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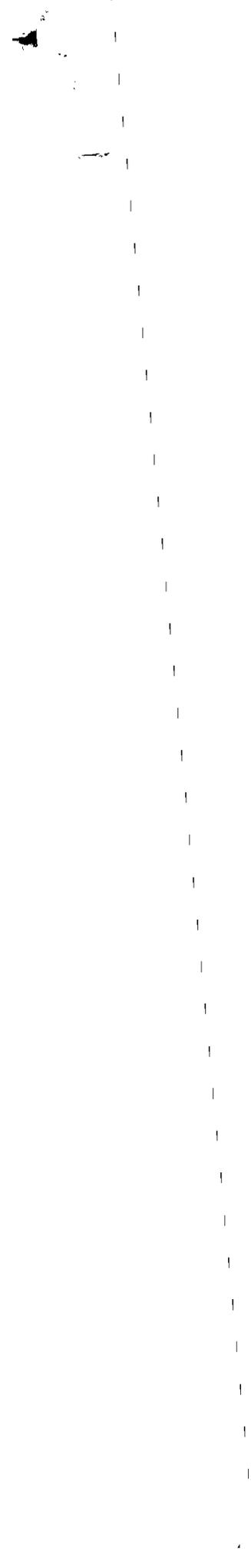


## TECHNICAL REPORT

# Development of a Prototype Service-Life Indicator for Organic Vapor Respirators

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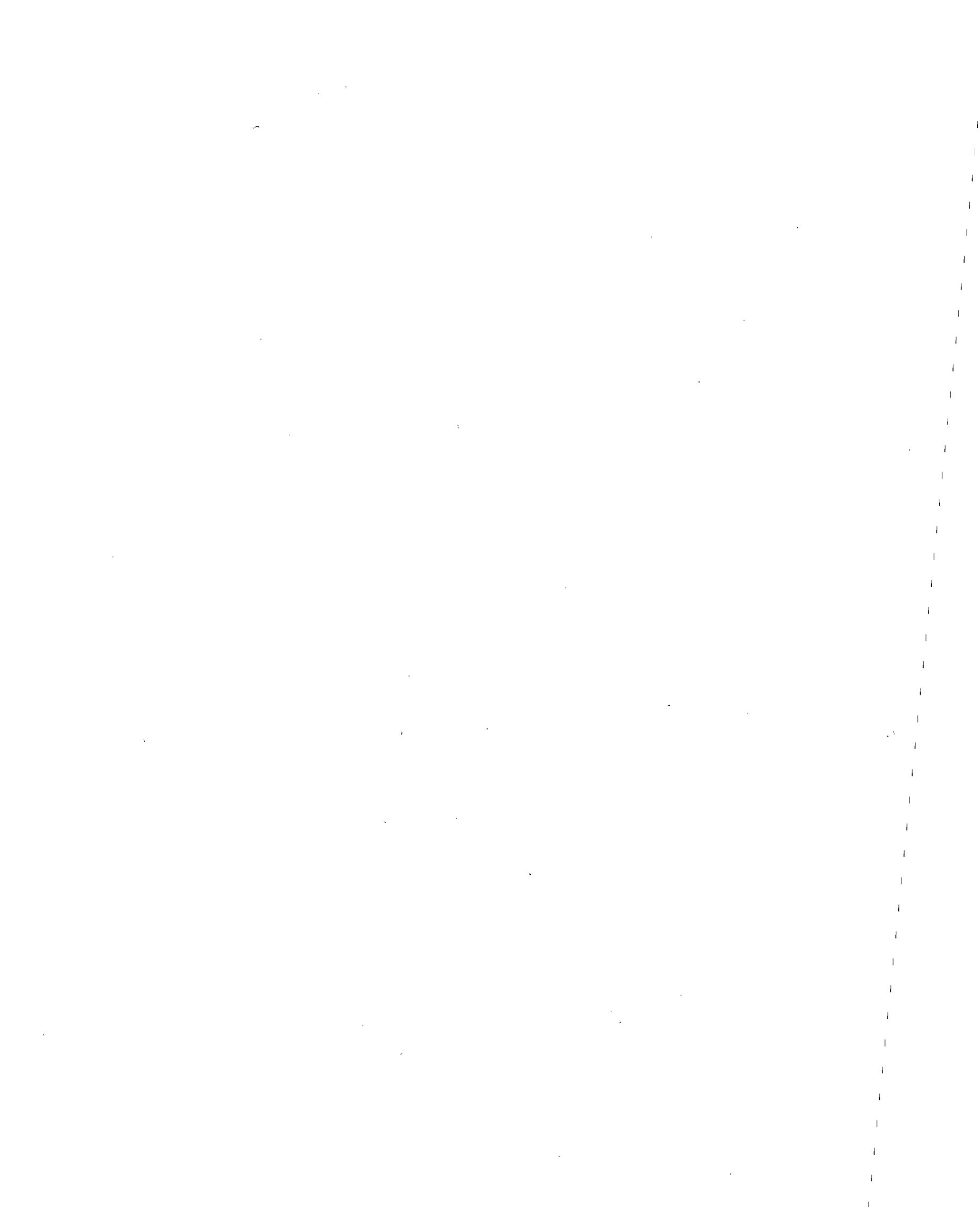
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REPORT DOCUMENTATION PAGE		1. REPORT NO.	2.	3. PB91-136309
4. Title and Subtitle Development of a Prototype Service-Life Indicator for Organic Vapor Respirators			5. Report Date August 1978	
7. Author(s) Anonymous			6.	
9. Performing Organization Name and Address NIOSH 4676 Columbia Parkway Cincinnati, OH 45266			8. Performing Organization Rept. No. 78-170	
12. Sponsoring Organization Name and Address NIOSH 4676 Columbia Parkway Cincinnati, OH 45266			10. Project/Task/Work Unit No.	
15. Supplementary Notes			11. Contract(C) or Grant(G) No. (C) 210-76-0163 (G)	
16. Abstract (Limit: 200 words) A NIOSH sponsored effort to develop and test a prototype service life indicator for organic vapor air purifying respirators is reported. A series of performance requirements for an end of service life indicator (ESLI) was developed which addressed indicator characteristics, specificity, reliability, respirator fit, weight, impairment of vision, durability, breathing resistance, temperature and humidity, electrical components, and toxic materials. A theoretical evaluation of various detection approaches was conducted to select a specific developmental approach. It was found that the metal oxide gas sensor (MOGS) merited further assessment because of its low cost, commercial availability and desirable nonspecificity. Also, catalytic oxidation was studied. Experimental evaluation showed that the MOGS responded to a large number of organic vapors within a relatively small concentration range. A prototype ESLI incorporating the MOGS was designed and constructed. The device consisted of a belt or shirt pocket mounted battery pack connected to a detector/indicator unit fitted between the respirator facepiece and the chemical cartridge. It is recommended that the ESLI be tested under actual use conditions, and that the MOGS detector be tested against additional challenge atmospheres.			13. Type of Report & Period Covered	
17. Document Analysis a. Descriptors NIOSH-Publication, NIOSH-Contract, Contract-210-76-0163, Safety-equipment, Personal-protective-equipment, Air-quality-control, Protective-equipment, Respiratory-protective-equipment,			14.	
b. Identifiers/Open-Ended Terms				
c. COSATI Field/Group				
18. Availability Statement AVAILABLE TO THE PUBLIC		19. Security Class (This Report) UNCLASSIFIED		21. No. of Pages
		20. Security Class (This Page) UNCLASSIFIED		22. Price

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DEVELOPMENT OF A  
PROTOTYPE SERVICE-LIFE INDICATOR  
FOR ORGANIC VAPOR RESPIRATORS

Arthur D. Little, Inc.  
Acorn Park  
Cambridge, Massachusetts 02140

Contract No. 210-76-0163

U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE  
Public Health Service  
Center for Disease Control  
National Institute for Occupational Safety and Health  
Division of Physical Sciences and Engineering  
Cincinnati, Ohio 45226

August 1978

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NIOSH Project Officers: Alan Gudeman  
Eugene R. Kennedy, Ph.D.

**DHEW (NIOSH) Publication No. 78-170**

## ABSTRACT

Existing Federal regulations limit the application of organic vapor air-purifying respiratory protective equipment to use for protection against contaminants which possess adequate inherent warning properties (e.g., odor and irritation). Due to the difficulty in objectively measuring the adequacy of warning properties, and the tendency of exposed individuals to acclimate or undergo sensory fatigue, it is desirable to provide an active warning signal which would warn of respirator sorbent breakthrough.

This report describes an experimental effort to develop and test a prototype service-life indicator for organic vapor air-purifying respirators. The work undertaken included development of desired performance requirements for an end-of-service-life indicator (ESLI), followed by a theoretical evaluation of various detection approaches (based on available data). Finally, a prototype ESLI was constructed and tested under laboratory conditions.

This report was submitted in fulfillment of Contract No. 210-76-0163, under the sponsorship of the National Institute for Occupational Safety and Health.

## ACKNOWLEDGMENTS

The Program Director at Arthur D. Little, Inc., for this work was R. Scott Stricoff, and coordination of chemical systems work was provided by Donald B. Lindsay. Arthur D. Little staff members making substantive contributions to this work include Clark F. Grain, Martin L. Cohen, Herbert H. Loeffler, Emmett M. Smith, and Kenneth R. Sidman. The Arthur D. Little project team wishes to thank Alan Gudeman and Eugene R. Kennedy, Ph.D., of NIOSH, (who served as NIOSH Project Officers) for their assistance during our efforts.

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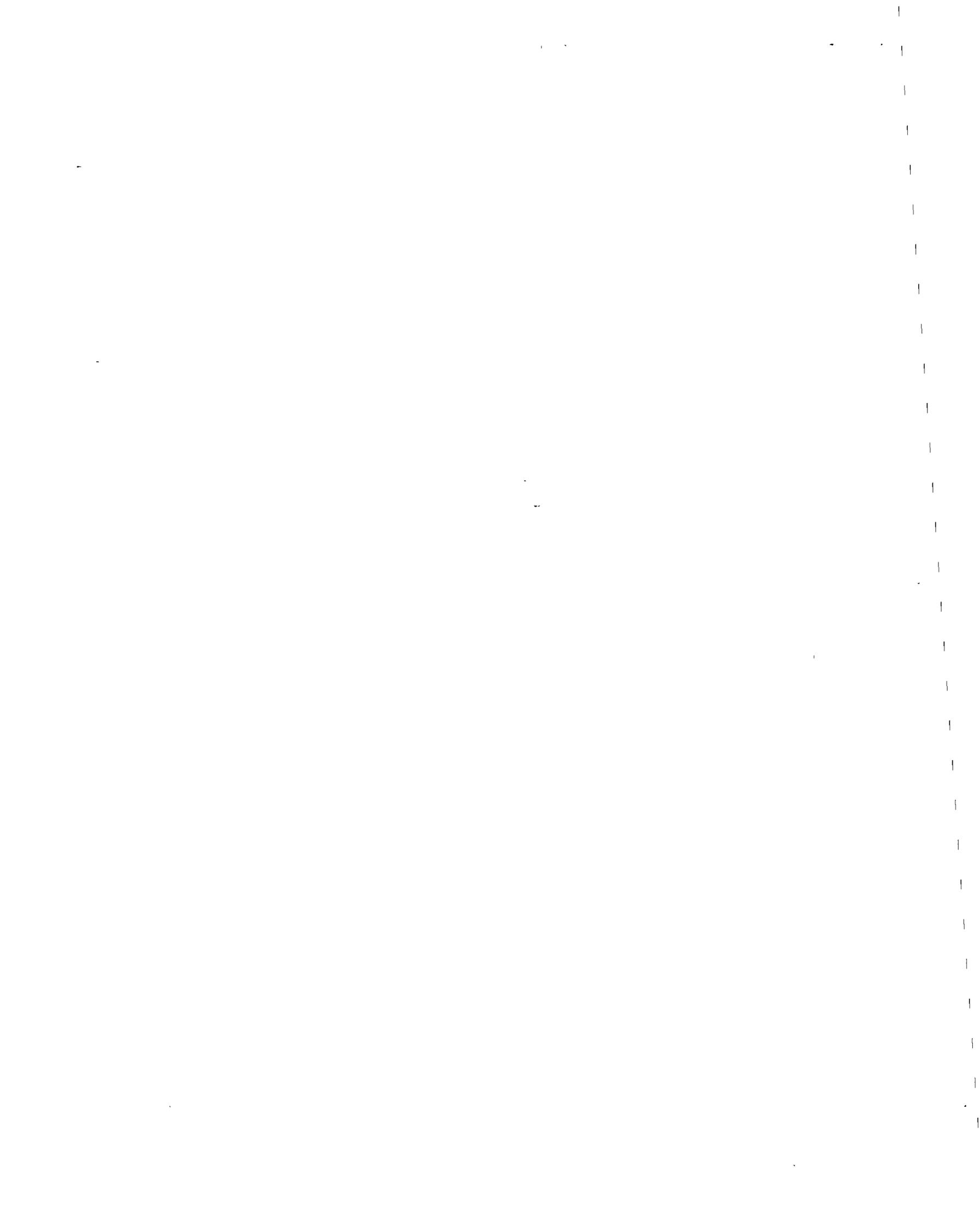
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## 1. SUMMARY

