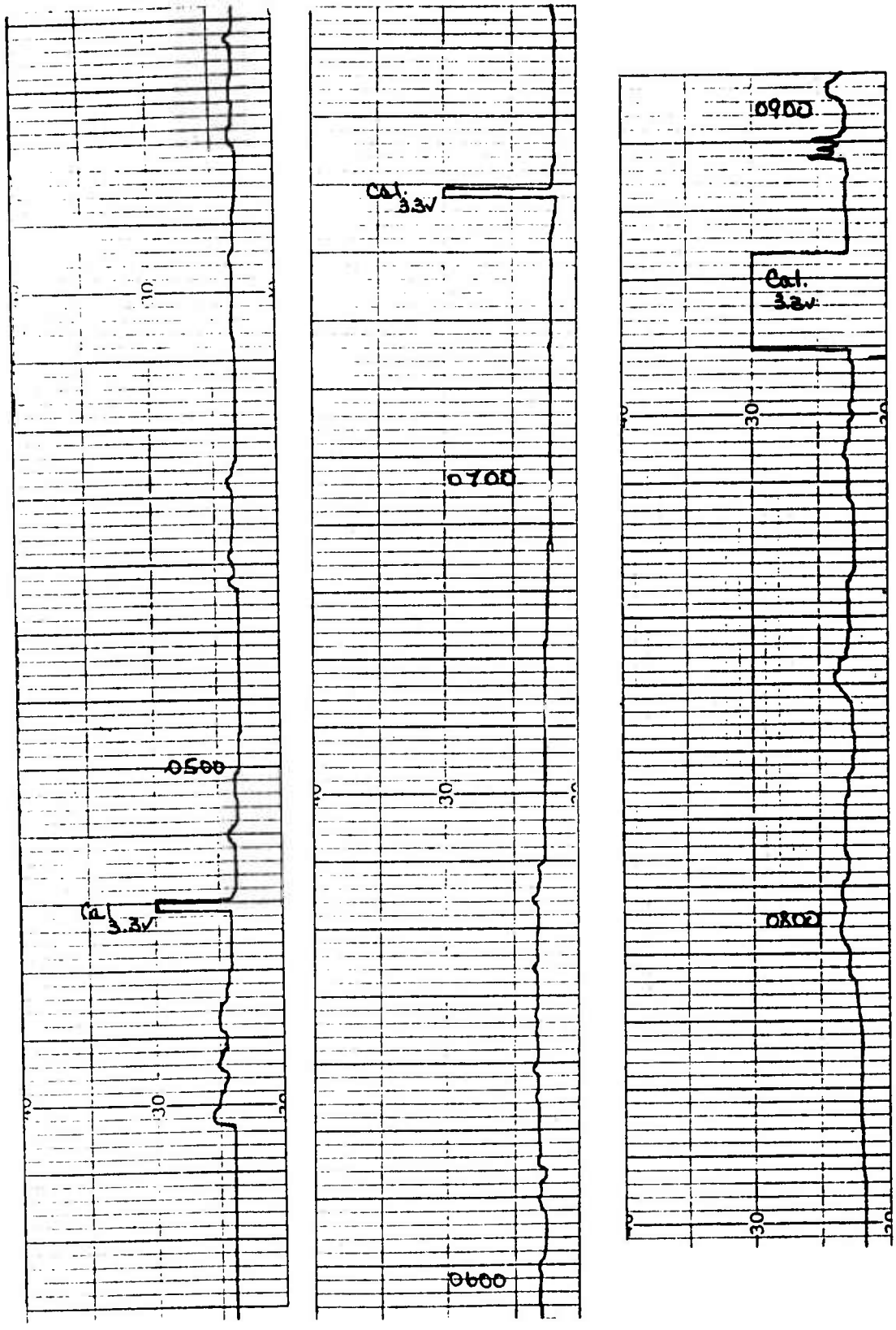


Figure 29b

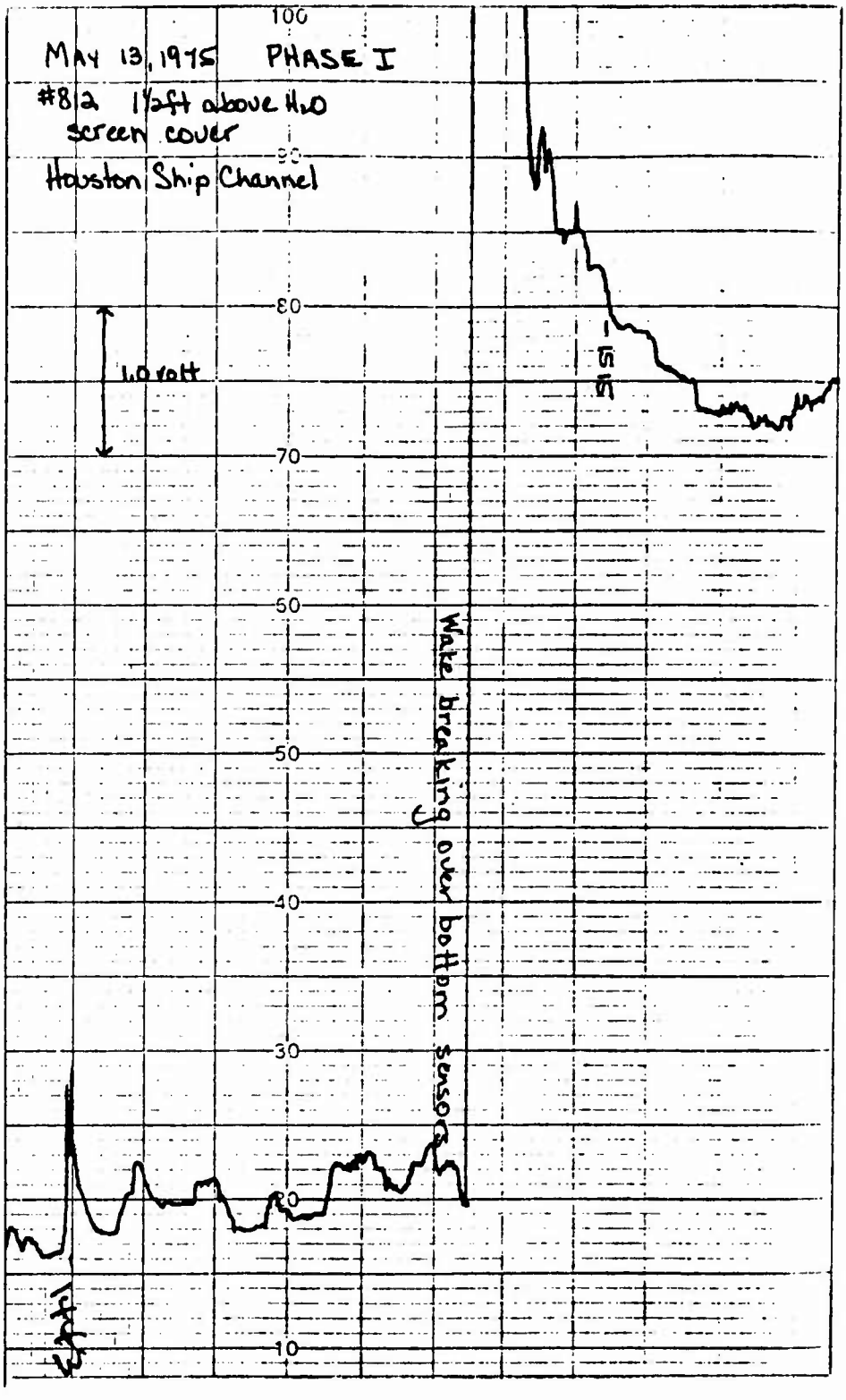


Figure 30. TGS No. 812 sensor with screen cover showing the effect of water splashing on the sensor.

As may be seen, the sensor shorted out and the baseline voltage rose at least 8 V. Recovery of this sensor was slow. From this it was concluded that the 50-mesh screen wire did not offer enough protection from splashing water.

At this point, the remaining 50-mesh screen sensors were covered with 1.0-mil polyethylene bags held on with rubber bands. Response of these sensors with standard vapors was greatly reduced unless long periods of exposure were used. These covered sensors were unsatisfactory since the bags tended to trap water instead of keep it out; the use of room temperature vulcanizing (RTV) silicone rubber to seal on the bags may have caused problems because the fume given off by the curing rubber caused high baseline voltages with the sensors. Curing of the rubber seals in an oven should remove the troublesome vapors.

The most satisfactory of the sensor covers used in this test were the PVC cylinders which were open at the bottom with wire screen. These sensors gave smaller responses to the hydrocarbon vapors and were slower to respond; but they were out of service only momentarily when they were completely submerged (see Figure 31).

The optimum packaging of the sensors on buoys has not yet been established; it should be noted, however, that sensors on the 4- and 6-ft levels did not fail in any of the tests. Since responses were better at the 4-ft level, it is proposed that further tests be done with sensors 3 to 4 ft above the water.

d. Interference problems: In the Houston Ship Channel, responses have been noted to various air pollutants, including those coming from an acrolein plant, those from a gas odorizing plant, gasoline engine exhaust, and diesel engine exhaust. Figure 32 presents portions of response curves for three sensors operated simultaneously in the Boat Town Dock during the early morning hours when the air was relatively quiet. It may be seen that the curve for the TGS No. 202 sensor gave large responses whereas neither the No. 812 nor the No. 711 sensors gave large responses. Since no observers were on duty at that hour, we can only guess as to the reason the responses were different: (1) according to the company literature, the TGS No. 202 sensor has an extreme sensitivity for carbon monoxide whereas the other two sensors do not; and (2) another explanation for the differences in response may be that different concentrations of the pollutant vapors reached the different sensors. This latter explanation, however, seems unlikely to be correct since all sensors had the PVC cylinder covers and since the No. 202

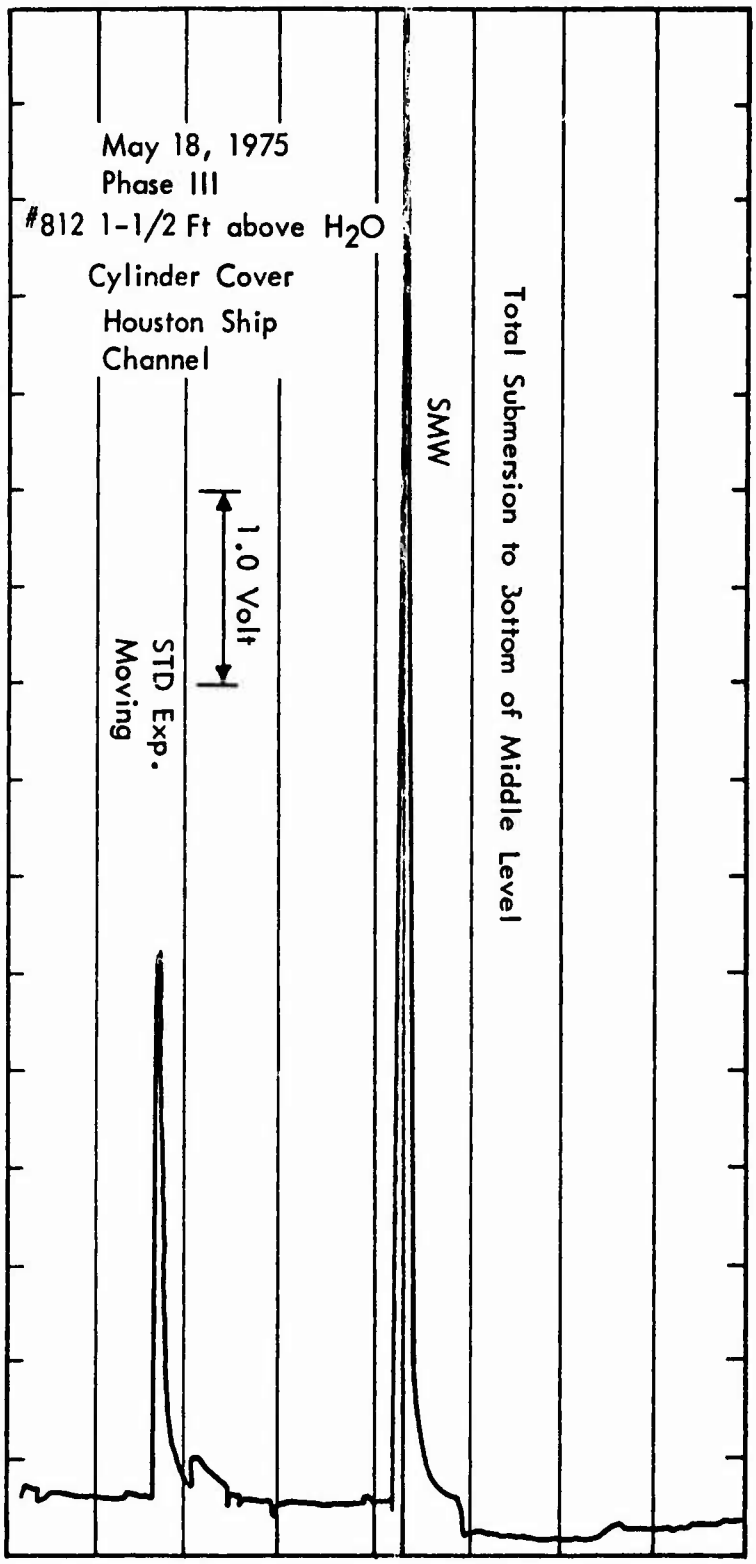


Figure 31. TGS No. 812 sensor with PVC cylinder showing the effect of total submersion in water.