### 1.1 Introduction

Current regulations addressing the certification of air-purifying respiratory protective equipment (30 CFR 11) limit the use of such apparatus to situations in which the airborne contaminant of concern possesses "adequate warning properties." Various reviews on warning properties of chemicals (i.e., odor and irritation) led NIOSH to conclude that these properties were not a reliable indicator of the air-purifying cartridge's saturation and that there was a need for an indicator that would provide a positive warning to the respirator user when his sorbent ceased to afford the desired level of protection. This study was conducted to develop a prototype end-of-service life indicator (ESLI) for organic vapor respirators.

### 1.2 Approach

Three major tasks were undertaken during the study. First, a series of desired performance requirements was prepared. These requirements addressed operational and design factors, and served as goals during prototype development.

Second, a theoretical evaluation was made of various detection approaches. This evaluation was made to select a specific approach for further development.

Finally, a prototype service-life indicator was constructed and tested under laboratory conditions. Following these tests, observations were made regarding appropriate use conditions and certification procedures.

### 1.3 Results

A series of desired performance requirements was developed. These requirements addressed:

- Indicator Characteristics
- Specificity
- Reliability
- Respirator Fit
- Weight
- Impairment of Vision
- Durability

- Breathing Resistance
- Temperature and Humidity
- Electrical Components
- Toxic Materials

During the theoretical evaluation of alternative detection systems, the applicability of each of six alternative techniques was studied. The metal oxide gas sensor (MOGS) was selected for further assessment due to its commercial availability, low cost, and desirable non-specificity. In addition, it was decided that some further evaluation of catalytic oxidation would be useful.

Experimental evaluation showed that the MOGS responded to a large number of different classes of organic vapors within a relatively small concentration range. Although humidity did tend to reduce MOGS sensitivity, the detection of organic vapors in a humid atmosphere remained possible.

A prototype ESLI incorporating the MOGS was designed and constructed. This device consisted of a belt or shirt pocket-mounted battery pack connected by wires to a detector/indicator. The detector/indicator unit was contained in a cylindrical housing that was fitted between the respirator facepiece and the chemical cartridge. The indicator provides a signal (a flashing light) when vapor is present, and a distinctive signal (a steady light) when the battery power is low.

#### 1.4 Conclusions and Recommendations

It is technically feasible to develop an end-of-service-life indicator for organic vapor respirators. It is recommended (1) that the prototype be tested under actual use conditions, and (2) that the MOGS detector be tested against additional challenge atmosphere in order to better understand the capabilities and limitations of the prototype device.

## 2. INTRODUCTION

### 2.1 Background

Respiratory protective equipment can be divided into two classes: air-purifying equipment and atmosphere-supplying equipment. The latter category of device supplies clean air to the user, drawing upon either a remote air supply, a portable tank, or a chemical oxygen-regenerating system. The air-purifying device cleans ambient air that is drawn through a filter or chemical cartridge by the user during inhalation. A variety of air-purifying respirators are available to provide protection against various types of particulates, gases and vapors, or particulate/vapor mixtures.

Two widely utilized types of air-purifying respirators are the chemical cartridge respirator and the gas mask, each of which may provide protection against organic vapors. These devices may be submitted by their producers for testing by the National Institute for Occupational Safety and Health (NIOSH), and devices that pass NIOSH tests receive certification issued jointly by NIOSH and the Mining Enforcement Safety Administration (MESA) under Title 30, Part 11, of the Code of Federal Regulations (30 CFR 11).

Within 30 CFR 11, in addition to respirator certification requirements, there are several limiting provisions that restrict the conditions under which various types of respirators can be employed. One limitation placed upon organic vapor chemical cartridge respirators and gas masks is that these devices may not be utilized for protection against airborne contaminants which have "poor warning properties." The term "poor warning properties" is not defined in 30 CFR 11, and no examples of substances which have either adequate or inadequate warning properties are provided.

In undertaking the Standards Completion Program in 1974, a joint working group of professionals representing the Occupational Safety and Health Administration (OSHA) and NIOSH developed a set of guidelines on respirator selection (the Respirator Decision Logic) designed to ensure the consistent specifications for allowable respirator usage during the development of individual health standards for 400 substances. This Respirator Decision Logic contained a definition of adequate warning properties, and cautioned that since "warning properties relying upon human senses are not foolproof," some method was needed by which an employee could detect respirator malfunction.

Consideration of various approaches to defining "warning property" indicated the desirability of developing an end-of-service life indicator to reduce dependence upon inherent warning properties. It was noted that the availability of an end-of-service life indicator (ESLI) for organic vapor respirator cartridges and canisters would

permit the use of air-purifying respirators in situations where they are currently not recommended (i.e., where contaminants lack inherent warning properties) upon NIOSH approval of ESLI-equipped respirators.

## 2.2 Objective and Scope

To encourage the study of respirator service life indicators, NIOSH sponsored this study to develop and evaluate a prototype indicator system.

The work program began with the development of a performance specification for an ESLI for organic vapor air-purifying respirators. These criteria addressed considerations including detector sensitivity and reliability, non-specificity, and effectiveness.

Next, an evaluation was conducted of candidate systems for detection and indication. Candidate systems included those already in use, proposed by others, or possibly adaptable from other applications. Chemical, physical, and electronic systems were evaluated relative to the criteria established above. A detailed ESLI design was prepared, and a prototype developed. The detection and indication system was tested under a variety of conditions.

At the conclusion of the study, recommendations were made regarding the capabilities and limitations of ESLI's for use in the industrial environment. Also, recommendations addressing the performance requirements for the approval testing of ESLI's were made.

### 3. ACCOMPLISHMENTS

#### 3.1 Development of Performance Criteria for an Ideal System

##### 3.1.1 Introduction

At the initiation of this program, several ideal performance characteristics were defined to serve as design goals during the development of a prototype ESLI. While it was recognized that no single ESLI might satisfy all of the ideal characteristics, it was necessary to establish these criteria as a yardstick against which the adequacy of any proposed design could be measured. An ESLI that successfully satisfied all of the ideal design criteria would permit the safe use of air-purifying respirators for protection against contaminants which do not have adequate inherent warning properties, thus permitting one to dispense with consideration of warning properties in respirator selection. Performance characteristics specifically excluded considerations of cost since this study was viewed as a demonstration of technical feasibility.

##### 3.1.2 Indicator Characteristics

###### Criteria

An ESLI must provide an active indication of the end of sorbent life. It must not require any action by the user to indicate warning. The ESLI must give a visual signal within the user's field of vision or by an equivalent signal (e.g., audible alarm).

###### Rationale

One of the objectives of an ESLI is that it should provide a reliable indication of respirator sorbent depletion. To be reliable, the indicator must not depend on any administrative or procedural protocol in providing warning. The ESLI must be an active indicator that will intrude upon the user's sphere of attention with no specific interrogation required.

##### 3.1.3 Specificity

An ESLI must be as non-specific as possible. While the universal ESLI would be the most desirable device, an ESLI that is less than universally applicable is acceptable since it will be more readily achievable than a universal ESLI and can be useful in many industrial environments. The acceptable use conditions for any such ESLI should preferably be described in terms of classes of contaminants against which the ESLI is and is not effective. These classes may be described in terms of charcoal breakthrough times, TLV's, physical properties, chemical families, etc.

### Rationale

For any ESLI that is developed, the capabilities and limitations of the system must be fully explained, and the use conditions must be fully understood in order to avoid misuse. Good industrial hygiene practice in general, and safe respirator use practice in particular, would suggest that anyone employing respirators should know the chemical composition of his workplace environment. Given this information, if the acceptable use conditions for an ESLI are known, it can be easily determined whether or not the ESLI is acceptable in any specific workplace. The recognition that a universal ESLI may not be practical is a pragmatic step toward the development of a device that will have real applications.

#### 3.1.4 Reliability

##### Criteria

An ESLI must be produced in accordance with established quality control procedures. Based upon the service life of each ESLI component and upon anticipated use conditions, the useful life of the ESLI must be specified.

Consideration must be given to potential interference with ESLI performance by undetected substances as well as by mixtures of detectable vapors. Environments in which ESLI performance is hindered must be identified.

### Rationale

Safe use of an ESLI requires that it be highly reliable. The potential user must be made aware of the possible use conditions that would give rise to false positive and negative responses.

#### 3.1.5 Respirator Fit

##### Criteria

No component of the ESLI, or of the devices utilized to attach the ESLI to the respirator, shall interfere with the effectiveness of:

- a) the facepiece to skin; or
- b) the respirator's headstraps or harnesses.

### Rationale

The adequacy of the fit of air-purifying respirators is recognized as being of primary importance in determining respirator effectiveness. The introduction of an ESLI to either the respirator cartridge or canister or to the respirator facepiece could interfere with the

respirator's fit by either physically displacing the seal, or by causing discomfort that would inhibit or discourage proper tightening of the respirator headstraps. This design characteristic is considered to be a performance specification that serves as a guideline regarding the ESLI's attachment to the existing respirator.

### 3.1.6 Weight Distribution

#### Criteria

The ESLI shall be supported so as not to change the weight distribution of the respirator to the detriment of facepiece fit.

#### Rationale

The introduction of an ESLI into the respirator cartridge and/or facepiece could introduce weight that would either pull the facepiece away from the face or would alter the stability of the headstrap. The ESLI weight and weight distribution and suspension must be designed so that facepiece fit will not be compromised.

### 3.1.7 Impairment of Vision

#### Criteria

The ESLI must not interfere with required lines of sight.

#### Rationale

ESLI components must be positioned so that they will not interfere with the vision of the respirator user. This is not to be interpreted as contradicting the requirement that an ESLI be located within the user's field of vision. An indicator located within the field of vision need not cause significant visual impairment.

### 3.1.8 Durability

#### Criteria

Any ESLI component that is permanently installed in the respirator facepiece must be capable of withstanding cleaning with detergent. Any ESLI component must be capable of withstanding dropping from a height of 6 feet.