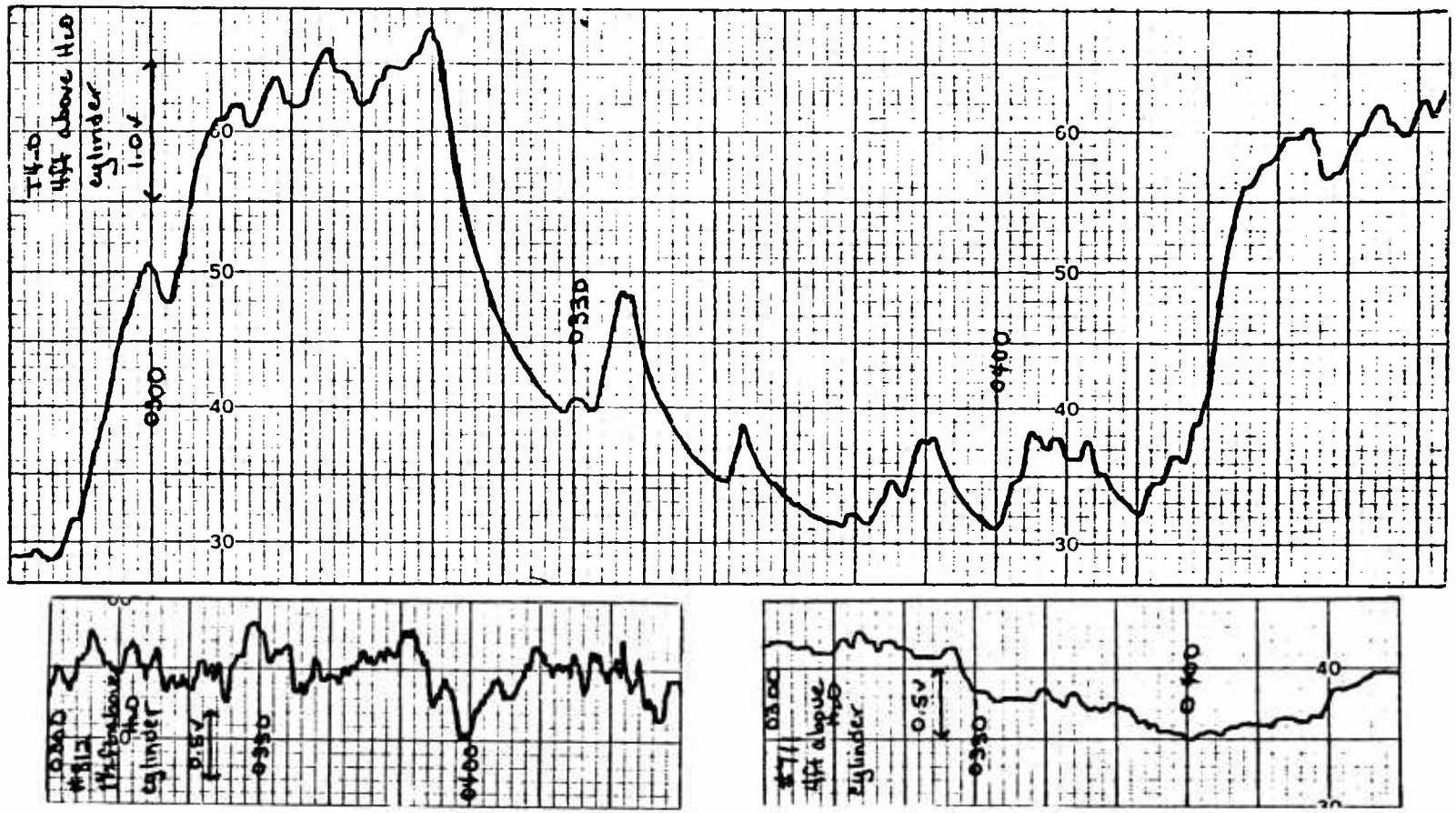


Figure 32. Simultaneous baseline tracings of sensors TGS No. 202 (upper) TGS No. 812 (lower left) and TGS No. 711 (lower right) in Boat Town Dock (boat was operating on shore power). Chart speed was greater for upper curve.

which responded well was less than 24 in. from the sensors which gave weak responses. As a result of this experiment, it was decided that the TGS No. 202 was less suitable than the other two sensors for use on buoys.

e. Comparison of the TGS No. 812 and the TGS No. 711 sensors: Figure 33 shows the tracings obtained in the Houston Ship Channel from the TGS No. 812 and the TGS No. 711 sensors joined together so that responses to specific pollutants can be compared. Time is shown on the charts and was used to help align the specific events. The abbreviation "Cal" at 11:05 hr indicates the calibration of the electronics and recorder package by momentarily substituting a known voltage for the sensors voltage. These fixed voltages enable the calculation of the actual voltages for each sensor at any time during the tests. At about 11:40 hr, the two sensors were given standard exposures to 1 ml of JP-4 and 20 ml of water in a 500-ml jar. Both sensors gave large responses instantaneously; however, the TGS sensor No. 711 recovered much more slowly than the TGS No. 812 sensor. This was not an altogether unexpected finding since it was known that the TGS No. 711 sensor was operating at a lower temperature and was reported to require the momentary application of a higher heater voltage to obtain rapid heat cleaning of the sensor surface.

At approximately 12:40 hr, brown oil was spotted on the water. The responses to this oil were quite disappointing; however, samples of this oil were collected and brought back to the laboratory where they were tested with the TGS sensors under laboratory test conditions. These samples gave better responses in the laboratory; but the small magnitude of the responses indicated that these were low in volatile materials.

Blue oil was seen on the water at about 13:50 hr; here again, it was judged that this was either motor oil or a residual oil with low vapor pressure. At 14:10 hr, near the Armco Steel plant, oil was spotted on the water and was reported by radio to the Coast Guard. This spill was estimated to have amounted to several gallons and it produced responses of more than 1.0 V with the TGS No. 812 sensor, indicating that it was a fresh spill and contained some larger proportion of volatile materials than was present in the brown and blue oils seen earlier.

At 17:00 hr and also at 17:05 hr, no oil was seen but good responses were obtained to exhaust from a tug boat and also from the exhaust of the boats which had congregated at Riverside Inn.

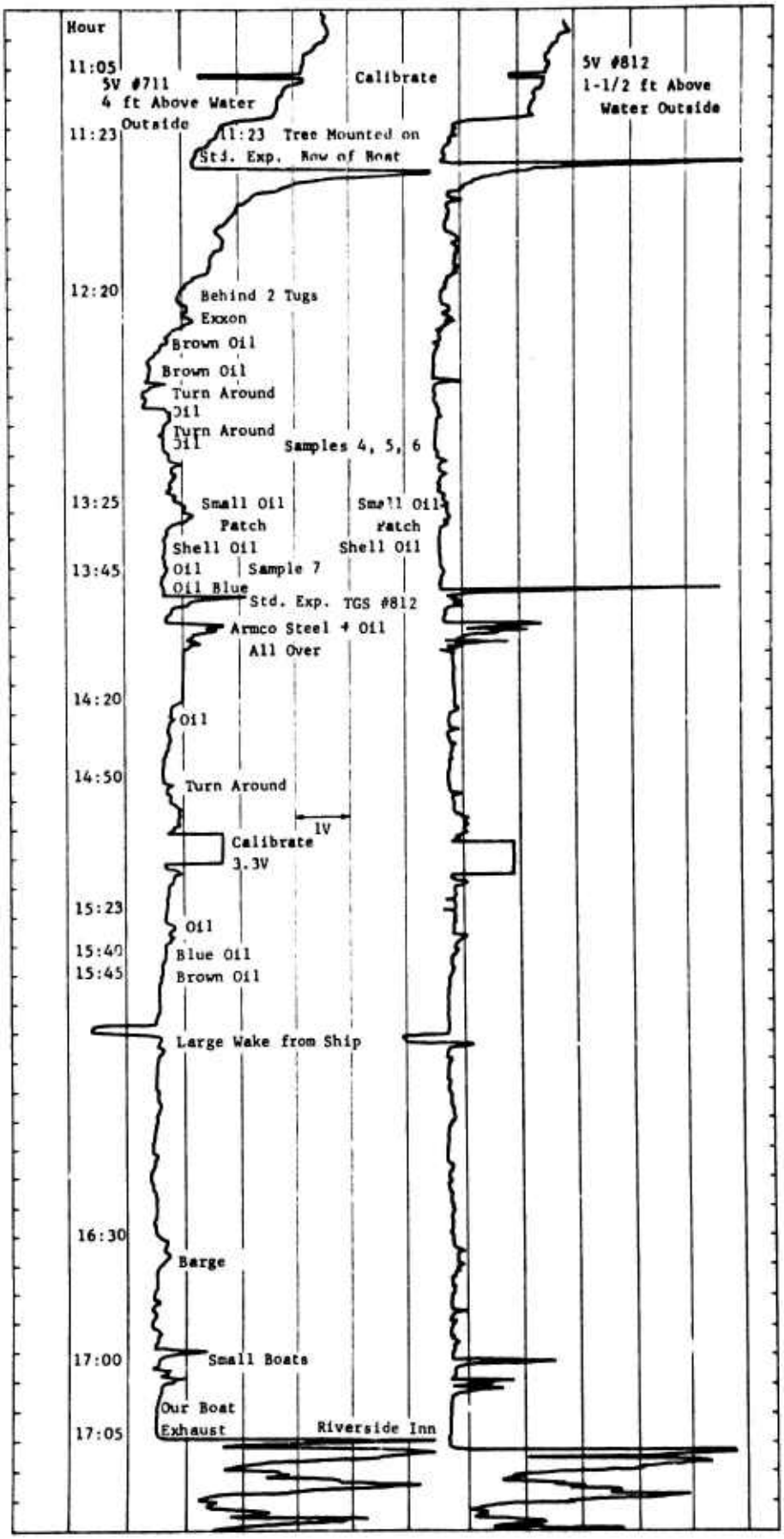


Figure 33. Side-by-side comparison of two 5-V TGS sensors (No. 812 and No. 711) operating from a boat moving at 5 knots/hr in the Houston Ship Channel (see text for details).

On the basis of the data presented, it was concluded that the No. 812 sensor was superior to the No. 711 sensor because: (1) the No. 812 sensor recovered more quickly following exposure to hydrocarbon vapors; (2) because there was less fluctuation in the baseline voltages; and (3) the responses to oil were as large or larger than the responses with the No. 711 sensor. The failure of either sensor to give large responses to the oil spills is attributed to the (1) presence of wind moving at 3-13 knots, which diluted the vapors, (2) the movement of the boat at 1-1/2 to 5 knots through the oil slicks, (3) the absence of a high proportion of volatile hydrocarbons in the oils spilled, and (4) the failure of the vapors to reach the sensors quickly due to the use of plastic cylinders and screens over the ends of the cylinders. That is, the vapors diffused to the sensors so slowly that the response was reduced.

III. SUMMARY OF LABORATORY AND FIELD TESTS

After laboratory and/or field testing of the Esso oil-on-water piezoelectric sensor system, the Wesmar Water Surveillance Monitor (the Adhistor), and the TGS semiconductor gas sensors, the following conclusions have been made:

1. The piezoelectric sensor system with the silicone-rubber-coated quartz crystal sensor is able to respond to hydrocarbon vapors by changing its vibrational frequency. In the apparatus submitted to MRI for evaluation, changes in crystal frequency also occurred as a result of changes in temperature and humidity; and these were only partially compensated for through the use of reference crystals exposed to the same or a protected environment. As a result of difficulty in maintaining a stable baseline voltage with the system in environmental testing during both cold and warm days and the lack of an alarm logic to signal the presence of a spill, MRI concluded that the piezoelectric system was not yet ready for buoy testing. This conclusion was reached without consideration of the weight, complexity, or probable costs of units for use on buoys.

2. Studies of the Environmental Measurement Systems Water Surveillance Monitoring System which utilized an "Adhistor" sensor for sensing hydrocarbons on water were undertaken because the company claimed outstanding performance for their instrument and because it offered a potential method of lowering the power requirements for buoy-mounted sensors. Studies with this system at MRI were conducted at the same time that developmental work was proceeding at the Environmental Systems Laboratories with the result that on three occasions, the company

submitted new sensors claimed to possess "quicker response" capabilities, "greater sensitivity," and "temperature compensation." On the basis of incomplete data submitted by the EMS Company, the Wesmar sensor was taken to the Houston Ship Channel for a side-by-side comparison with the TGS semiconductor sensors. On the basis of this test, it was concluded that this sensor system (1) was too slow in its response to hydrocarbons, (2) possessed less sensitivity than the TGS sensors, (3) on several occasions failed to respond to oil on water which had been detected by the TGS sensors, and (4) gave baseline fluctuations which exceeded the responses to oil which were observed. It was concluded that this system was not applicable for use on buoys. Although the Wesmar sensor had been reported capable of detecting oil spills while it was submerged in water, our preliminary laboratory tests failed to confirm this report. The sensor did respond when liquid hydrocarbons contacted it; but the recovery of the initial baseline took hours or days, depending upon the nature and amount of the hydrocarbon.

3. The Taguchi Gas Sensors (TGS) supplied by the Figaro Engineering Company were chosen by MRI for extensive field testing and for use in a prototype pollution sensor system for use on buoys. This selection was based upon extensive testing both in the laboratory and also in the marine environment. A few of the reasons for this selection are listed below:

*The sensors are sensitive to hydrocarbon vapors at levels as low as 5-25 ppm.

*The sensors give baseline voltages which are stable and reproducible for extended time periods.

*Temperature and humidity have little effect on the baseline voltage. The electrical noise produced by wind is readily eliminated by protecting the sensors from direct blasts of air.

*The responses are short and usually reach a maximum in a few seconds.

*Recovery after exposure is rapid and complete.

*The sensors are known to retain their sensitivity for periods of at least 6 months of continuous operation.

*The sensors are inexpensive with cost-per-sensor ranging from $2.00 for the 1.0-1.5 V heater models up to $7.00 for the 5-V heater models.

*The sensors recover their sensitivities even though totally immersed in sea water.

*The heaters require only about 0.4 W during operation.

*The sensor itself can serve as a relay so that alarms or other signalling devices may be operated without relays or sophisticated electronics.

IV. RECOMMENDATIONS

Experiments described in this report show that the TGS sensors have much promise for use on buoys for pollution surveillance. However, several tasks remain to be completed before the full potential of these sensors can be realized. We are now recommending the completion of the remaining tasks which are described here:

Task I - Design and construct an experimental prototype oil detection buoy using a 12-V battery power supply and TGS sensor with its electronics package. The TGS sensor should be packaged so as to provide the maximum protection from the water without unduly blocking the movement of vapors to the sensor. Cables are to be used to transmit signals to the recorders.

Task II - Install the prototype buoy system in a suitable test site, possibly the Missouri River, where the buoy sensor electronics and sensor packaging can be checked. After all systems are functioning in a reliable manner, move to other test sites for additional checkout.

Task III - Conduct long-term field evaluation including some additional effort close to the laboratory and as much time as possible in a marine environment in which oil spills occur frequently. Testing in the Houston Ship Channel is recommended. Total test time should exceed 6 months.

Task IV - On the basis of the long term field evaluation design an operational prototype of the buoy-mounted sensor for incorporation in battery powered Coast Guard Aids-to-Navigation Buoys. This task should include the preparation of design layouts, drawings, and the design interfacing with Coast Guard telemetry systems.

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1. Tetsuro Seiyama, Akio Kato, Kiyoshi Fujiishi, and Masanori Nagatani, "A new detector for gaseous components using semiconductor thin films," Anal. Chem. 34, 1502-1503 (1962).

2. Tetsuro Seiyama and Shuichi Kagawa, "Study on a detector for gaseous components using semiconductive thin films," IBID. 38, 1069-1073 (1966).

3. Varga, G. M., Jr., and A. R. Garabrant, "Development of a Piezoelectric Oil on Water Detector for Coast Guard Use." Esso Research and Engineering Company, Contract No. DOT-CG-31530-A, Monthly Progress Report No. 3, page 6, 31 May 1973.

APPENDIX I

THE WESMAR ADHISTOR WATER SURVEILLANCE MONITOR (WSM-350 and VM-400)

* Facts Regarding the WSM-350 Sensor

* Operational Instructions for Water Surveillance Monitor WSM-350

* Performance Test by Environmental Measurement Systems

ENVIRONMENTAL MEASUREMENT SYSTEMS

A DIVISION OF WESMAR

905 Dexter Avenue North • Seattle, Washington 98109 U S.A • Telephone: (206) 285-1621 • Cable WESMAR • Telex 329509

FACTS REGARDING THE WSM-350 SENSOR

The WSM-350 sensor represents a totally new art with world-wide patants that may be used to detect and measure differences in the environment. To our knowledge, the WSM-350 sensor is the only device that is capable of operation in two environmental mediums, vapor and fluid. Since the physiochemical adsorption characteristics are the same in both mediums, the sensor will also respond in air or in water. In air, the sensor is designed to monitor levels of pollutants usually in parts per million whereas in water, the sensor would be asked to detect normally in a percentage figure. The world-wide patented sensor is desirable in that it is considered intrinsically safe while monitoring combustible atmospheres and fluids.

Some of the major classes or organic solvents that the sensor will respond to are Aliphatic Hydrocarbon, Cyclic, Ethers, Esters, Aromatic Ketones and Halogenated Hydrocarbons. Since these organic vapors and solvents are the product of oil, then oil itself is detected in the fluid state as well as in its many vapor states that are cracked off from the crude fluid. Products such as gasoline are easily detected in both states.

The sensor is essentially operating at ambient temperatures and is a conductor in air and in water. When the sensor is exposed to an adsorbate of higher Van der Waal's-a-constants, the conductivity of the sensor will change in response to the quantity of adsorbate present. In air, the sensor is usually made to respond to Van der Waal's-a(attractive force) scale above 9.00, therefore gases such as oxygen, nitrogen, bethane, methane will not cause the sensor to react. The sensors, designed for the medium of water,which is 5.464 on the Van der Waal Attractive Force Scale, are designed to operate above nine (9) on the scale.

Some of the gases or fluid solvents that may be detected in either medium are acetic acid (17.39), acetone (13.91), benzine (18.00), carbon tetrachloride (20.39), kerosene, gasoline, vinyl chloride, ethyl alcohol and many others. Any adsorbate determined from Van der Waal's-a constants above nine may be readily detected and monitored in an intrinsically safe manner.

In fluids as in gases, the WSM-350 sensor is not affected physically by most acids and alkalines. The viscosity of the adsorbate naturally would affect the adsorption function that would return the sensor to a pure water condition.

ENVIRONMENTAL MEASUREMENT SYSTEMS

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OPERATIONAL INSTRUCTIONS FOR WATER SURVEILLANCE MONITOR, WSM-350

The WSM-350 is complete with the meter, recorder, alarm, sensitivity adjustments and electronics in one enclosure plus three (3) ceramic (waterproof) sensors and seven (7) regular sensors, each with a 40' cable and connector.

TO OPERATE

1. Select sensor and insert into receptacle on front panel of unit (lower right hand corner).
2. Turn power switch on, indicated by amber light. Unit is powered by regular 115V.
3. Adjust ZERO adjustment (calibrater) so meter needle is on '0'.
4. Turn MULTIPLIER PPM switch to 'A'.
5. Turn VANDERWAAL'S CONSTANT switch to '10'.
6. Adjust ALARM SET POINT to 5 as reflected on meter dial face, 'A' scale. Push knob in and turn to set. Needle point will return to '0'. Check ALARM SET POINT anytime by pushing in knob. Alarm point may be set at any point on meter face; 5 is the average setting.
7. OVERRIDE switch deactivates the horn. The red alarm will continue to stay lit until the vapor clears.

The WSM-350 is now operative and will respond to vapor/fluid with a rating of nine (9) or higher on Van der Waal's Constant for Gases (chart enclosed). Note: there are numerous pollutants that the WSM-350 detects in addition to the gases listed on Van der Waal's chart.

The WSM-350 can be adjusted for sensitivity by the MULTIPLIER switch and VANDERWAAL'S CONSTANT switch. The MULTIPLIER switch has 5 settings, A-B-C-D-E ranging from the most sensitive 'A' to the least sensitive 'E'.

VANDERWAAL'S CONSTANT has 6 settings, 10-20-30-40-50-60, ranging from the least sensitive '10' to the most sensitive '60'.

If is is desirable to overlook a certain amount of pollutants, such as fumes from an outboard motor, then set for a less sensitive setting.

Start with the MULTIPLIER on 'A' and VANDERWAAL'S CONSTANT on '60'. When the unit is operating and the meter indicator goes to the right, the sensitivity must be lessened. This is done by:

1. Turn VANDERWAAL'S CONSTANT from 60 to 50. Continue to 10 or until the meter indicator is off right side.

(CON'T)

(CON'T)

2. If it is still too sensitive, return switch to 60 and adjust MULTIPLIER to B. Then continue through to 60 to 10 range on VANDERWAAL's CONSTANT again. Repeat the procedure all the way to 'E' on the MULTIPLIER if necessary or until you have determined what concentration of oil or gas you wish to detect. Then set the ALARM SET POINT accordingly.

CAUTION:

1. Do not submerge the SENSOR directly in a pollutant, such as in a container of oil or gasoline. This in effect 'drowns' the sensor and it takes a long while for it to recover (return to a normal state).
2. Keep the extra SENSORS away from vapors while not in use. They 'sense' at all times and if one is saturated prior to being attached to the WSM-350 for operation, you will receive an incorrect reading until the SENSOR clears itself.
3. When a new SENSORis attached always calibrate it by setting the ZERO adjustment to '0'.

POINTS TO REMEMBER

1. The ceramic SENSORS are waterproof but will allow fumes in.
2. Try to keep ceramic SENSOR either below the water's surface or just above it. It will work either way. If it is on the water's surface, the oil will cling to it longer after the oil spill has been dispersed and it will take longer to clear itself of the fume.

The unique qualities of the WSM-350 are:

1. Low electrical current consumption requiring less than 50 micro-ampheres.
2. Intrinsically safe, there is no heat or combustion required to operate.
3. SENSORS can be made to operate in the medium of air or in the medium of water.
4. The SENSOR will detect toxic as well as explosive gases and fluids.

ENVIRONMENTAL MEASUREMENT SYSTEMS

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March 4, 1975

Dr. Louis Goodson
Midwest Research Institute
425 Volker Blvd.
Kansas City, MO 64110

EMS 3162

Dear Dr. Goodson;

The Water Surveillance Monitor, WSM-350 (Vapor Monitor, VM-400) was shipped today per our telephone conversation yesterday. This unit is available at no charge to Midwest Research or the U.S. Coast Guard and may be used as long as you or the Coast Guard is testing it as an oil detection system.

The results we obtained from our testing were most gratifying. The data is as follows:

1. Response time to #2 Black Oil — 40 seconds
   Response time to #6 Dieseline — 5 seconds
   Response time to Crude Oil — 20 seconds

2. Parts-Per-Million scale registered:

#2 Black Oil	10 minutes	25 PPM
#6 Dieseline	10 minutes	325 PPM
Crude Oil	10 minutes	200 PPM

Conditions for tests were: one milliliter of oil on water surface area of 10,000 square inches, outside with 8 m.p.h. wind in temperature range of 32°F to 48°F over a 20 hour period for each oil with the sensor mounted 6 inches above the water surface.

As the test data reflects, we have made vast improvements in the system over the original unit in response time and stability. This has been accomplished without affecting the advantage of lower current requirements of 50 micro ampheres for the sensor.

I'm glad we were able to accomplish these improvements in time for your March 17th test. Please call anytime you have a question or desire additional information.

Very truly yours;

ENVIRONMENTAL MEASUREMENT SYSTEMS

J. Bruce Orkney
General Manager

JBO/bl
cc: Lt. George White

APPENDIX II

THE TAGUCHI GAS SENSORS (TGS)

* General Specifications

* TGS No. 308

* TGS Current Production

* TGS No. 711

* TGS No. 812

1. The Principle of TGS Sensor

In general once a gaseous molecule is adsorbed on the surface of a semi-conductor, an electric charge transfer occurs between the surface of the semi-conductor and the adsorbed molecule, owing to the difference of the electron energy between them.

For example, when oxygen in air is adsorbed on the surface of n-type semi-conductor device like TGS electrons move from the device to the adsorbed gas, and as a result of this, oxygen is adsorbed as a negative charge. Hence the density of the conduction electron in a space-charge layer of the semi-conductor decreases and then the conductivity also decreases.

Consequently, the oxygen pressure in the atmosphere and the conductivity of the device are mutually related, so the partial pressure of oxygen being lowered as shown in Fig. 1, decreases the value of the electric resistance of the device.