#### Rationale

A properly maintained respirator will be cleaned periodically. If the ESLI has components that are permanently installed in the respirator facepiece, these components will be subjected to cleaning along with the facepiece itself. Such cleaning should not disable the ESLI.

Any equipment utilized in an industrial environment will be subject to rough handling at times. The ESLI must be sufficiently durable to withstand dropping without breakage.

#### 3.1.9 Breathing Resistance

##### Criteria

An ESLI system shall not increase breathing resistance through the respirator by more than 10% over the resistance of a device not equipped with an ESLI. In no case should the breathing resistance of an ESLI respirator system exceed the limits specified in 30 CFR 11.

##### Rationale

The amount of work required to breathe against the increased resistance of an air-purifying respirator during a complete work shift may cause fatigue among employees. The extent to which an ESLI increases this burden should be minimized.

#### 3.1.10 Temperature and Humidity

##### Criteria

An ESLI system should work at environmental conditions bounded as follows: a) temperature, 0-40°C; b) humidity, 0-100% RH. If any other temperature or humidity limits apply, they should be noted on the ESLI label.

##### Rationale

Respirators may be used in a wide variety of environmental conditions. An ESLI system should be effective at as broad a range of temperatures and humidities as possible.

#### 3.1.11 Electrical Components

##### Criteria

Any electrical power supply and electrical components of an ESLI shall conform to the applicable provisions of the National Electrical Code and shall be "intrinsically safe." The electrical system of the ESLI shall include a positive warning mechanism for automatically indicating a loss of power to the user.

##### Rationale

The introduction of an electrical system into a respiratory protective device should not subject the user of the respirator to any new safety hazards. In addition, an ESLI that is dependent upon electrical power

should permit its user to detect the loss of power so that he is aware that his service-life indicator is not operational.

### 3.1.12 Hazardous Materials

#### Criteria

The ESLI must not expose, or potentially expose, its user to hazardous concentrations of substances other than those in the ambient environment.

#### Rationale

The objective of the ESLI/respirator system is to protect the user against hazardous environments. Any system that introduces new hazardous substances into the worker's environment is not consistent with the objectives of the ESLI/respirator system.

### 3.2 Theoretical Evaluation of Alternative Detection Systems

The second task of the ESLI development program involved the selection of an appropriate and effective technological basis for the detection of breakthrough of toxic gases in the air-cleaning element of an air-purifying respirator. Evaluation of detection techniques began with the following list of candidates:

- Adsorption on Organic or Inorganic Semiconductors
- Catalytic Oxidation
- Air Ionization
- Electrochemical Effects
- Infrared or Ultraviolet Absorption
- Oxidation-Reduction Reactions

Based upon previous work, the first two items on this list appeared, at the outset, to have the best characteristics for the desired purpose. Review of basic principles, and careful consideration of ways in which each of these principles might be employed, tended to confirm these initial impressions. Among characteristics desired of an ESLI were simplicity and reliability of operation, the invoking of a warning signal which would be both automatic and unmistakable, and initiation of the warning device without dependence upon any initiative by the user (i.e., a spontaneous signal). No promising approaches to the solution of these problems were found through the use of infrared or ultraviolet absorption systems, air ionization techniques, or electrochemical effects. Chemical reactions (primarily oxidation-

reduction) that produce dramatic changes in visible color were considered, as was one entirely new concept, the piezoelectric microbalance. Adsorption on semiconductors was subdivided into two categories, one consisting of the heated metal oxide semiconductors, commonly known as "Figaro" detectors or "Taguchi gas sensors," and the other being the photoconductive devices. Evaluation of these candidates was based upon literature search, theoretical considerations, and a limited amount of laboratory experimentation. The results of these assessments are summarized in the following section.

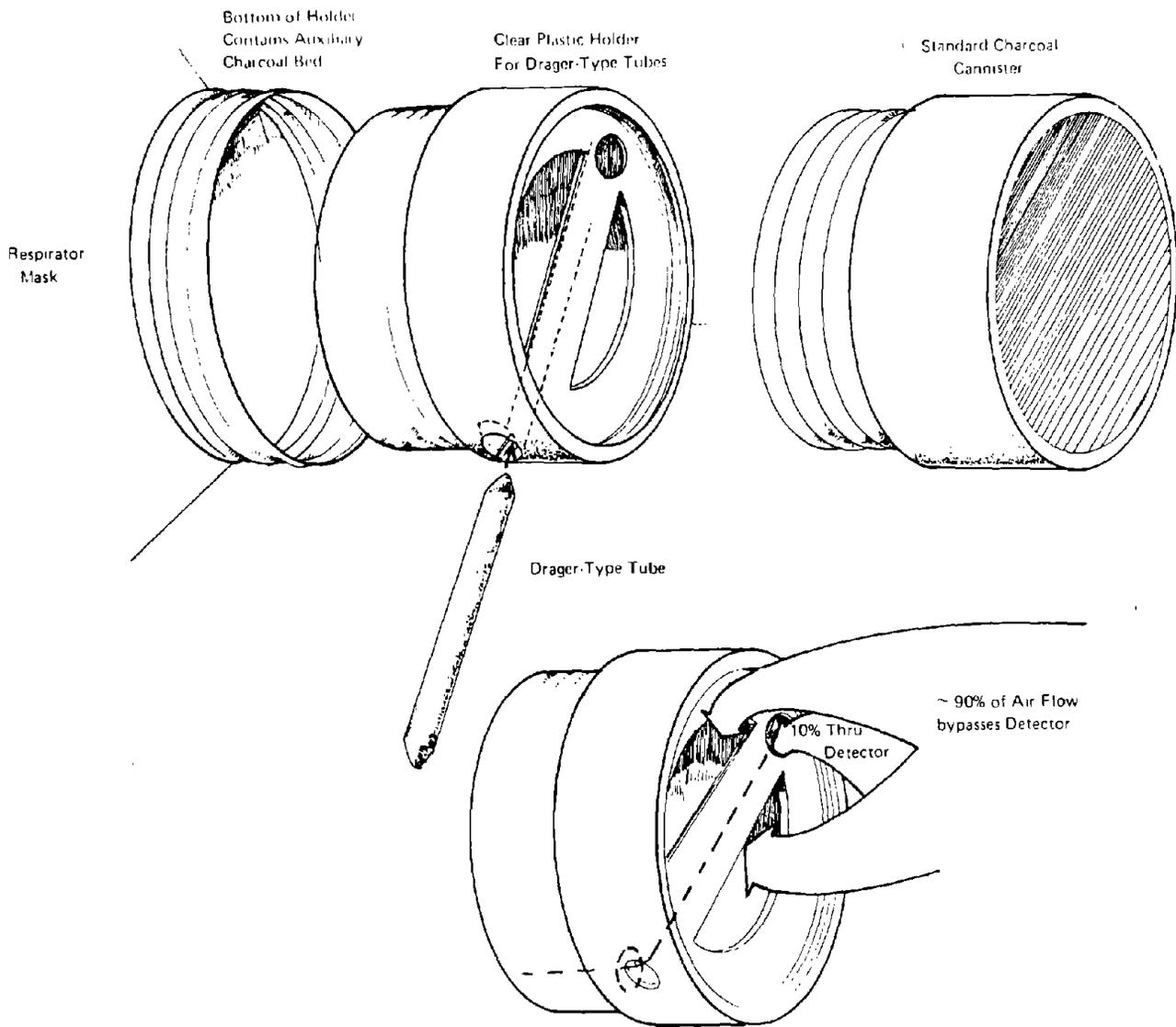
### 3.2.1 Color-Forming Reaction

A color-changing breakthrough indicator initially appeared to be an attractive possibility because of its relative simplicity, ruggedness, and low cost. Questions were raised, however, regarding the sensitivity and specificity of this approach, and in the end this detection technique was rejected because the limitations were judged to be severe, and because of difficulties in providing a suitable indicator that was complementary to this type of detection.

Figure 1 shows a possible embodiment of the colorimetric approach, illustrating the simplicity of the concept. A standard charcoal cartridge is mounted in a clear plastic holder into which a Drager-type colorimetric indicating tube may be mounted. Air flow through the charcoal cartridge is split so that 90% flows straight through the plastic holder (and through an auxiliary charcoal bed) while the remaining 10% of the flow is diverted through the detector tube. When the absorption capacity of the cartridge is exhausted, hydrocarbon vapors enter the tube and trigger the color change.

Very low triggering concentrations could produce visible color changes if the detector tubes could be designed so that a low hydrocarbon concentration would initiate a chemical reaction causing rapid color change in the entire tube. For example, the tube might contain zeolite- or carbon-type molecular sieves onto which a potent reagent was absorbed. If this reagent could be easily and specifically displaced by the hydrocarbon, then a fairly rapid and intense response of the tube would be produced.

The colorimetric indicator concept, despite possible disadvantages related to its lack of sensitivity and its selectivity, did satisfy some of the principal objectives of an ESLI, and probably could be made to satisfy all of the requirements for some limited number of reactive substances. Further investigation into this area of technology has been suspended due to the relatively small number of applicable substances and also because of the disappointing experience of organizations such as the U.S. Army (Edgewood Arsenal) in this area of technology.



**FIGURE 1**  
**DRAGER-TYPE TUBE CONCEPT.**

### 3.2.2 Piezoelectric Microbalance

In essence, the piezoelectric microbalance is simply an electro-mechanical means of measuring the mass of a very small quantity of matter. As little as a few picograms ( $10^{-12}$  g) of material can be measured, provided that the sample can be collected on the surface of a small quartz crystal. Detection and measurement of the added mass is possible by virtue of the slight alteration the addition produces in the vibrational frequency imposed on the quartz crystal by an applied electrical AC frequency in the range of 9-15 MHz.

For use as an ESLI detector, the microbalance requires the additional capability of selectively and efficiently collecting the organic vapors of concern. This capability can be provided, at least for some of the compounds, by the application of selective sorbents as coatings on the piezoelectric crystal.<sup>(1)</sup> Some of the common sorbents and stationary phases used in gas chromatography have been found to be effective in this regard. For example, materials such as squalane, silicone oils and apiezon grease have been used to collect hydrocarbons, while polyethylene glycol, dinonylphthalate, and alkyl sulfonates are effective for polar materials.<sup>(1)</sup> Certain inorganic salts (especially the halides of transition metals, lanthanides, and actinides) have been used as specific collectors for organophosphorous compounds.<sup>(2)</sup>

A desirable attribute for an ESLI detector is reversibility. That is, the detector should be able to respond continuously to fluctuations in the concentration of detectable vapors, or at least be able to be returned easily to a "zero" reading after each positive indication or "alarm". None of the sorbents cited is capable of what might be called "real time response," although some of them could conceivably be cleaned by heating or by purging with appropriate solvents. Alternatively, the entire sorbent coating could be removed and replaced in order to restore the detector's initial sensitivity. One concept which was put forth, but which was not tested, was that of coating the piezoelectric crystal with a solid semipermeable polymer which, when exposed to certain vapors, would absorb them, thus experiencing a measurable increase in mass. The sorbed vapor would be discharged either by purging in streams of a clean inert gas, or by mild heating, or both, thus giving the detector unit an acceptable degree of reversibility. Although this idea is appealing from a theoretical basis, proof of its effectiveness would require a major experimental program to develop a suitable detector.

Some of the advantages of piezoelectric mass detection for an ESLI are the small size and high sensitivity of the sensor, the relative simplicity of associated electronics, and the small power consumption. Also, depending on the nature of the sorbent applied to the crystal's surface, a considerable range of selectivity could be provided for substances that would be sorbed (and desorbed) by charcoal.

Among the limitations of the piezoelectric approach are the probable difficulty in discharging the sorbed substances from the surface coating, and the possibility that false-positive signals would be given by collection of unrelated substances such as water vapor, liquid droplets, or solid aerosol particles. Because the mode of action of the coated piezoelectric mass sensor is substantially different from that of any other system considered in this program, this type of device might be useful for some toxic vapors that are adsorbable on charcoal, but are not detectable by those other systems. Therefore, although it was not studied further in this program, it is suggested that the piezoelectric mass detector should be considered in any subsequent investigation.

### 3.2.3 Catalytic Detectors

Catalytic detectors operate by measuring the amount of heat liberated when an organic molecule reacts exothermically with an oxidant. In a gaseous atmosphere containing oxygen and small amounts of oxidizable organic vapors or gases, this reaction can be made to occur selectively at the surface of a suitable solid catalyst. This catalyst, which must ordinarily be maintained at some elevated temperature (usually above 300°C), must then be associated with a sensitive temperature-sensing element which can measure the small amount of additional heat produced by the catalyzed reaction. In effect, the sensor unit must be a miniature calorimeter, capable of measuring temperature changes resulting from the evolution of heat at levels as low as 100 kilocalories per mole.

In order for the sensor to operate continuously as a detector of oxidizable vapors, both the organic molecules and atmospheric oxygen molecules must be able to be adsorbed momentarily on the catalytic surface. The reaction products must not be strongly sorbed, however, since they must be discharged in order to make room for the arrival of new reactants. The temperature of the catalyst is controlled at a point high enough to assure that the rate of the reaction exceeds that of the diffusion of molecules in the gas phase to, and away from, the surface. The amount of heat produced is then directly proportional to the amount of oxidizable components in the gaseous atmosphere around the detector. In modern devices of this kind, two kinds of catalytic substances have been shown to be effective: the so-called "platinum metals" (platinum, rhodium, palladium and iridium); and a class of transition metal oxides, the best known of which are the Hopcalites, complex mixed oxides of copper and manganese. The platinum metals are generally formed into fine filaments which can be heated by their own resistance to an electric current, and whose temperature changes due to the occurrence of oxidation reactions on their surface, can be detected as changes in resistivity. The Hopcalite type of catalyst, which is inherently a poor thermal conductor, must be used as a coating on a heated thermistor, a requirement that imposes practical difficulties on its operation and limitations on its sensitivity.

Catalytic detectors are mainly useful for measuring concentrations of oxidizable gases in ranges below the lower explosive limits (LEL) of those substances in air. The lowest concentration of any gas that can be measured in air is limited by the signal-to-noise ratio of the temperature sensor. Inasmuch as these devices are operated at elevated temperatures, most of the noise is produced by thermal effects, and although these effects can be reduced by proper insulation and by using stabilized power supplies, it is generally not possible to accurately measure concentrations of oxidizable vapors below about  $10^{-3}$  x LEL.

The main deficiency of catalytic detectors lies in their susceptibility to interference from certain gaseous substances that are much more strongly adsorbed on the catalyst surface than either the gas to be measured or oxygen. These strongly adsorbed gases limit the area of the surface available for adsorption of the oxidizable gas of interest and, therefore, reduce the signal. Furthermore, if the interfering molecules are oxidized on the catalyst surface to yield a strongly adsorbed solid product, a cumulative reduction in surface area occurs which is not reversible, thus effectively poisoning the surface. Although some protection might be afforded through the use of semi-permeable membranes as filters to exclude these substances, the technique is not sufficiently selective for general use since membranes tend to differentiate substances mostly on the basis of molecular weight. Although Hopcalite catalysts are satisfactory for use in purification of air contaminated with oxidizable organic substances, they are not commonly used as detection elements, and are judged to be inferior to the platinum filament type of sensor.

In considering the possible use of a Hopcalite detector system for ESLI service, it was felt that such a system was probably not feasible for the following reasons:

- 1) The catalyst's high operating temperature ( $>300^{\circ}\text{C}$ ) would require a relatively large amount of power.
- 2) A thermistor or thermocouple would have to be coupled closely to the catalyst in order to detect the small temperature changes due to oxidation of vapors.
- 3) The temperature change through the catalyst itself would be slow since it is an insulator.
- 4) The catalyst is relatively insensitive to halogenated hydrocarbons.

In most respects, the use of a platinum wire catalyst as an ESLI sensor appears much more feasible than the use of the metal oxide catalyst. Although the temperature requirements for the two catalysts are similar, the platinum filament is heated due to its own resistance and the change in platinum wire resistance is readily measurable, so

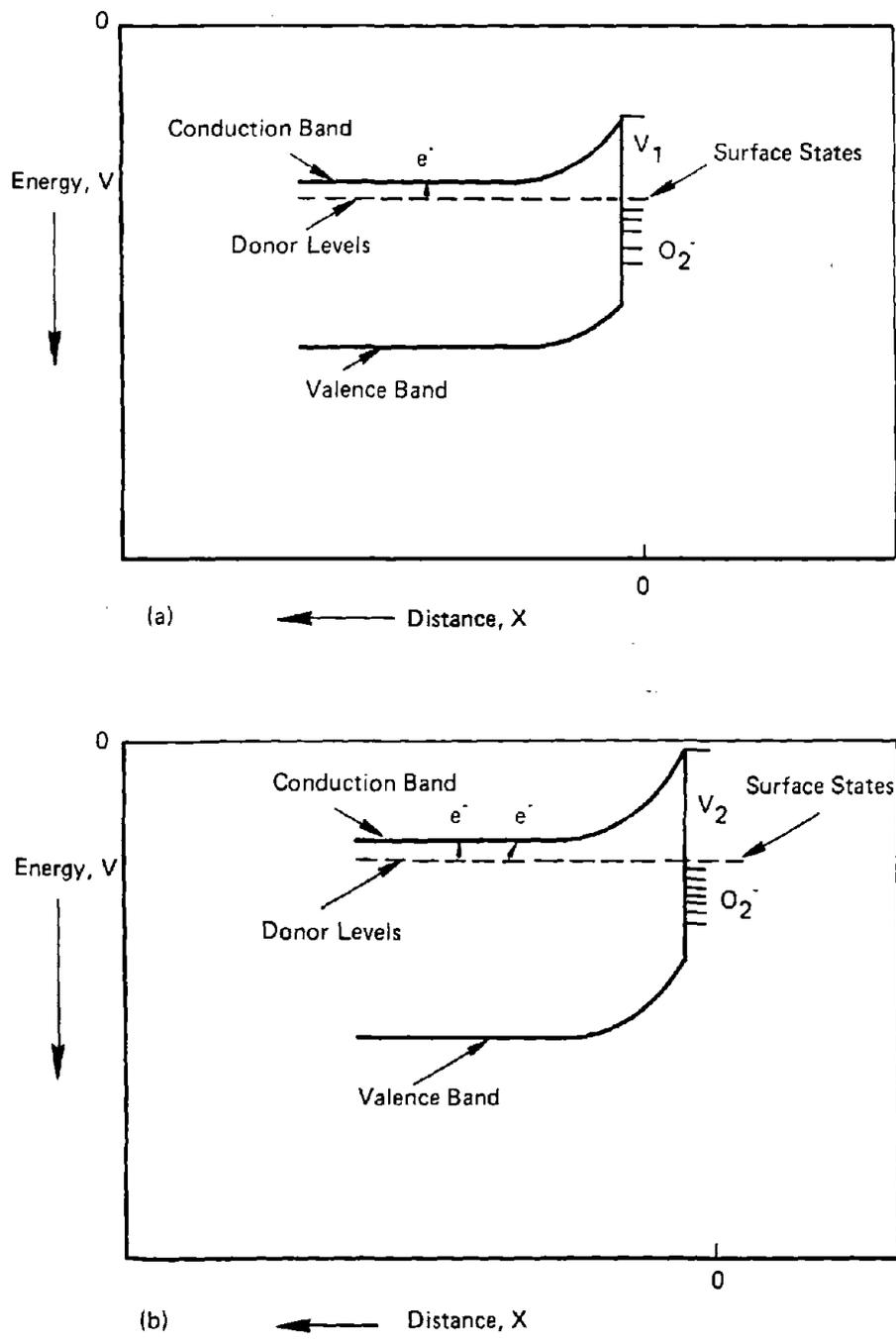
the catalyst and the heat sensor are intrinsically combined. The platinum filament is a good heat conductor and the temperature (and resistance) change can therefore be detected rapidly. Finally, commercial versions of portable explosive gas detectors using the hot platinum wire system are considered readily amenable to miniaturization. Instead, the platinum elements used in commercial units are small enough to use directly in any preliminary experimental program of gas detection.

#### 3.2.4 Heated Metal Oxide Semiconductors

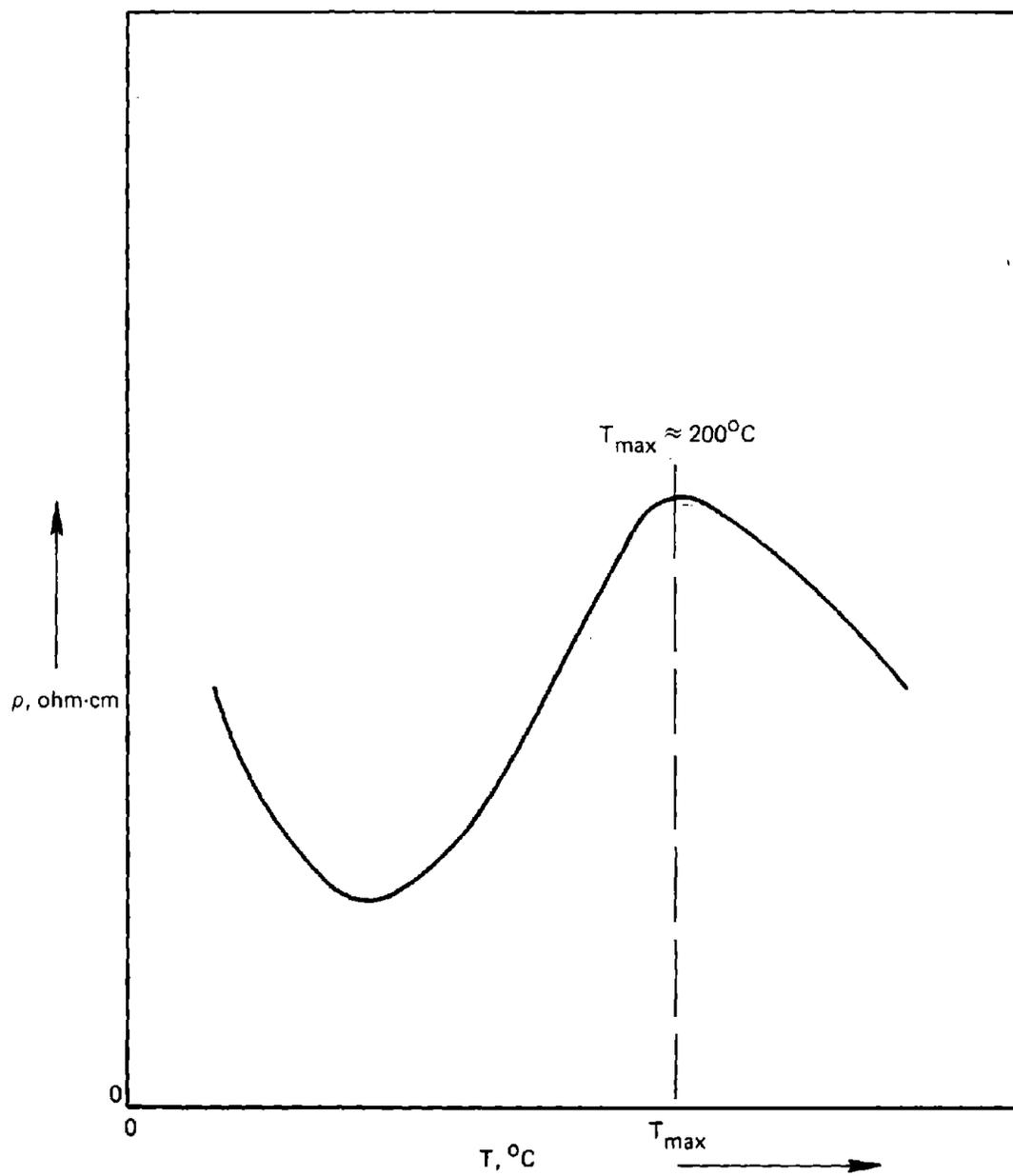
The effectiveness of a device known as the Metal Oxide Gas Sensor (MOGS) as a detector for organic vapors and gases is based upon the semiconductive properties of an n-type metal oxide, namely stannic oxide,  $\text{SnO}_2$ , crystalline lattice ("doping"). The electrical resistivity of this material can be varied over a wide range extending from that associated with electrical insulators to the low values of metallic conductors. When the material is lightly doped ( $\sim 10^{16}$  ions/cm<sup>3</sup>), such that its room temperature resistivity is in the range of about  $10^3$  ohm-cm, it becomes useful as a detector of oxidizable gases in air.