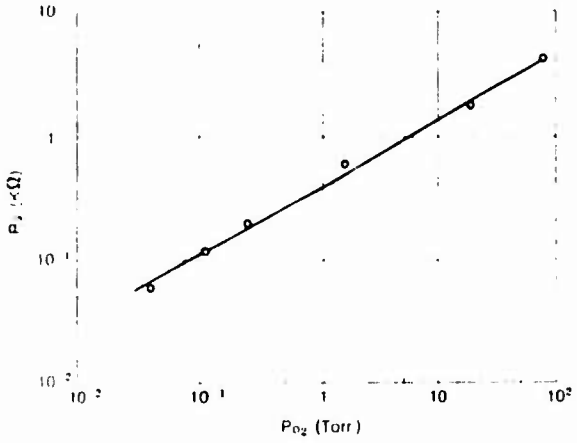


FIG. 1. RELATIONSHIP BETWEEN THE RESISTANCE OF TGS (Rs) AND THE PRESSURE OF OXYGEN (Po_2).

◆**Sample:** #308
◆**Test condition:** VC 10V D.C. / VH 1.2V D.C. / RL 4KΩ

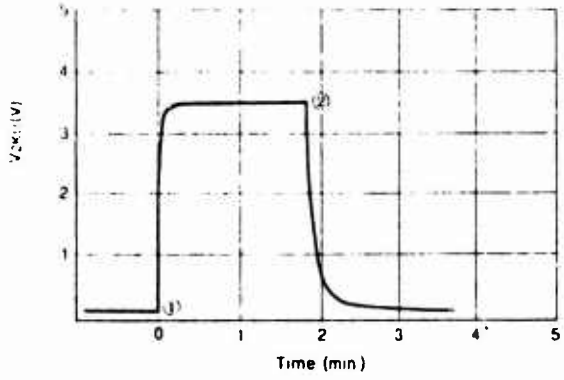


FIG. 2. RESPONSE CURVE AGAINST ISOBUTANE.

◆**Sample:** #308
◆**Test condition:** VC 10V A.C. / VH 1.2V A.C. / RL 2KΩ
◆**Measuring procedure:**
(1) Put the TGS into a hermetic-sealed test box containing 1000 ppm of isobutane
(2) Take it out promptly in a few minutes.

Since the partial pressure of oxygen in air is nearly constant, the amount of oxygen adsorbed to the device and the mode of its adsorption remain stable at a certain condition, maintaining the device at a constant temperature by means of heating. At a result of this, the conductivity also remains constant.

Under these conditions, when combustible gases such as hydrogen, carbon monoxide and others exist in air, these gases are adsorbed on the surface of the semi-conductor as a positive charge and make the density of the conductive electron increase in a space-charge layer so that the conductivity increases in proportion to the concentration of a gas.

These mechanisms are strictly the adsorptive and desorptive reaction of gases on the surface of the device, so its response speed is quite fast under a certain degree of high temperature (200°C~400°C), therefore, the TGS sensor on the market also shows its remarkable response speed.

In addition it keeps a stationary resistance value in response to the concentration of a gas when it is placed for a long time under a sensitive state in the air containing combustible gases.

When the combustible gases are faded away and fresh air is restored, its resistance value promptly returns to its original state. Fig. 2 shows the characteristics of its response and restoration of model 308 against isobutane gas.

2. The Structure of TGS Sensor

Fig. 3 shows the schematic illustration of TGS sensor. Its device is massive and contains coils, which operate as heater and electrode simultaneously.

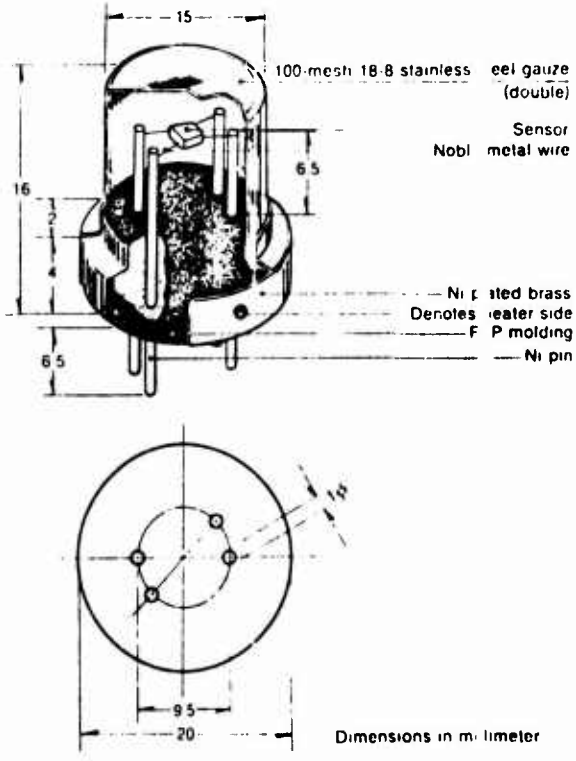


FIG. 3. STRUCTURAL SPECIFICATIONS.

The resistance value of these coils are both approximately 2Ω and made of an alloy of iridium and palladium. The wire's diameter is 90μ.

Both ends of these coils are welded on the pins. The pin is made of nickel and its diameter is 1 mm. The configuration of 4 pins used is arranged to match the socket intended for a 7-pin miniature vacuumtube. The hold-strength of the pin against its base is above 5 kgs.

The base is made of polyethylene terephthalate reinforced with glass-fiber, so it can withstand temperatures as high as 240°C without deformation.

The cap is made of double 18-8 stainless steel 100 mesh per inch net for explosion proof. Our test proves that it can intercept a fire occuring inside the sensor from sparking outside even in a mixture of hydrogen of 2:1 ratio.

The above mesh is fixed to the base by a ring. This ring is made of nickel-plated brass. Pressed on the ring is a heater mark, which shows the sensor's heater coil side for heating up the afore-mentioned device.

10 pieces in a random sampling was tested under the conditions indicated in Table I by an official institute and the result obtained proves no craking and breaking occured on welding joints and bodies of the sensors.

TABLE I VIBRATION AND SHOCK TEST

1. VIBRATION TEST	
◆ Conditions:	
Frequency	1000cpm
Total amplitudes	4mm
Duration	1hr.
Direction of vibration	Vertical
2. SHOCK TEST	
◆ Conditions:	
Acceleration	100G.
Number of shock times	5

3. A Basic Measuring Circuit

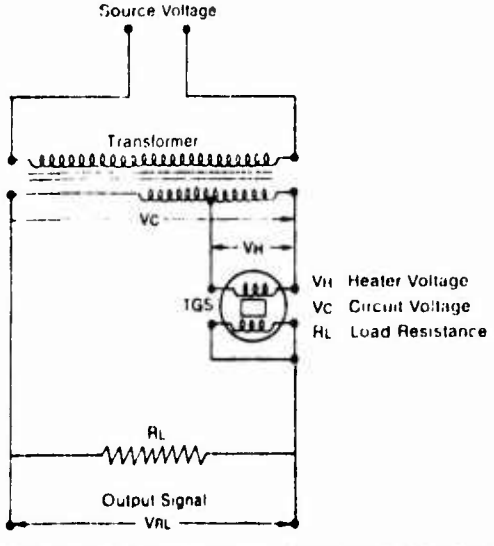


FIG. 4. BASIC MEASURING CIRCUIT WITH TGS SENSOR.

TGS sensor keeps its certain resistance value in fresh air, so a certain amount of current flows in the circuit.

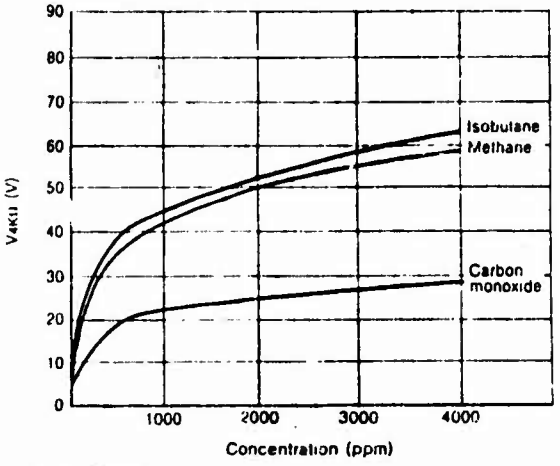
Under this condition, once any combustible gas, such as hydrogen, carbon monoxide or others, contacts the sensor, the resistance value of the sensor decreases according to the concentration of the gas or gases concerned. Then the change of the resistance value appears as the variation of voltage across the load resistance of RL.

Vh (Heater Voltage), Vc (Circuit Voltage) and RL (Load Resistance) are specified beforehand by the supplier according to each model.

4. The Sensitivity Characteristics

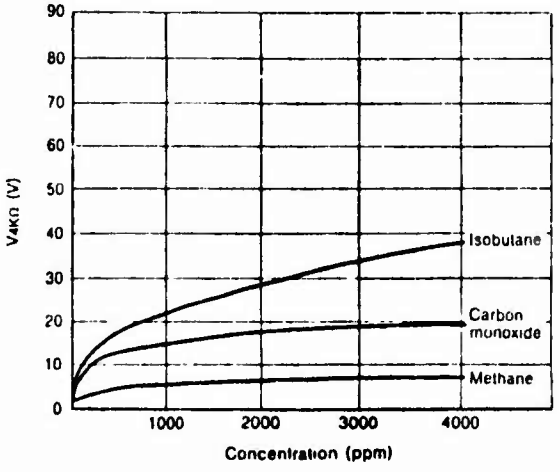
TGS sensor shows its variation of the resistance against all sort of combustible gases, but its sensitivity characteristics to each of them differs according to the model used.

Fig. 5-1~5 show the sensitivity curves of each model against typical gases.



5-1. TGS #109

◆Test condition: Vc 100V A.C. / VH 1.0V A.C. / RL 4KΩ
Temperature 24°C
Relative humidity 57%



5-2. TGS #105

◆Test condition: Vc 100V A.C. / VH 1.0V A.C. / RL 4KΩ
Temperature 23°C
Relative humidity 72%

FIGARO Technical Report

FIGARO ENGINEERING INC.
3 15 6 HIGASHITOYONAKA, TOYONAKA CITY,
OSAKA, JAPAN
CABLE FIGARO TOYONAKA
TELEPHONE . 068 49 2156

T.G.S. CURRENT PRODUCTION(Autumn 1972)

	FOR HIGH VOLTAGE APPLICATION			FOR LOW VOLTAGE APPLICATION	
CODE NO.	#109	#105	#102	#202	#308
FORMERLY	M or BM	L or BL	CM	—	—
BASIC CIRCUIT (A) CIRCUIT VOLTAGE (V_C)	100V	100V	100V	10V	10V
(B) HEATER VOLTAGE (V_H)	1.0V	1.0V	1.0V	1.5V	1.2V
(C) LOAD RESISTANCE (R_L)	4KΩ	4KΩ	4KΩ	2KΩ	2KΩ
WARM UP TIME	Approx. 2 min.	Approx. 1'. min.	Approx. 5 min.	Approx. 5 min.	Approx. 2 min.
TEST GAS	0.1% Isobutane	0.1% Isobutane	0.1% CO	0.1% CO	0.1% Isobutane
V_{R_L} * (A) IN FRESH AIR	Less than 15V	Less than 5V	Less than 15V	Less than 1V	Less than 1V
(B) IN 0.1% TEST GAS	30V ~ 50V	10V ~ 30V	25V ~ 45V	2V ~ 5V	1.5V ~ 4.5V
APPLICATIONS	•General purpose. •Gas detector.	•Automatic ventilation. •Smoke detector •Gas detector.	•CO detector. •Smoke detector.	•CO detector. •Smoke detector.	•General purpose. •Gas detector.
REMARKS	•High output signal can activate alarm directly	•Very stable in use.	•Long warm up time Delay circuit recommended	•Long warm up time. Delay circuit recommended.	•Short warm up time.

* Output voltage measured across (R_L) on basic circuit.