Figure 2a depicts the electronic band structure of lightly doped  $\text{SnO}_2$  at room temperature. The incorporation of small amounts of the dopant introduces electron donor levels close to the conduction band. As long as the donor levels are located no more than 0.1 eV below the conduction band at room temperature, a fraction ( $\sim 10\%$ ) of the electrons in the donor levels will be thermally excited to the conduction band, thereby substantially increasing the bulk conductivity. In the absence of an electric field or optical excitation, and in the presence of atmospheric oxygen, the donated electrons will be compensated by the chemisorption of oxygen on the surface. Adsorbed oxygen acts as an efficient electron trap, so the region near the surface becomes depleted of electrons, causing the energy bands to bend upward, i.e., the region near the surface becomes more positive on the energy scale depicted in Figure 2a. The net result is that an energy barrier is set up that inhibits further flow of electrons.

Figure 2b depicts the situation at higher temperatures, when a larger number of electrons are thermally excited to the conduction band. When this occurs, more oxygen is chemisorbed until at some temperature,  $T_{\text{max}}$ , all available surface adsorption sites are occupied. If the temperature is increased beyond that necessary to achieve saturation of the surface with adsorbed oxygen, the concentration of bulk electrons increases, but since there can be no additional chemisorption of oxygen, the resistivity decreases. The effect of temperature upon the electrical resistivity of  $\text{SnO}_2$  is shown schematically in Figure 3. In normal operation, the temperature of the surface is held constant, ideally, for most purposes, in the vicinity of  $T_{\text{max}}$ .



**FIGURE 2**  
 **$\text{SnO}_2$  BAND STRUCTURE AT (a) ROOM TEMPERATURE ( $\sim 25^\circ\text{C}$ )**  
**AND (b) HIGH TEMPERATURE ( $\sim 200^\circ\text{C}$ ). IN THE FIGURE,  $V_2 > V_1$ .**



**FIGURE 3**  
**RESISTIVITY OF MOGS VS. TEMPERATURE.**

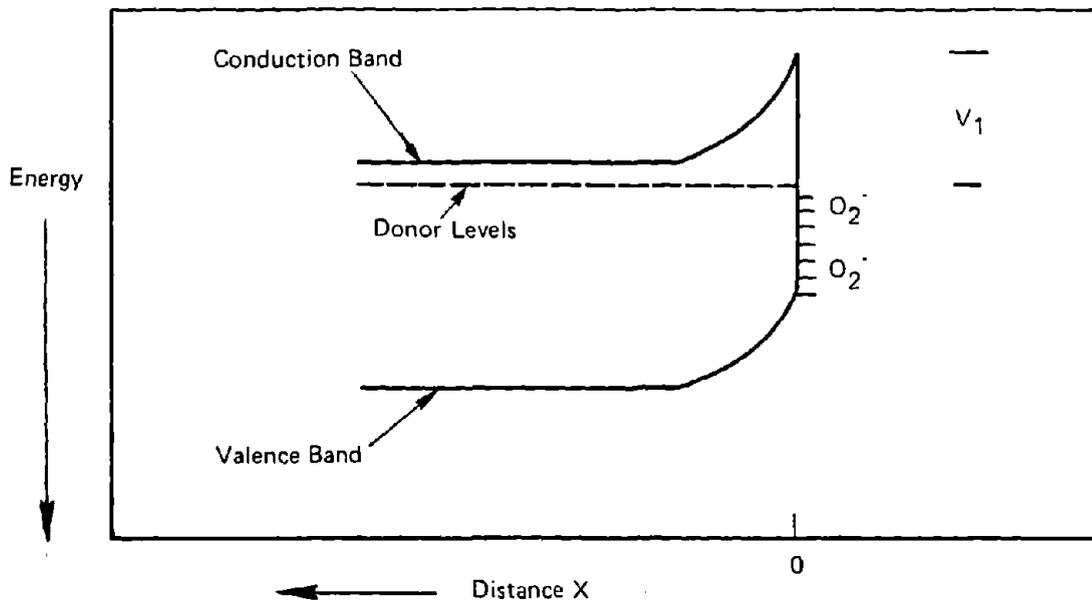
When oxidizable organic molecules approach the SnO<sub>2</sub> surface, the chemisorbed oxygen reacts with them, thereby releasing the oxygen's trapped electrons to the conduction band. At a given concentration of oxidizable gas, this process quickly attains a steady state in which the normal population of adsorbed oxygen molecules is effectively decreased because of the continuing reaction. This results in a decrease in bulk resistivity of the semiconductor which can be detected via a bridge circuit, for example. When the concentration of organic vapor decreases, the population of adsorbed oxygen from the atmosphere on the surface increases, more conduction band electrons are thus trapped, and the resistance returns to its former low value. Maintaining the temperature of the SnO<sub>2</sub> in the vicinity of T<sub>max</sub> assures an optimal balance of adsorption, desorption and reaction rates for most circumstances. The oxidation of an organic molecule will obviously be aided by the higher temperature, and the concentration of reactive oxygen on the surface will be maximized because of the increase in electropositivity of the surface resulting from the thermal excitation of a larger number of electrons under an applied DC field.

The chemisorption and desorption of oxygen on the SnO<sub>2</sub> surface obey a logarithmic rate equation of the type  $d\rho/dt \sim \exp(-bt)$ , where  $\rho$  is the resistivity,  $b$  is a constant, and  $t$  the time. This type of behavior is the direct result of the building up of an energy barrier (band bending) as adsorption proceeds, such that as each oxygen molecule traps an electron the probability of another electron surmounting the barrier decreases. The same rate law is followed in desorption and release of electrons back to the conduction band as the released electrons originate from progressively deeper energy levels. It can be shown that the time dependence will lead to a logarithmic dependence of the resistivity upon the concentration of organic vapor, i.e.,  $\rho \sim \log C$ . This means that there will be a relatively large change in resistivity at low concentrations of oxidizable vapor, a property that is advantageous for rapid detection of low concentrations.

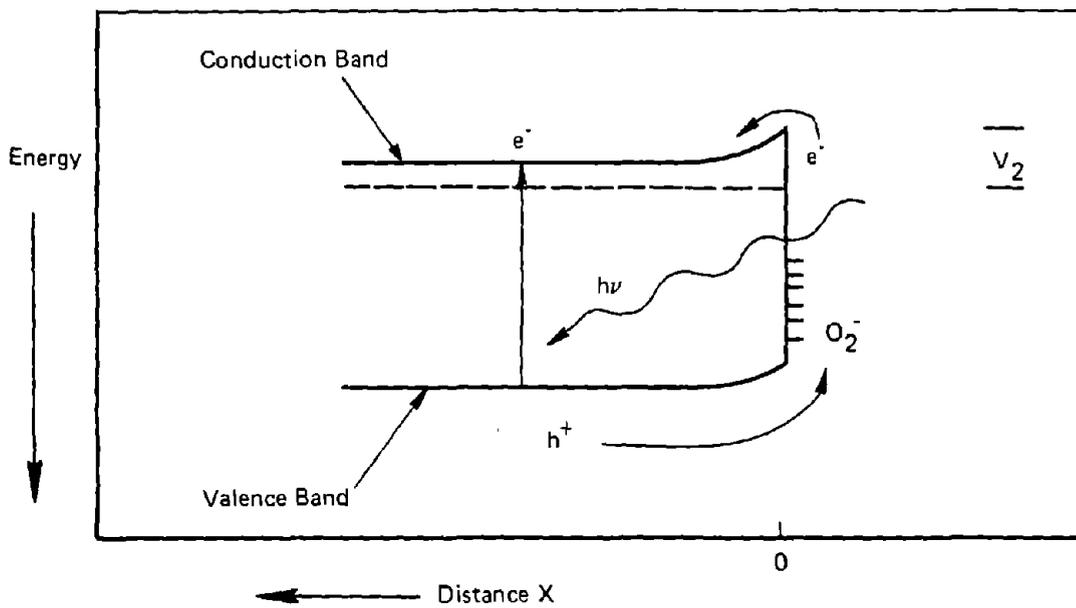
### 3.2.5 Photoconductors

Oxide semiconductors such as ZnO, TiO<sub>2</sub> and Cu<sub>2</sub>O exhibit a photoconductive effect at or near room temperature which could be useful in the detection of some organic vapors. The photoconductive effect in ZnO and TiO<sub>2</sub>, which are n-type semiconductors, has been studied by a number of investigators,<sup>(3-9)</sup> and a reasonable picture of the processes occurring during excitation by light has emerged. The mechanism that seems to be favored was first enunciated by Morrison<sup>(3)</sup> for ZnO, and later expanded on by Melnick<sup>(4)</sup> and by Medved.<sup>(5)</sup>

The mechanism proposed for ZnO is as follows: Figure 4 shows the relative positions of the energy bands of a photoconductive n-type oxide in the dark and under illumination. Under illumination and in the presence of some oxygen, the conductivity increases compared to what it would be in the dark because of the increased electron



(a)



(b)

FIGURE 4  
 BAND STRUCTURE OF n-TYPE OXIDE AT  
 (a) IN THE DARK AND (b) UNDER ILLUMINATION. IN THE FIGURE,  $V_2 < V_1$ .

population and because the minority carrier (a hole in the case of n-material) has interacted with chemisorbed  $O_2^-$ , yielding molecular oxygen. The interaction of the hole with  $O_2^-$  prevents recombination with the light-induced electrons. When the illumination is stopped oxygen will return to the surface and become chemisorbed as  $O_2^-$ . The  $O_2^-$  will trap an electron in the process, thereby reducing the conductivity. A similar mechanism has been proposed for the photoconductive effects in  $TiO_2$ . (6, 7)

If a vapor or gas that is a stronger electron acceptor than oxygen approaches the illuminated semiconductor surface, it may combine with the excess electrons, thereby reducing the conductivity. This effect has been observed for  $N_2O$  over  $ZnO$ . (10) It is reasonable to suppose that organic vapors containing carboxyl, nitryl, and nitro groups would be the most sensitive while amines and ethers, for example, would be least sensitive.

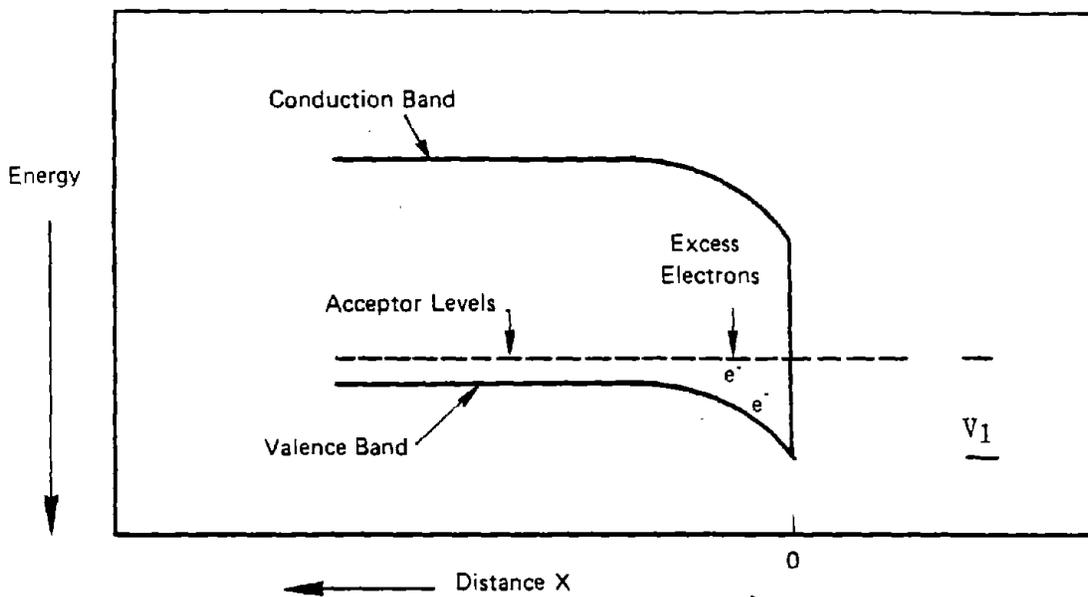
$Cu_2O$  is a p-type semiconductor whose conductivity is enhanced in the presence of oxygen. (11) One might envision a situation as shown in Figure 5 in which, in the absence of atmospheric oxygen and in the dark, the region near the surface is rich in electrons. As  $Cu_2O$  is a hole conductor, this would mean that the conductivity would be relatively low. With oxygen present, one would expect chemisorption and trapping of electrons near the surface such that the conductivity is increased. The role of photoexcitation is not clear as there is no evidence of adsorption-desorption effects on the photoconductivity of  $Cu_2O$  analogous to  $ZnO$  and  $TiO_2$ .

One might speculate, however, by noting that since the majority charge carrier in  $Cu_2O$  is an electron hole, a vapor or gas that will donate or inject electrons into the  $Cu_2O$  should reduce the photoconductivity. The injected electrons will act as recombination centers, thereby reducing the number of photo-induced holes. Thus, one might expect, for example, that electron donors such as organic amine vapors would be detected with high sensitivity, while electron acceptors should have little or no effect.

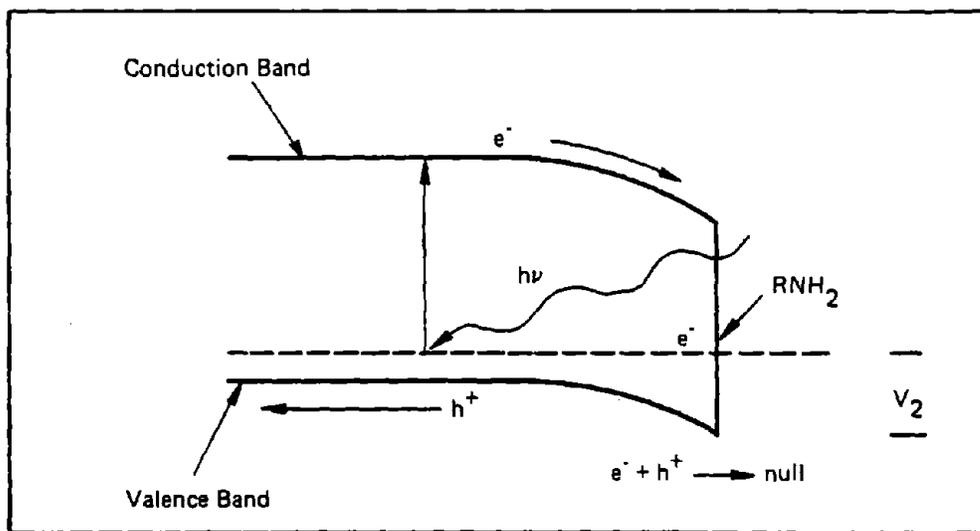
Oxide photoconductors offer some advantages over doped  $SnO_2$  devices, one of which is that of operation at ambient temperature. A light source is, of course, necessary, but this may be provided at a saving in power relative to a heating element. Possible disadvantages for purposes of an ESLI, however, include the restriction of sensitivity to specific classes of vapors and gases and the possibility of irreversible poisoning of the surface by strongly adsorbed species.

### 3.2.6 Summary

The metal oxide gas sensor (MOGS) was judged to have several important advantages for incorporation in an ESLI. The MOGS is commercially available, and generates a change in electrical resistivity which can



(a)



(b)

FIGURE 5  
SCHEMATIC BAND STRUCTURE OF  $\text{Cu}_2\text{O}$  (a) DARK (b) ILLUMINATED;  $V_2 < V_1$ .

be readily utilized to activate a buzzer, light bulb, or other warning signal. Available MOGS's are low in cost (approximately \$3 each), and require little in the way of instrumentation. Furthermore, these sensors are non-specific, responding to a wide variety of organic vapors. The principal disadvantage perceived in the MOGS was the large current drain caused by the high operating temperature.

While catalytic oxidation detectors require a stable power supply and good insulation to produce accurate sensing of low gas concentrations, this type of detector is low in cost, readily adaptable to positive indication, and non-specific.

While it was recognized that there were a number of approaches meriting further study, the metal oxide gas sensor and catalytic oxidation detector were selected for further experimental evaluation during this program. This evaluation is described in the following section.

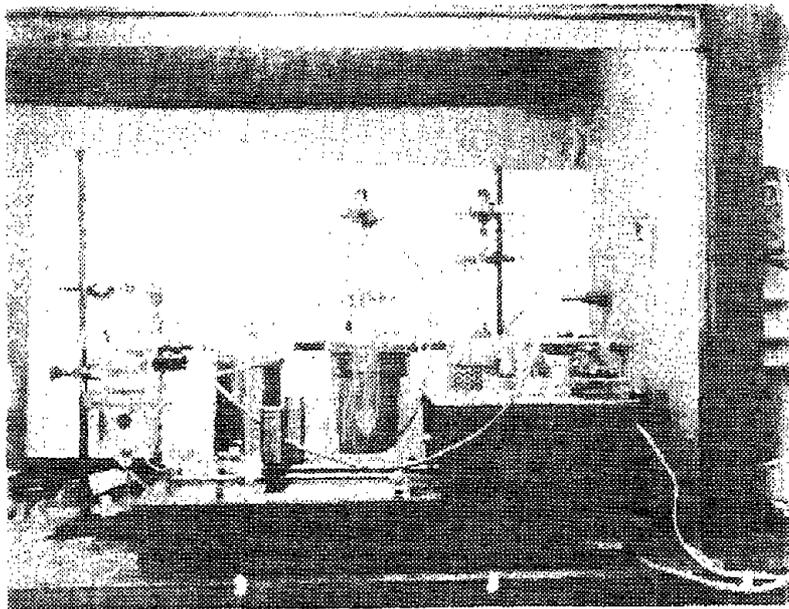
### 3.3 Experimental Evaluation of Preferred Approaches

#### 3.3.1 Heated Metal Oxide Semiconductors

##### 3.3.1.1 Experimental approach

Evaluation of both the metal oxide detectors and the catalytic detector was conducted utilizing a simple air train constructed from one-half inch diameter glass tubing. The tubing was fitted with an infusion port for the introduction of vapors at a controlled rate, and sampling ports to direct a portion of the air stream to the sample chamber. Laboratory air, filtered through a system consisting of a rough filter, drying agent, particulate filter and a final carbon filter, was generally maintained at a flow rate of 100 cc/min. Vapors were introduced at controlled rates using a calibrated Harvard syringe drive.

The sample chamber consisted of a plastic (polymethyl methacrylate) cylinder whose dimensions were 3 inches in diameter and 6 inches long. The chamber could be divided into two sections by the placement of a typical charcoal respirator cartridge at its midpoint. Thus, by introducing air into one end of the cylinder and venting it from the opposite end, the air in the second section would be purified by the charcoal trap, irrespective of the vapor concentration in the first sections. This allowed us to establish "true" operating background levels for the respirator cartridge and was particularly useful in determining the effect of water vapor on the performance of the sensor. A photograph of the apparatus is shown in Figure 6.



**FIGURE 6**  
**PHOTOGRAPH OF TEST APPARATUS.**

### 3.3.1.2 Sensitivity

The specific sensor that was evaluated is manufactured by the Figaro Engineering Co., and is sold under the name of "Figaro Gas Sensor," or the "Taguchi Gas Sensor" after its inventor, N. Taguchi. Initial testing was done using circuitry based upon a design which was provided by the manufacturer. A schematic of the circuit is given in Figure 7. This circuit permits one to measure the voltage drop across a variable resistor. The voltage drop is directly related to the resistance changes occurring when oxidizable organic vapors are detected.

Figure 8 shows typical results obtained on some selected vapors. By defining the detection limit as "that concentration which yields a potential drop of 1 volt," we were able to determine rough detection limits for a variety of organic vapors in air. The substances tested, which are listed in Table 1, were chosen to represent a wide variety of types of organic compounds. The compounds are also sufficiently volatile to exist in air at concentrations exceeding their TLV's or OSHA standards. The fact that the sensitivity of the MOGS to this wide variety of volatile compounds was nearly uniform shows that the presence of heteroatoms and functional groups has little effect on the performance of this type of detector. The resistivity of the detector is proportional to the logarithm of vapor concentration, so that the sensitivity of the detector is highest at low vapor concentrations. The sensitivity range for some compounds is two or three times that of others, largely because of saturation at higher concentrations. For example, at ~ 150 ppm of vapor the voltage drop for trichloroethylene is 3.5 volts, while that for n-butyl alcohol at the same concentration level is 6 volts.

With improved circuitry featuring temperature compensation, a stabilized voltage supply, and variable trigger levels, the detection limits were redetermined on a few of the materials and are shown in parenthesis in Table 1. It should be noted that these data were obtained with unamplified signals. It should be possible, perhaps with an amplified differential signal, to obtain further improvements in detection limits.

### 3.3.1.3 Interferences

The most important interfering substance is water vapor. Some inorganic gases such as CO, SO<sub>2</sub>, H<sub>2</sub> and NH<sub>4</sub> will elicit a response, but since the inhalation of these gases is not desirable, the fact that they are detected at some concentration may not be considered disadvantageous. Water vapor, however, is neither toxic nor hazardous and hence can truly be classified as an interference.