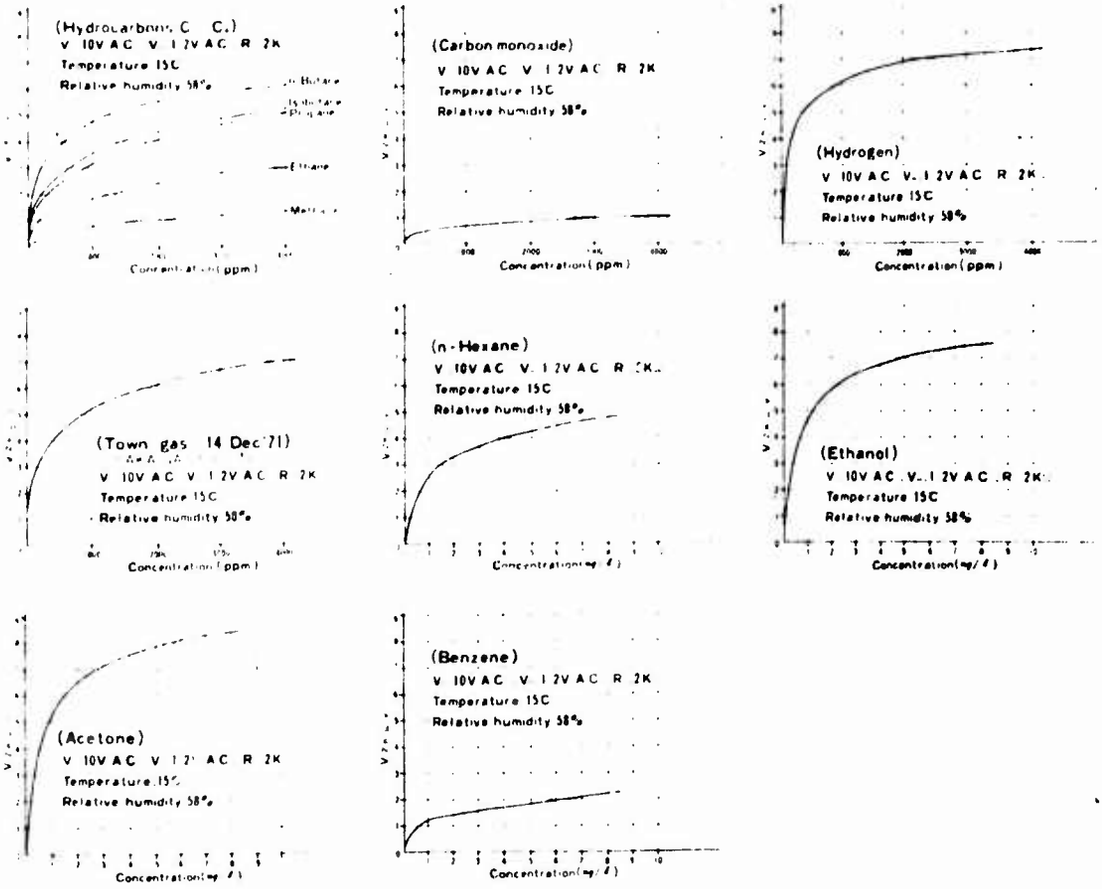
[NOTE] Please refer to relevant FIGARO TECHNICAL REPORT for fuller details.

FIGARO Technical Report

FIGARO ENGINEERING INC.
3-15-6 [illegible] TOYONAKA, TOYONAKA
OSAKA JAPAN
CABLE FIGARO TOYONAKA
TELEPHONE 06849 2156

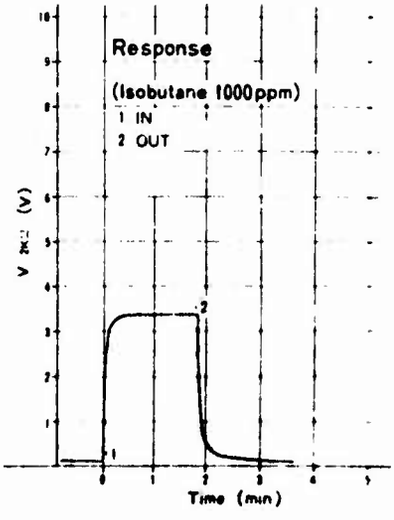
No.7

T.G.S.=308



- **Response**
- **CIRCUIT FOR MEASUREMENT:**
  Fig. 1 (V_C, 10V AC; V_H, 1.2V AC; R_L, 2KΩ)
- **MEASURING PROCEDURE:**
  (1) Put the T.G.S. into a hermetic-sealed test box containing 1000 ppm of isobutane, and take it out promptly in a few minutes.
  (2) Record the change of output voltage ($V_{2K\Omega}$)

- **Warm-up time**
  About 2 minutes or less.



FIGARO

Technical Report

No.7

FIGARO ENGINEERING INC.
3 15 6 HIGASHITOYONAKA TOYONAKA CITY,
OSAKA, JAPAN
CABLE FIGARO TOYONAKA
TELEPHONE 068 49 2156

T.G.S.#308

FOR LOW VOLTAGE APPLICATION

■ **Applications**

Detection of LPG or other kinds of combustible gases.

■ **Basic circuit for application**

V_C (Circuit voltage) : 5 ~ 30V (AC or DC)
V_H (Heater voltage) : 1.2V (AC or DC)
R_L (Load resistance) : 2KΩ

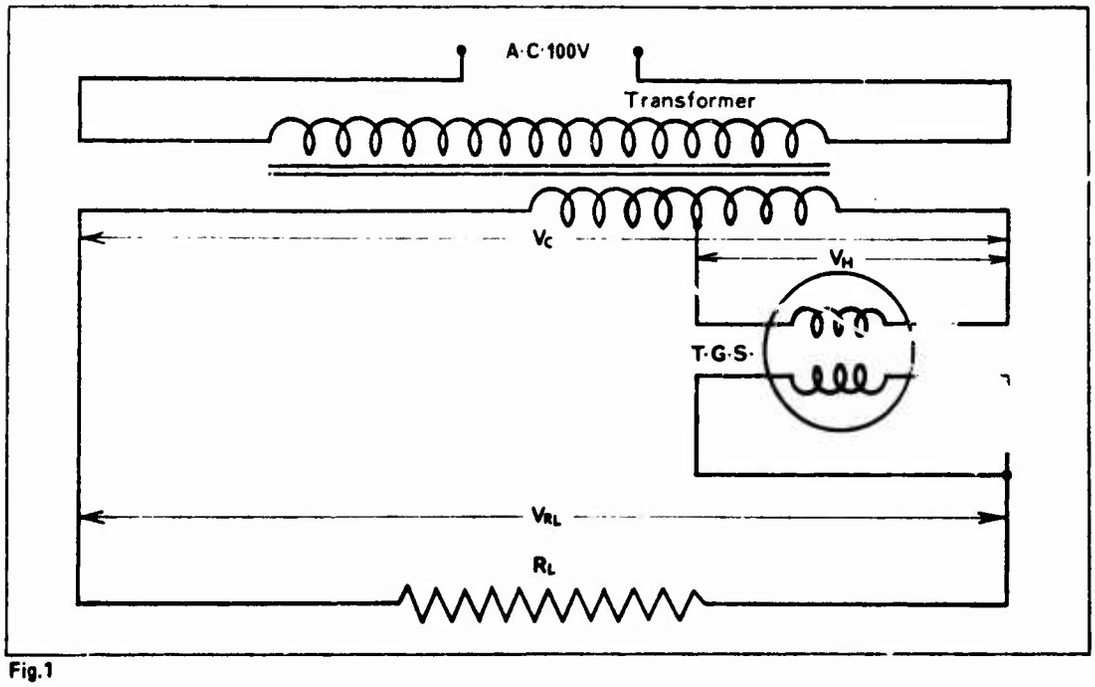


Fig.1

■ **Sensitivity**

- **CIRCUIT FOR MEASUREMENT:**
  Fig. 1 (V_C, 10V AC; V_H, 1.2V AC; R_L, 2KΩ)
- **MEASURING PROCEDURE:**
  (1) Put the T.G.S. into a hermetic-sealed testbox filled with fresh air.
  (2) Supply a sample gas (In case of liquid sample, evaporated at 100°C)
  (3) Measure output voltage at the ends of 2KΩ resistor ($V_{2K\Omega}$)

FIGARO Report April, 1975 FIGARO ENGINEERING INC.

NEWLY DEVELOPED

FIGARO GAS SENSOR #711 & #812

High Sensitivity Carbon Monoxide Sensor TGS #711

This semi-conductor sensor has high sensitivity to Carbon Monoxide (CO) and can readily detect low level CO concentrations. Several tens ppm of CO can be detected without difficulty.
Suitable applications for the #711 sensor include monitoring the toxic level of CO present, making ventilation fans automatic, controlling engine exhaust gases, smoke detection etc.

General Purpose Sensor TGS #812

This semi-conductor sensor is designed for general purpose detection. Its main feature is the inclusion of an isolated heater powered from a 5 volt supply. This new heater arrangement is convenient for circuit design.

.....

It is essential that the design parameters supplied by the manufacturer be observed in order that the optimum benefit is derived from the Figaro Gas Sensor's characteristics.

FIGARO Report April, 1975 FIGARO ENGINEERING INC.

High Sensitive CO (Carbon Monoxide) Transducer

FIGARO GAS SENSOR #711

1. Distinctive Features

In comparison with conventional TGS sensors,

a. Has a high sensitivity to Carbon Monoxide (CO).
b. Has very slight response to Isobutane, Butane, Propane, Ethane, Methane, etc.
   Hence, it is capable of detecting several tens ppm of CO without difficulty.
c. Operates with 5.0V Heater Volts.
d. Has low power consumption. (Approx. one-third compared with conventional TGS sensors.)

Sensitivity characteristics for types #711 and #308 are shown in Figs. 1 and 2 respectively.

2. Configuration

As shown in Fig. 3. Current #711 sensors are shown in sketch (a), but future production will adopt the layout shown in sketch (b).

3. Electrical Specifications

* Heater Volts ..... 5.0V ± 0.2V
* Heater Power Consumption ... 250mW
* $R_{(CO\ 200)}$ ..... 1kΩ ~ 10kΩ
  This represents sensor resistance when exposed to 200-ppm CO in air.
* $R_{(CO\ 1000)}/R_{(CO\ 200)}$ .... Approx. 0.4
  This represents ratio of sensor resistance in 1000-ppm CO/sensor resistance in 200-ppm CO.
* Heat Cleaning Volts ..... 6.7V ± 10%
  A sensor which has been stored unenergized for a long time cumulatively adsorbs moisture and molecules from the air at ordinary temperature. Consequently it is necessary to remove these contaminants from the sensor by increasing the heater voltage for a short period. This process is termed "Heat Cleaning" by the manufacturer.
* Heat Cleaning Time ..... 1 minute
  Heat Cleaning is carried out by increasing the heater voltage from 5V to 6.7V for one minute after switch on.
  Test measurements may be made three minutes after completing Heat Cleaning.
* Dependency on Temperature and Humidity ..... Same as for conventional sensors.
* Circuit for Test Measurements... As shown in Fig. 4.

4. Recommended Testing Procedures

a. The sensor operates with either D.C. or A.C.
b. Set heater volts at 5.0V ± 0.2V using a stabilized supply.
c. To establish the sensor's characteristics its resistance may be measured as shown in Fig. 4.
d. When a digital multimeter is employed for resistance measurement, in general, the resistor under test is connected to the meter's built-in constant current source. The voltage developed across the resistor by this current is measured by the meter and displayed as resistance.
   When the sensor resistance (R) is measured on the digital multimeter with the constant current (I_S), Joule heat ($I_S^2 \cdot R$) will be generated in the sensor. Maximum heat will occur when the sensor has reached its highest resistance state in fresh air. Less heat will be produced as the sensor resistance falls due to the presence of deoxidizing gas.
   An excess of the current produces undesirable amount of heat in the sensor resulting in a deterioration of its long term stability. To avoid damage to the sensor's long term stability please ensure that not more than 0.5mA can be supplied by the multimeter employed.

e. A practical gas-leak detector can be produced by connecting a suitable switching circuit to the basic circuit shown in Fig. 5. This circuit is designed to produce an output proportional to the conductance of the sensor. A gas response characteristic obtained by this circuit is shown in Fig. 8 : The manufacturer can supply a gas sensor test unit and a gas test-box designed for the evaluation of the new sensors as per attached Figaro Report.

Figure 6 illustrates a practical circuit in which a switching circuit is connected to the circuit in Fig. 5. In this circuit the current flowing through the sensor is approx. 0.7/R. This approximates to 0.1mA in fresh air and increases when the sensor is exposed to gas. The maximum current which can pass through the sensor is limited by the values of V_C and R_{ADJ}.

Another practical circuit for gas-leak detector is shown in Fig. 7 This includes a series resistor connected with the sensor. Voltage across the resistor is used to trigger a thyristor. In this circuit a current of less than 1mA may pass through the sensor in fresh air rising to a maximum of 5mA in gas. No thermal damage of the sensor caused by undesirable amount of Joule heat will take place if the recommended component values are maintained. In Fig. 7 the circuit voltage may be increased to 30 volts provided that the series resistor is increased to ensure that the heating effect produced in the sensor does not exceed that experienced when using the standard circuit in Fig. 7.

The ratio of output-voltage change to gas-concentration change ($\Delta V_M/\Delta C$) in the circuit shown in Figs. 5 and 6 is greater than that ($\Delta V_{2k\Omega}/\Delta C$) in Fig. 7, where C denotes the concentration of gas. Hence the alarm level can be more accurately set when the circuit in Fig. 6 is used.

f. Table 1 is to show the recommended component values to be used in Figs. 6 and 7.

TABLE 1. RECOMMENDED COMPONENT VALUES FOR FIGS. 6 & 7

Figures	6	7
Heater volts V_H(V)	5±0.2	5±0.2
Heat Cleaning volts (V)	6.7V (±10%)	6.7V (±10%)
Circuit volts V_C(V)	10~15	10
Adjustable resistance value R_{ADJ} (kΩ)	100	–
Series resistor R_L (kΩ)	–	2

General Purpose Transducer

FIGARO GAS SENSOR #812

1. Distinctive Features

In comparison with conventional TGS sensors,

a. Designed for 5.0V heater operation instead of 1.0V, 1.2V or 1.5V as previously required.
b. Has improved long term stability.