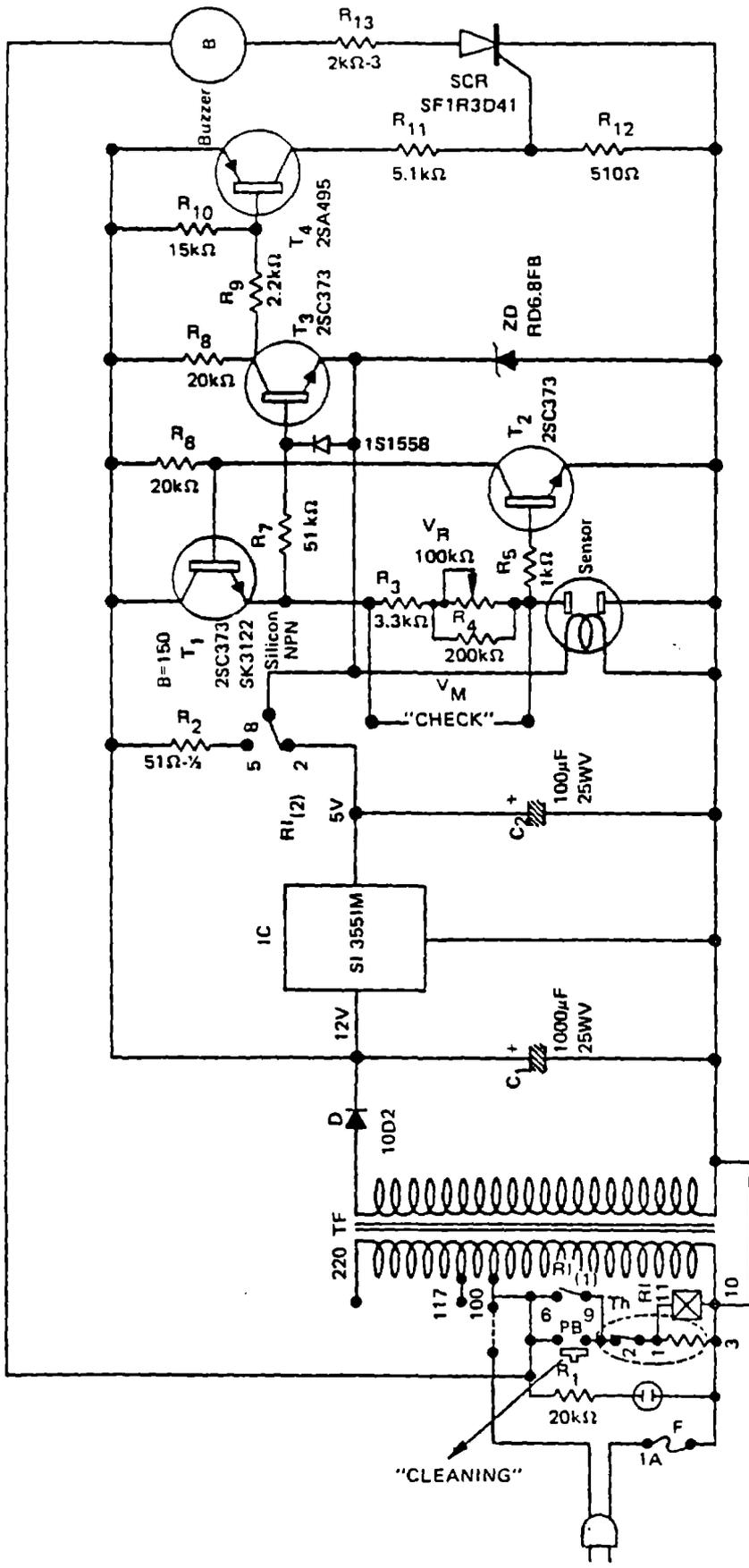
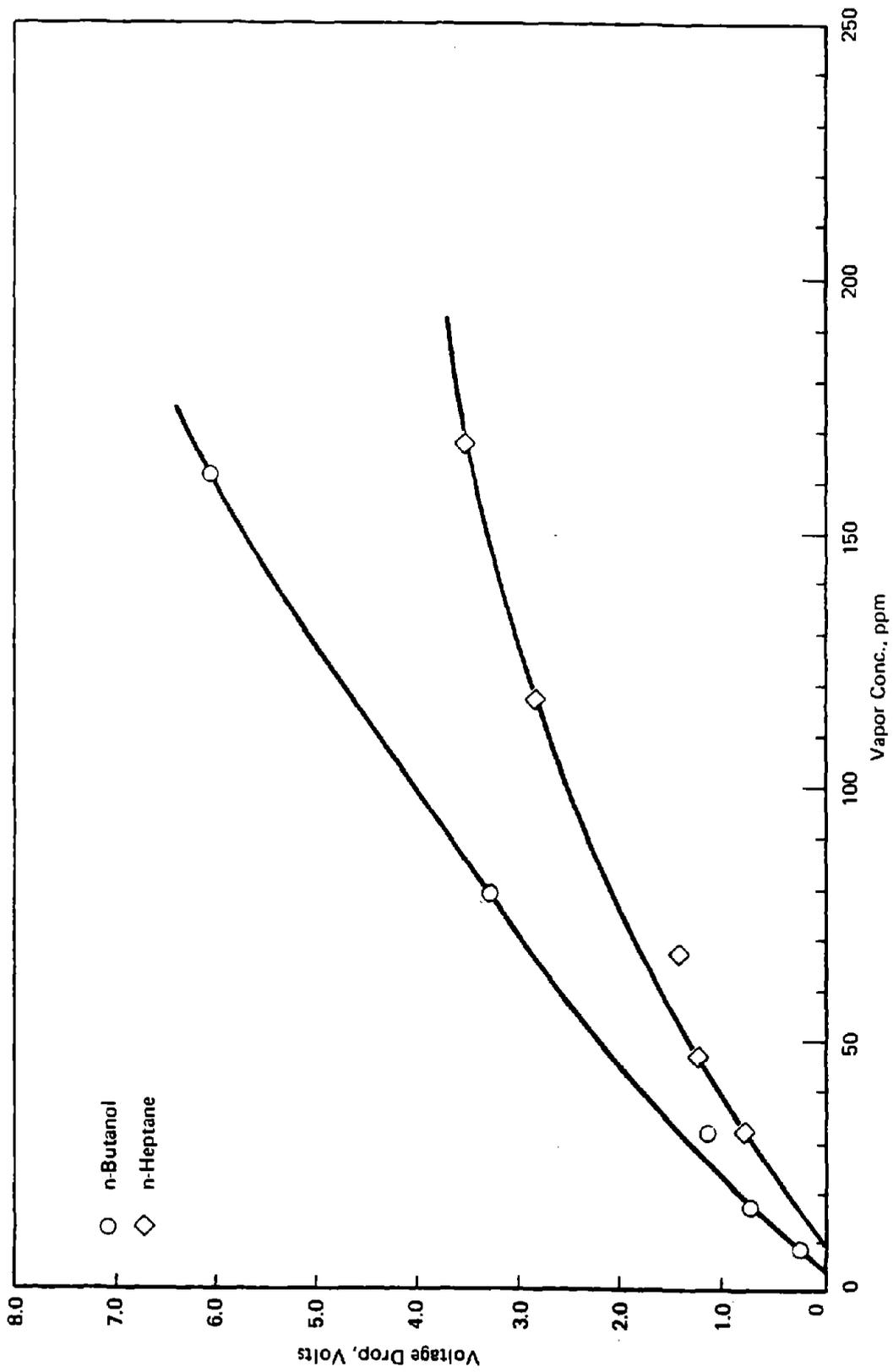


FIGURE 7 SCHEMATIC OF TAGUCHI SENSOR CIRCUIT



**FIGURE 8**  
**RESPONSE OF MOGS.**

Table 1

DETECTION LIMITS OF ORGANIC VAPORS BY MOGS

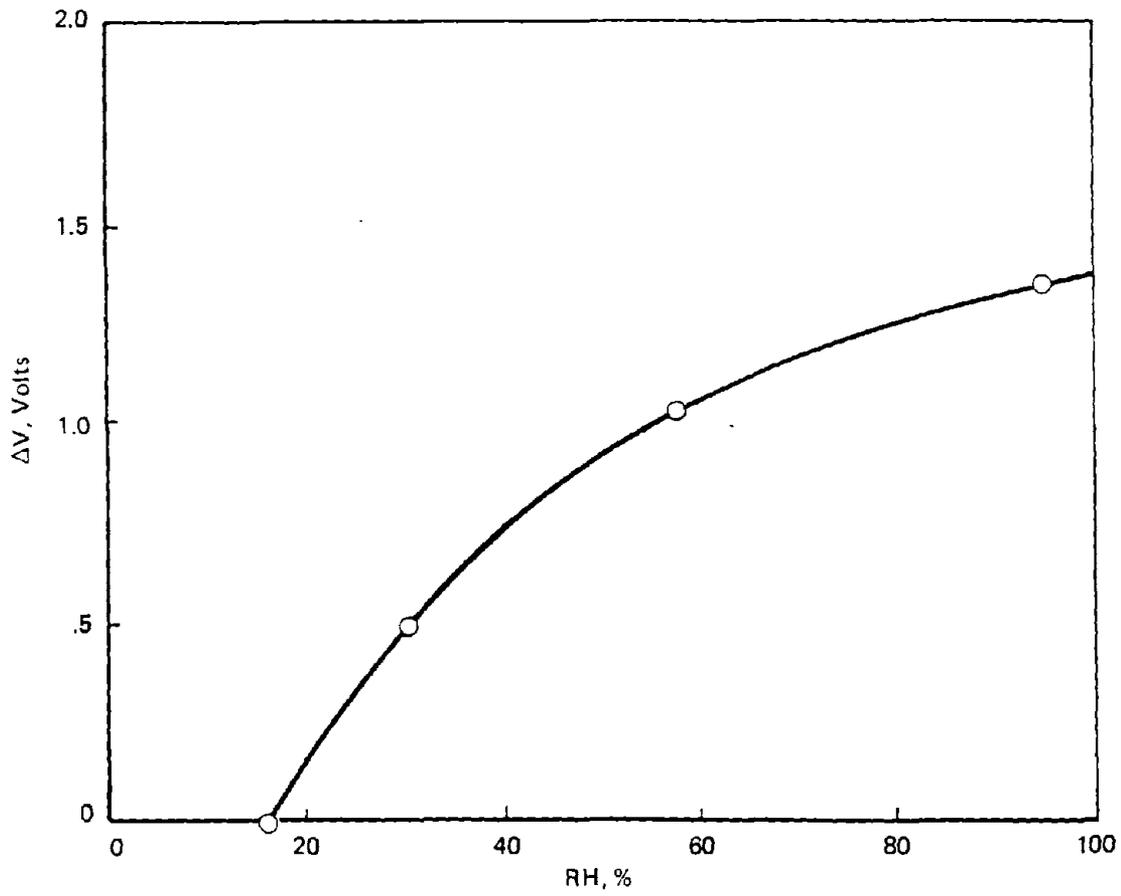
<u>Class</u>	<u>Compound</u>	<u>MOGS Detection Limit (ppm)</u>	<u>TWA OSHA Standard (ppm)</u>
Aliphatic Hydrocarbon	Heptane	40	500
Olefin	Styrene	40	100
Aromatic Hydrocarbon	Xylene	60	100
Aliphatic Amine	Diethylamine	40	25
Heterocyclic Nitrogen Compound	Pyridine	30 (13)	5
Heterocyclic Oxygen Compound	Tetrahydrofuran	60	200
Chlorinated Aliphatic Hydrocarbon	Trichloroethylene	80 (35)	100
Chlorinated Aromatic Hydrocarbon	O-Dichlorobenzene	40 (25)	50
Ketone	Methyl Isobutyl Ketone	40	100
Aliphatic Nitrogen Compound	Nitroethane	30	100
Aliphatic Oxygen Compound	n-Butyl Alcohol	20 (10)	100
Nitrile (Organic Cyanide)	Acetonitrile	40	40

Tests conducted during this program revealed that air saturated with water vapor at 35°C "uses up" approximately 25% of the total range of the detector's signal. Figure 9 shows the response of the detector to relative humidity levels ranging from 15% RH to 95% RH at 25°C. If an additional small quantity of organic vapor is present in such an atmosphere, the resultant signal is additive. There, if the water vapor concentration is reasonably constant, the increment due to the organic component can be reliably detected. Figure 10 illustrates the detectability of n-butanol and of o-dichlorobenzene in an air atmosphere saturated with water vapor at 95% RH.