2. Configuration

As shown in Fig. 3. Current #812 sensors are as shown in sketch (a), but future production will adopt the layout shown in sketch (b).

3. Electrical Specifications

* Heater Volts ..... 5.0 ± 0.2V
* Heater Power Consumption 620mW
* R (IB 1000) ..... 1kΩ ~ 10kΩ
  This represents sensor resistance when exposed to 1000-ppm Isobutane in air.
* R (IB 3000)/R (IB 1000) ..... approx. 0.55
  This represents ratio of
  sensor resistance in 3000-ppm Isobutane/
  sensor resistance in 1000-ppm Isobutane.
* Sensitivity Characteristics
  to various gases ..... as shown in Fig. 9.
* Warm-up Time ..... within 2 minutes.
* Dependency on Temperature
  and Humidity ..... Same as for conventional sensors.

4. Recommended Testing Procedures

a. The sensor operates with either D.C. or A.C.
b. Set heater volts at 5.0V ± 0.2V using a stabilized supply.
c. To establish the sensor's characteristics its resistance may be measured as shown in Fig. 4.
d. When a digital multimeter is employed for resistance measurement, in general, the resistor under test is connected to the meter's built-in constant current source. The voltage developed across the resistor by this current is measured by the meter and displayed as resistance.
   When the sensor resistance (R) is measured on the digital multimeter with the constant current (I_S), Joule heat ($I_S^2 \cdot R$) will be generated in the sensor. Maximum heat will occur when the sensor has reached its highest resistance state in fresh air. Less heat will be produced as the sensor resistance falls due to the presence of deoxidizing gas.
   An excess of the current produces undesirable amount of heat in the sensor resulting in a deterioration of its long term stability. To avoid damage to the sensor's long term stability please ensure that not more than 0.5mA can be supplied by the multimeter employed.
e. Figures 10, 11, 12 and 13 show practical examples of gas-leak detector circuit. Figures 14 and 15 show output voltage V_M and $V_{2k\Omega}$ in relation to gas concentration obtained from the circuits in Figs. 11 and 13 respectively. In addition gas response curves obtained from these circuits are shown in Figs. 16 and 17 respectively.
   In the circuits in Figs. 10 and 12 the ratio of the output-voltage change to gas-concentration change is relatively small resulting in poor repeatability in terms of alarm setting when compared with that produced by the cirucits in Figs. 11 and 13. The former circuits are practically convenient because of their simple construction. However, the circuit in Fig. 11 is recommended when the best repeatability in terms of alarm setting are required.

f. The circuits shown in Figs. 10 and 11 are designed to produce an output proportional to the conductance of the sensor. The constants applicable to these circuits are determined by consideration of the sensor's characteristics, in particular the value of current flowing through the sensor. In these circuits nearly 0.03mA of current flows through the sensor when placed in fresh air. The current increases as the concentration of gas increases, but it does not increase more than approximately 1mA being limited by circuit volts (V_C) and Adjustable Resistor (R_{ADJ}). When a circuit is designed in accordance with the component values given in Figs. 10 and 11 no deterioration of long term stability of the sensor due to the undesirable amount of Joule heat will occur.

g. Figures 12 and 13 include a series resistor connected with the sensor. The voltage across this resistor is used to trigger a thyristor. In both cases the circuit current in fresh air is less than 1mA and reaches maximum values of 1.25mA and 5.0mA respectively in gas.

No thermal damage of the sensor caused by the Joule heat will occur when the recommended component values are maintained. If any circuit changes are considered necessary e.g. changing the value of the series resistor or increasing V_C to a maximum of 30 volts, then the new heating effect produced in the sensor must be checked with a view to ensuring that the heat input does not exceed that experienced when using the recommended circuits.

h. Table 2 is to show the recommended component values to be used in Figs. 10, 11, 12 and 13.

TABLE 2. RECOMMENDED COMPONENT VALUES FOR FIGS. 10, 11, 12 & 13

Figures	10	11	12	13
Heater volts V_H(V)	5±0.2	5±0.2	5±0.2	5±0.2
Circuit volts V_C(V)	5	10~15	5	10
Series resistor R_L(kΩ)	–	–	4	2
Adjustable resistance value R_{ADJ}(kΩ)	50	100	–	–

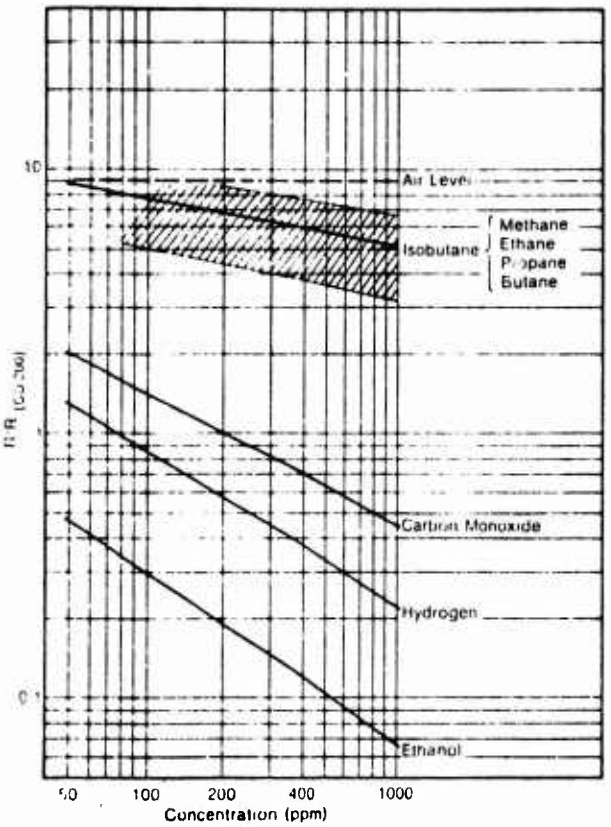


FIG. 1. RATIO OF RESISTANCE [R/R (CO 200)] vs. CONCENTRATION FOR #711.

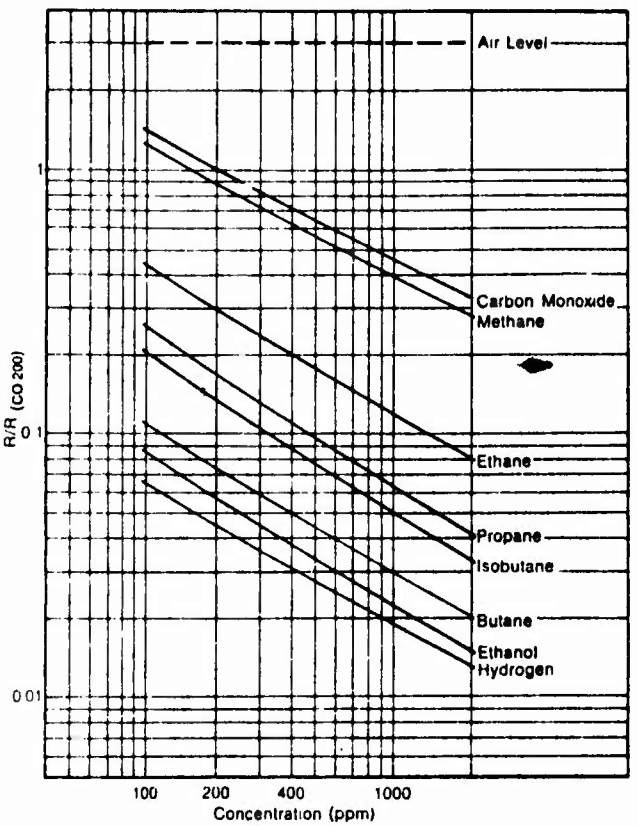
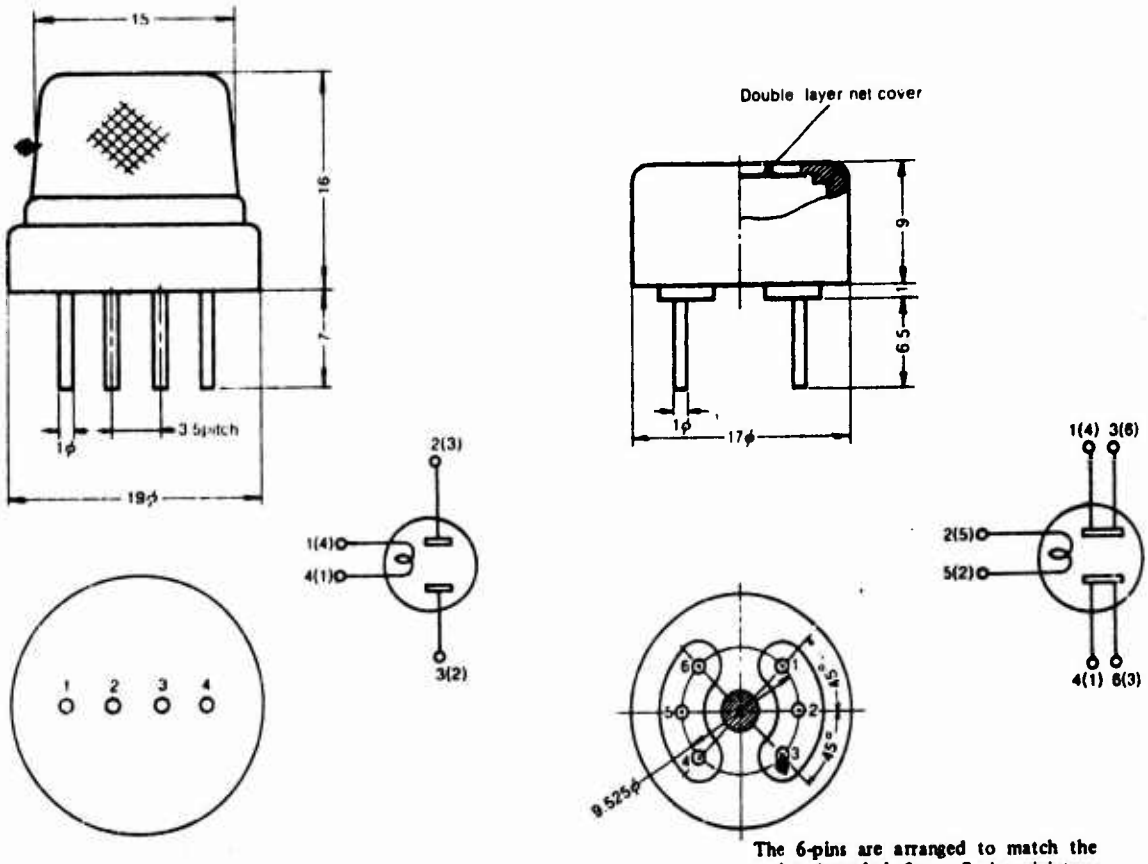


FIG. 2. RATIO OF RESISTANCE [R/R (CO 200)] vs. CONCENTRATION FOR # 308.

Sample Production (a)

Regular Production (b)



The 6-pins are arranged to match the socket intended for a 7-pin miniature vacuum tube.

Dimensions in millimeter

FIG. 3. CONFIGURATION OF # 711 & # 812.

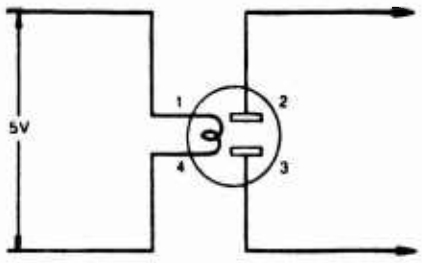
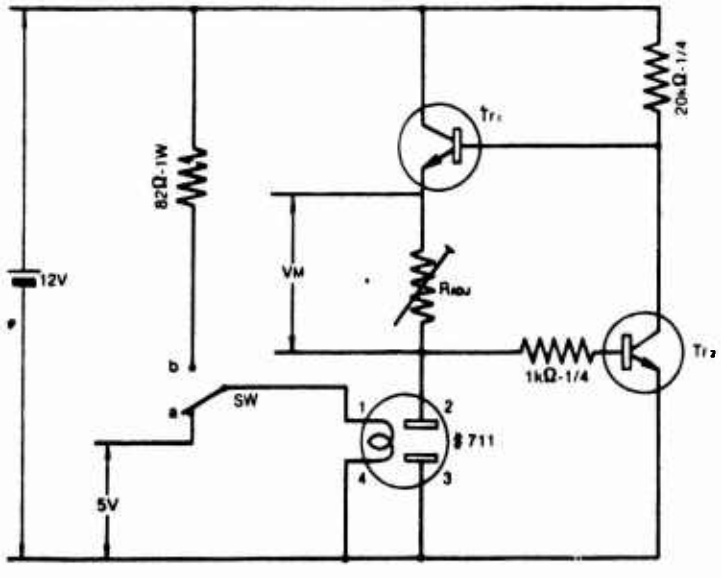


FIG. 4. CIRCUIT FOR MEASUREMENT.

Measure the resistance value across these electrodes (2, 3) employing a certain measuring current less than 0.5mA. For instance, read the value directly using a Digital Multimeter.



Suggestion: h_{FE} for Tr_1 and Tr_2 to be more than 200.

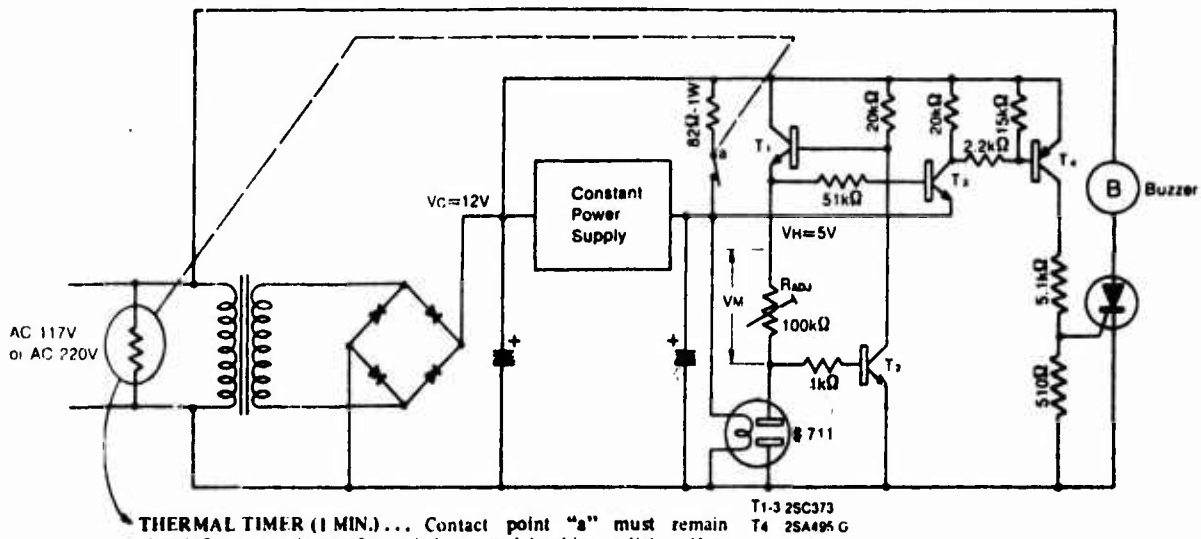
FIG. 5. AN EXAMPLE OF PRACTICAL DETECTING CIRCUIT.

Measuring Method

1. Construct a test chamber capable of being hermetically sealed, in which the sensor complete with this circuit and a stirring fan can be installed. The volume of the chamber should be measured and a gas injection inlet provided.
2. Inject a test gas of Carbon Monoxide through its gas inlet with a syringe so as the concentration of the gas in the chamber reaches 200ppm by volume, then adjust measuring voltage V_M so as to become 5V using volume $R_{ADJ}(k\Omega)$.
3. Inject additional test gas into the chamber repeatedly and read V_M against each concentration of the gas.
4. Plot the relationship between gas concentration (ppm) and measuring voltage $V_M(V)$ on a log-log scale. A straight line will be given in the range of 50 ~1000ppm of the gas.
5. The relationship between V_M and the sensor resistance $R(k\Omega)$ is expressed with a following equation:

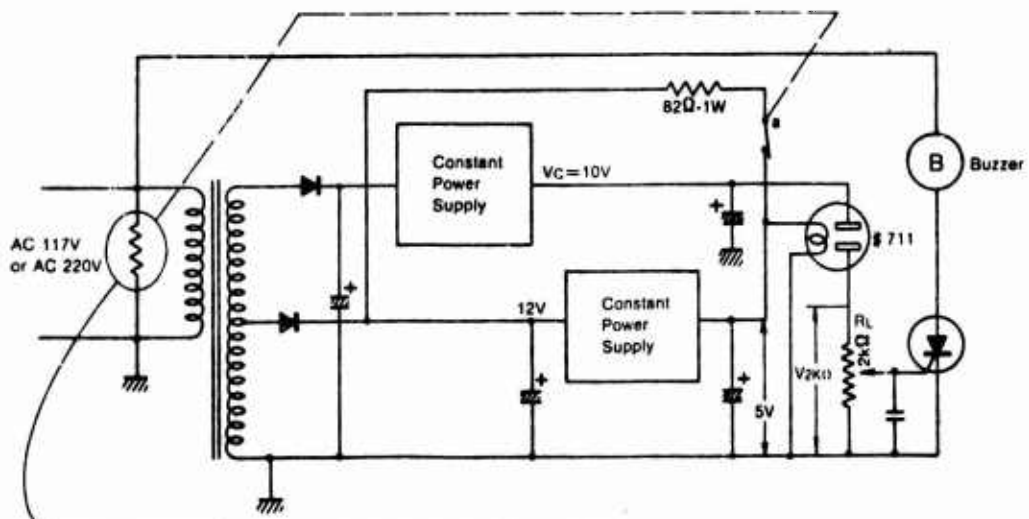
$$V_M \simeq 0.7 \times \frac{R_{ADJ}}{R}$$

6. Connect SW with point "b" at "Heat Cleaning" time for one minute. Usually SW must be in contact with point "a".



THERMAL TIMER (1 MIN.)... Contact point "a" must remain closed for one minute after switch on, and in this condition, Heat Cleaning for the Figaro #711 sensor is carried out. The voltage rating of the output circuit of the 5 volt constant supply unit must be in excess of 12 volts.

FIG. 6. AN EXAMPLE OF PRACTICAL CIRCUIT.



THERMAL TIMER (1 MIN.)... Contact point "a" must remain closed for one minute after switch on, and in this condition, Heat Cleaning for the Figaro #711 sensor is carried out. The voltage rating of the output circuit of the 5 volt constant supply unit must be in excess of 12 volts.

FIG. 7. AN EXAMPLE OF PRACTICAL CIRCUIT.

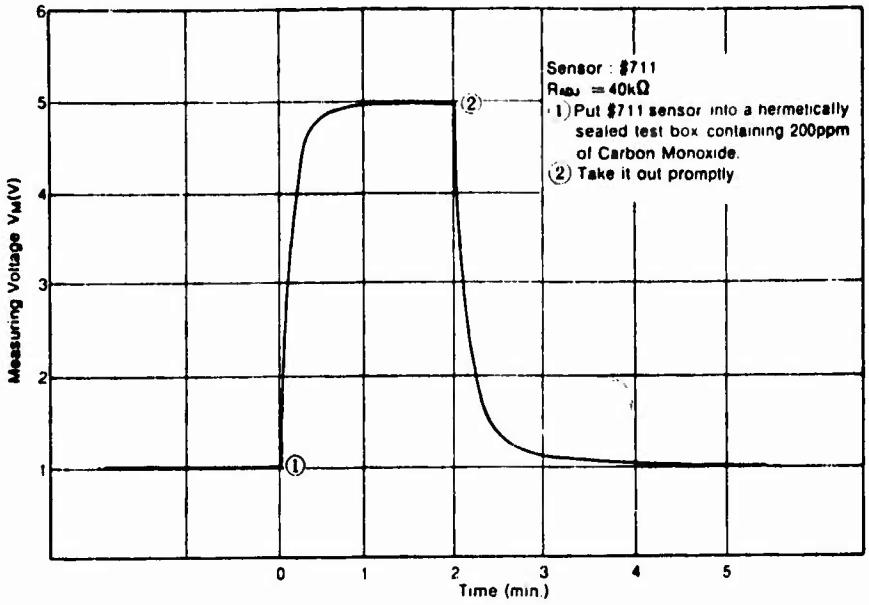


FIG. 8. RESPONSE CURVE AGAINST 200PPM OF CARBON MONOXIDE IN AIR.

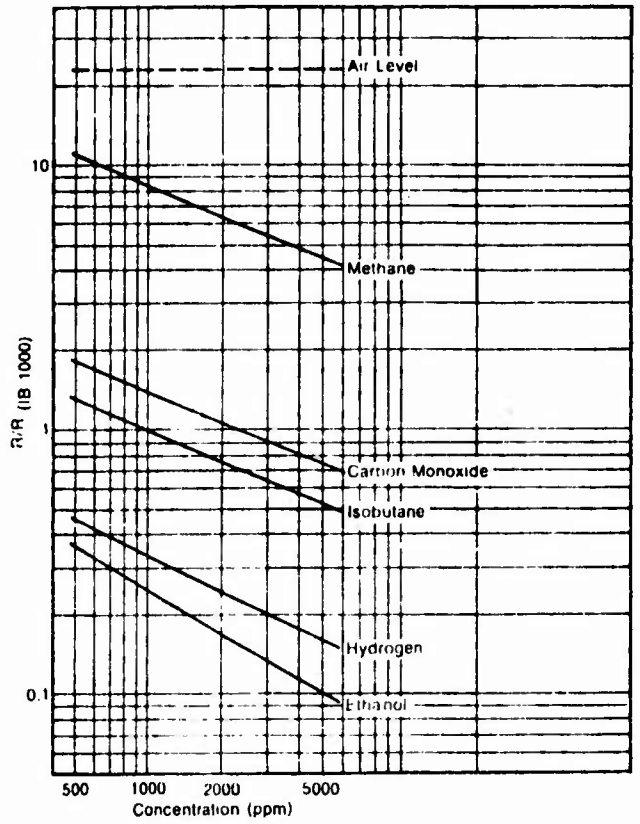


FIG. 9. RATIO OF RESISTANCE [R/R (IB 1000)] vs. CONCENTRATION FOR # 812.

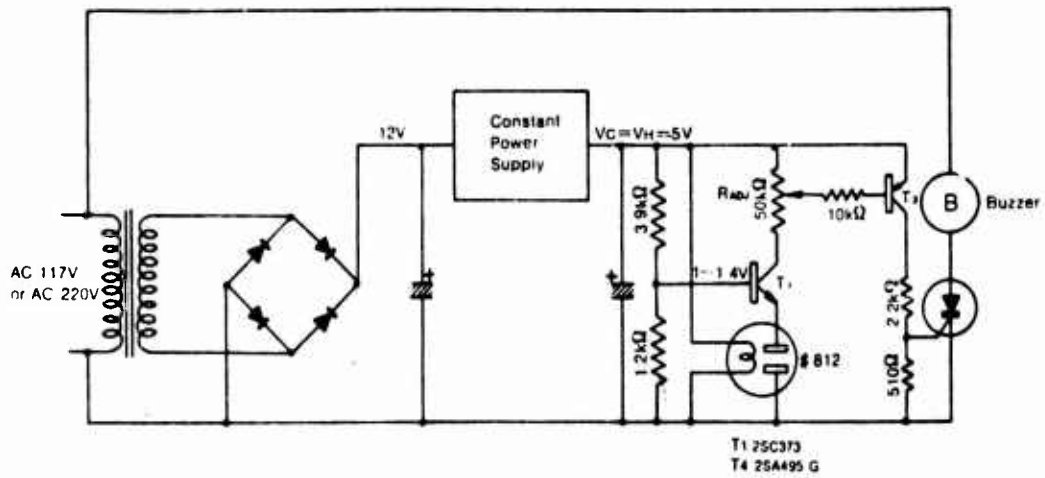


FIG. 10. AN EXAMPLE OF PRACTICAL CIRCUIT.

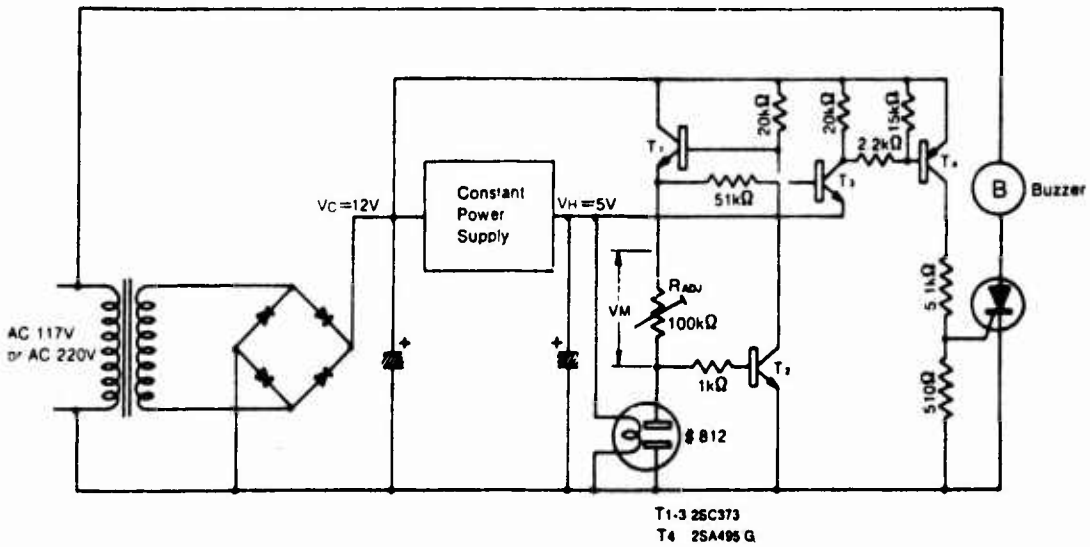


FIG. 11. AN EXAMPLE OF PRACTICAL CIRCUIT.

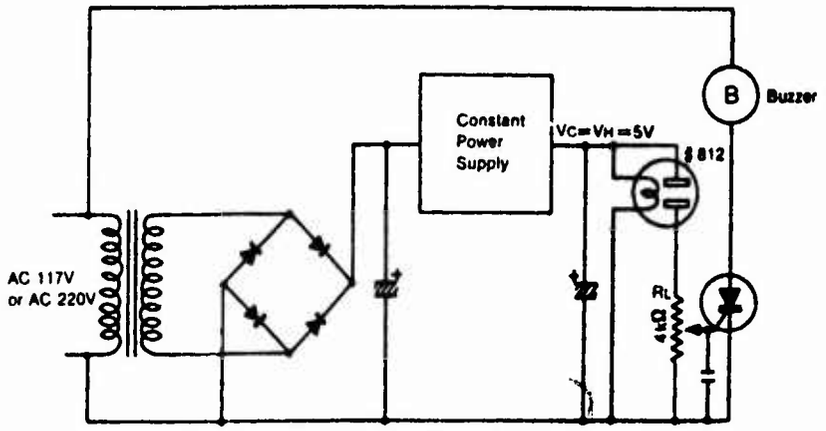


FIG. 12. AN EXAMPLE OF PRACTICAL CIRCUIT.

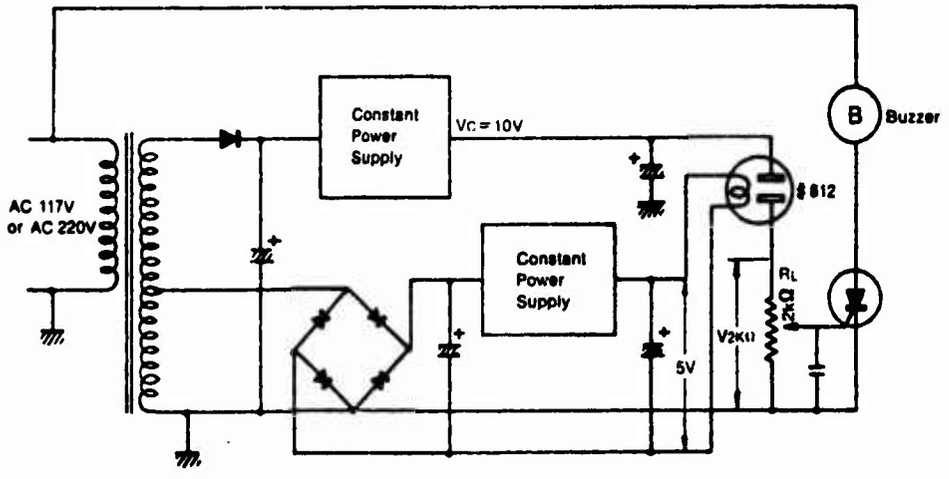


FIG. 13. AN EXAMPLE OF PRACTICAL CIRCUIT.

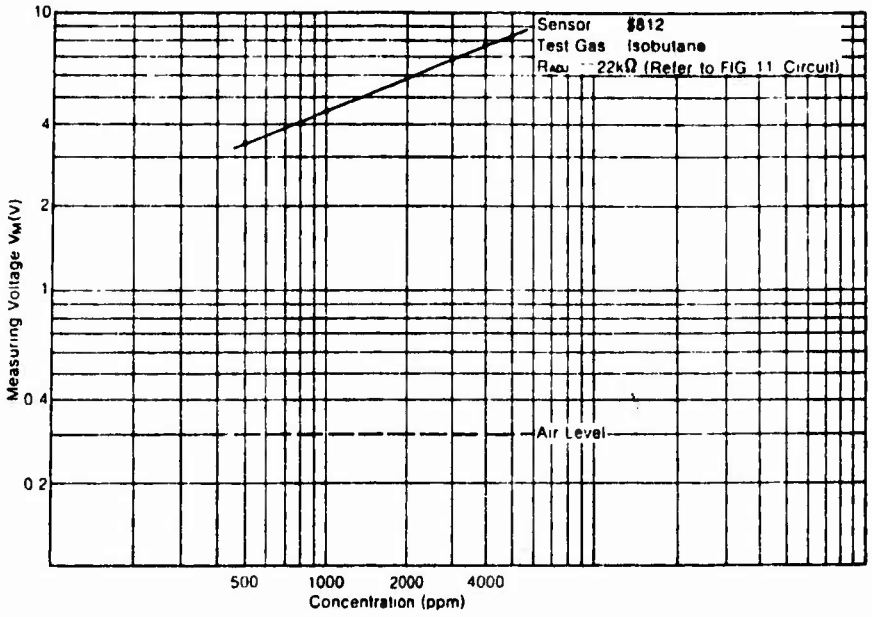


FIG. 14. MEASURING VOLTAGE vs. CONCENTRATION in use of FIG. 11. CIRCUIT.

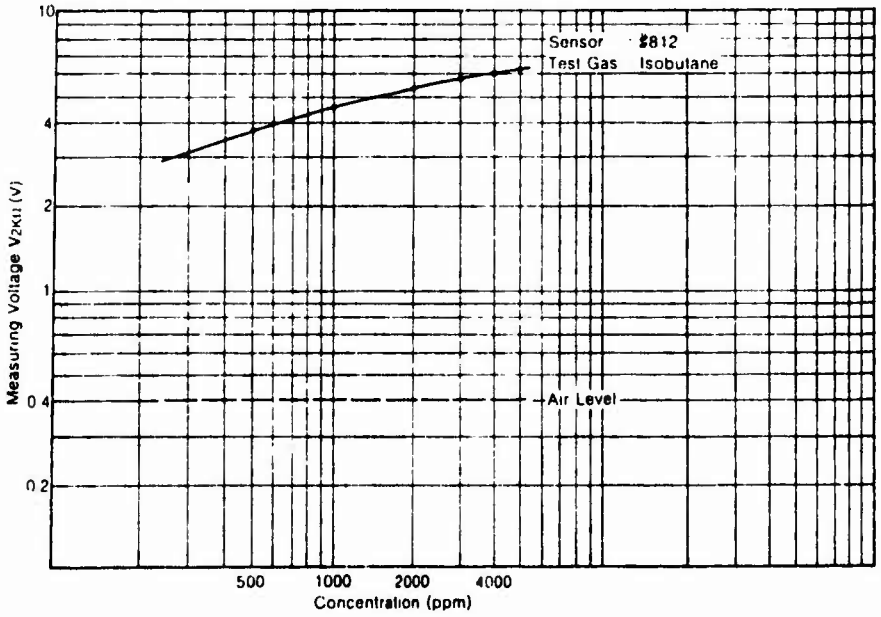


FIG. 15. MEASURING VOLTAGE vs. CONCENTRATION in use of FIG. 13. CIRCUIT.

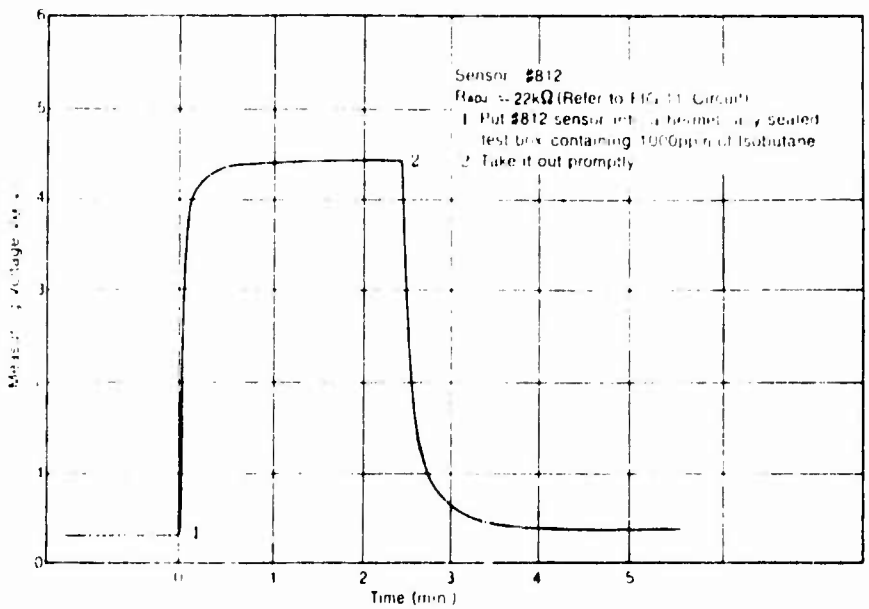


FIG. 16. RESPONSE CURVE in use of FIG. 11. CIRCUIT.

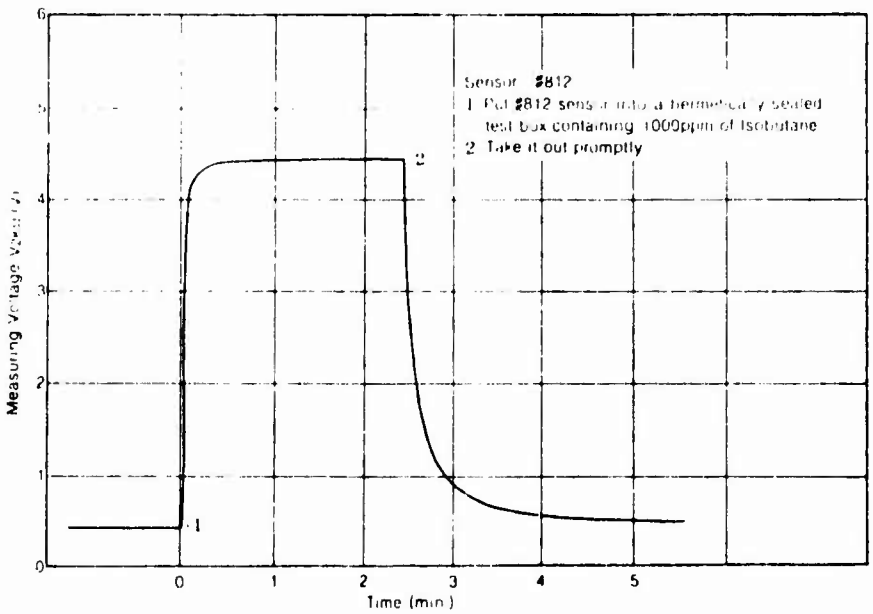


FIG. 17. RESPONSE CURVE in use of FIG. 13. CIRCUIT.

FIGARO Report April, 1975 FIGARO ENGINEERING INC.

Price/Delivery Information

for FIGARO Gas-Sensors #711 & #812

April 1, 1975

Type Number	FIGARO GAS-SENSOR #711	FIGARO GAS-SENSOR #812
Quantity Discount Price & Delivery	FOB Net Japan 1-99 pcs. @US$7.00 within 2 weeks 100-999 pcs. @US$5.30 within 3 weeks 1,000-9,999 pcs. US$3.60 within 4 weeks above 10,000 pcs. @US$2.70 within 4 weeks	FOB Net Japan 1-999 pcs. @US$3.00 within 2 weeks 1,000-9,999 pcs. @US$2.50 within 4 weeks above 10,000 pcs. @US$2.00 within 4 weeks
Specifications	As per attached Figaro Report	As per attached Figaro Report
Samples & Delivery	The manufacturer can supply a Gas Sensor Test Unit and a Gas Test-Box designed for the evaluation of the #711 and #812 sensors as per attached Figaro Report C & F * Set "A" ..... US$130.00 Gas Test-Box 1 pc. Gas Sensor Test Unit 1 pc. #711 sensor 10 pcs. * Set "B" ..... US$108.00 Gas Sensor Test Unit 1 pc. #711 sensor 10 pcs. * 10 piece Sample Shipment.. US $72.00	The manufacturer can supply a Gas Sensor Test Unit and a Gas Test-Box designed for the evaluation of the #711 and #812 sensors as per attached Figaro Report. C & F * Set "a" ..... US$ 90.00 Gas Test-Box 1 pc. Gas Sensor Test Unit 1 pc. #812 sensor 10 pcs. * Set "b" ..... US$ 68.00 Gas Sensor Test Unit 1 pc. #812 sensor 10 pcs. * 10 piece Sample Shipment.. US$ 32.00
	C & F * Gas Test-Box only ..... US$55.00 * Gas Sensor Test Unit only.. US$45.00 Shipment: Via Air Parcel Post Packing: Carton Box	
Payment	Please remit the amount by Mail or Telegraphic Transfer to The Sumitomo Bank Ltd ,Osaka Japan A/C No.146256662 or send Cashier's Check payable in Osaka, Japan directly to the manufacturer. Unable to accept a personal check or bank money order due to the time and cost involved in collection.	

*** Remarks:** We have neither representative nor distributor at home and abroad upon our marketing policy. So all inquiries and orders should be sent direct to us.

FIGARO ENGINEERING INC.
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