A reasonably constant signal due to water vapor could be subtracted electronically so as not to generate false positive signals, but some loss in sensitivity to organic vapors would result. Figure 11 illustrates this for n-butanol vapor. The data show the individual responses for water vapor at 95% RH for 10 ppm of n-butanol and for 30 ppm of n-butanol in dry air, all at 25°C. If the detection circuitry were adjusted to subtract the water vapor signal due to 95% RH, concentrations as low as 10 ppm of n-butanol would not be detected in any atmosphere containing water vapor at levels significantly lower than 95% RH. Adjustments to subtract out a smaller portion of the RH signal will obviously result in false positive signals whenever higher concentrations of water vapor are present.

The MOGS was incorporated into a circuit with stabilized voltage supply, temperature compensation, and variable trigger levels that allowed the determination of the detection limits for various organic vapors at trigger level settings corresponding to maximum sensitivity and at levels designed to mask out the presence of water vapor (~ 30,000 ppm). When the trigger level is set at maximum sensitivity, the output from the detector circuit is 3.8v in clean, dry air. A voltage drop of 0.1v to 0.2v will cause an alarm signal to be generated. When the trigger level is set to mask the water vapor signal, the output from the detector is 5v in a clean atmosphere, and a voltage drop of ~ 1.3v is required to generate an alarm signal. Data on trigger levels in humid air were obtained on n-butanol, trichloroethylene (TCE), and o-dichlorobenzene and presented in Table 2. It is concluded from these data that one can expect to be able to detect most oxidizable organic vapors at their OSHA standard levels (Table 1) even when masking of the water vapor response is required.

It is not clear whether the response to water vapor is caused by the same mechanism as attributed to organic vapors, i.e., oxidation of vapor by surface  $O_2^-$ , or whether the  $H_2O$  simply displaces the  $O_2^-$ , effectively acting as an electron donor. The latter mechanism appears more likely, as a relatively high concentration of  $H_2O$  vapor (~ 30,000 ppm) does not begin to saturate the detector whereas 2000 ppm to 5000 ppm of most organic vapors will cause saturation. If the water vapor were being oxidized, 30,000 ppm would certainly use up all of the chemisorbed oxygen.



**FIGURE 9**  
**VOLTAGE DROP VS. RELATIVE HUMIDITY.**

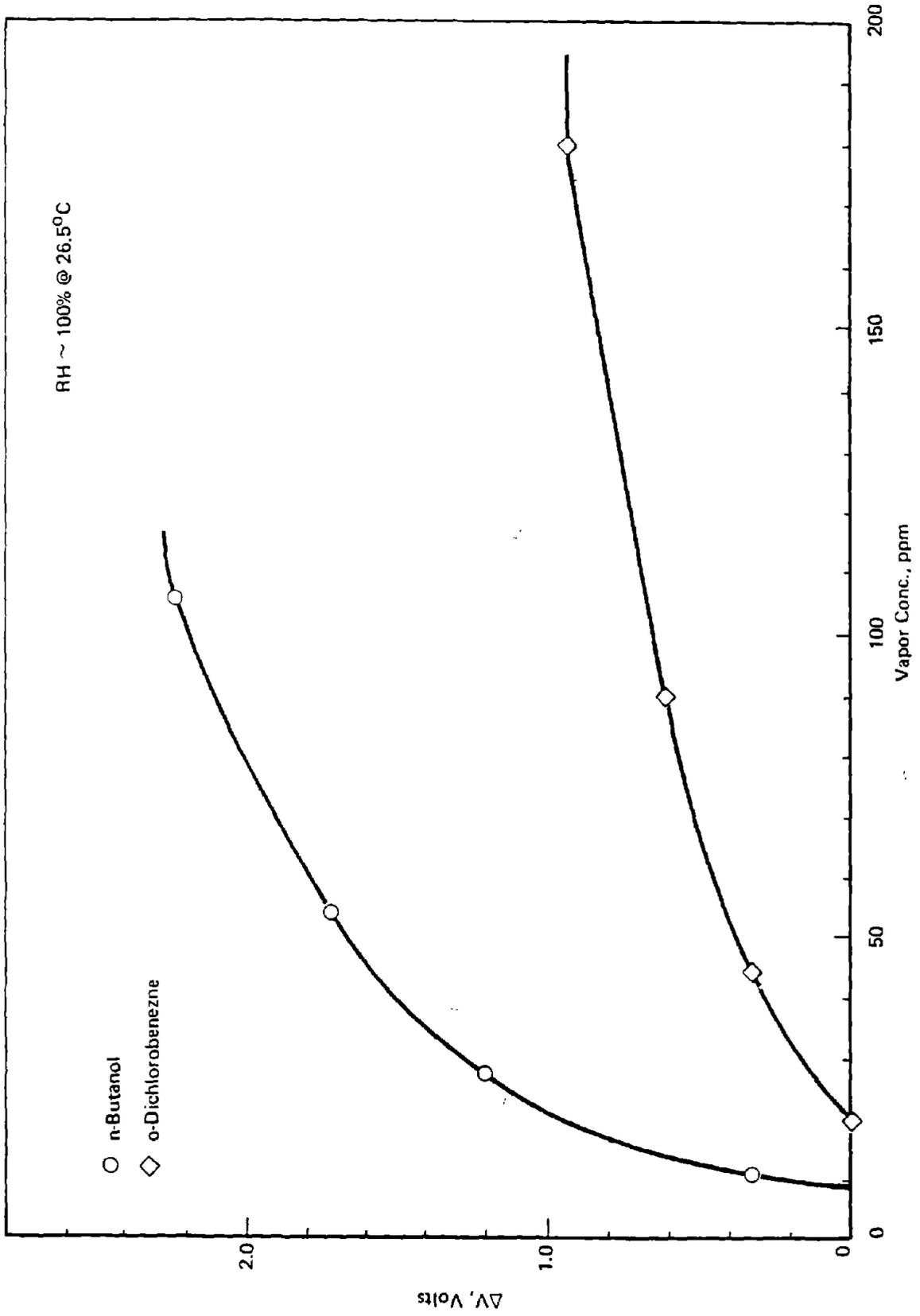
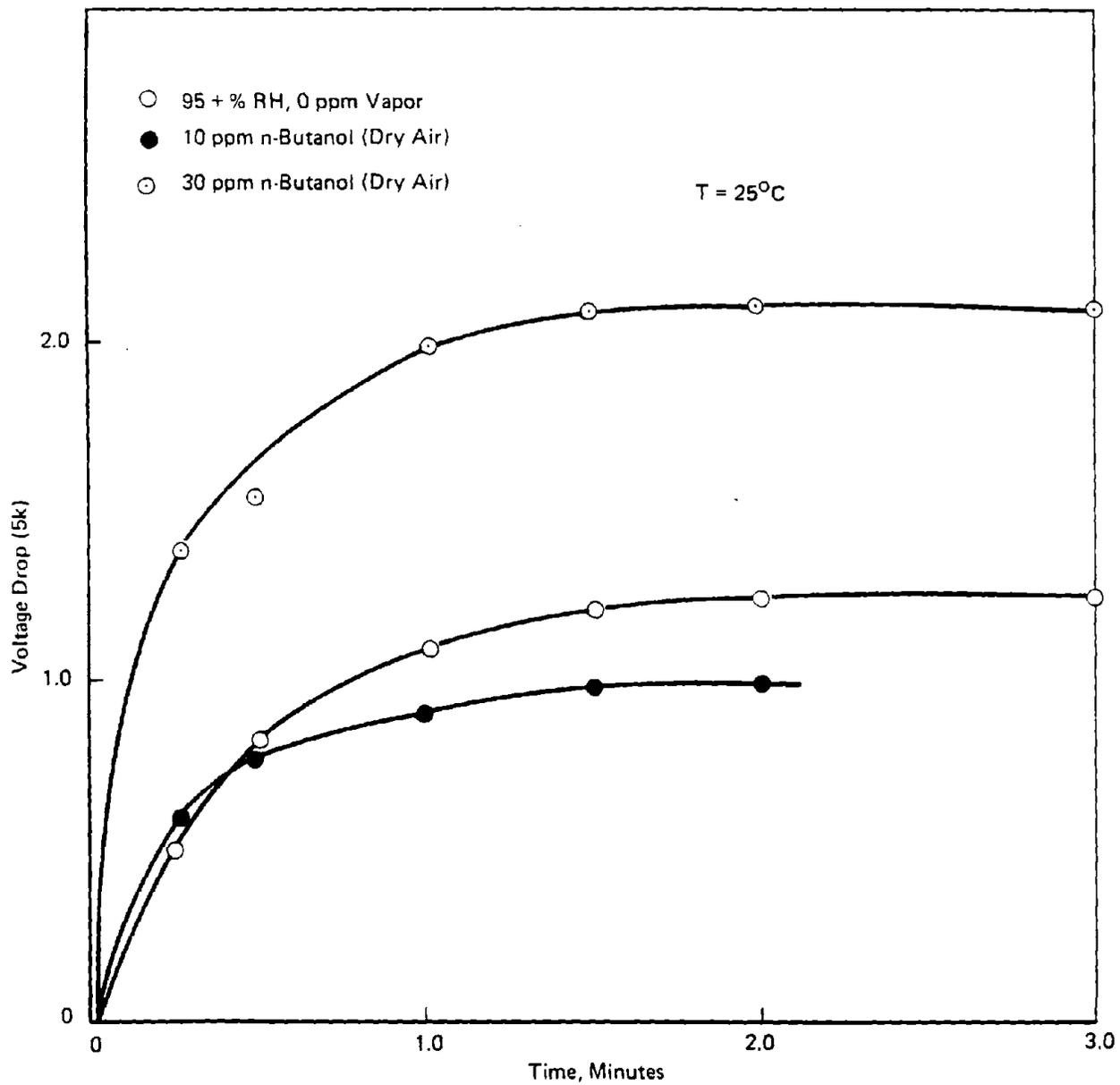


FIGURE 10  
EXCESS VOLTAGE DROP ABOVE WATER VAPOR SIGNAL.



**FIGURE 11**  
**n-BUTANOL RESPONSE RELATIVE TO WATER VAPOR RESONSE.**

Table 2

VAPOR CONCENTRATIONS REQUIRED TO ACTIVATE

FIGARO DETECTOR CIRCUIT

	Trigger Levels (ppm) for:	
	<u>n-Butanol</u>	<u>Trichloroethylene</u> <u>o-Dichlorobenzene</u>
Maximum Sensitivity	10	35      25
Water Vapor Threshold	30	90-110      45
OSHA Standard (TWA)	100	80      50

#### 3.3.1.4 Stability

The stability of the MOGS device is a function of the ambient temperature and the constancy of the heater temperature. Reference to Figure 3 shows that in the operating range of the device, the resistivity is a quite sensitive function of temperature and small deviations in temperature will result in relatively large changes in resistivity. When a thermistor and a voltage stabilizer were included in the detection circuit, the output of the MOGS remained constant in clean, dry air for many hours. The stability of the MOGS has been tested in such a circuit for periods up to 48 hours, with less than 0.1v variation in output voltage (3.8 volts) noted.

#### 3.3.1.5 Toxic By-products

Tests were conducted with o-dichlorobenzene to determine if phosgene, a likely toxic by-product, was generated when the vapor came in contact with a MOGS device. Air containing 1000 ppm of o-dichlorobenzene was passed through the sample chamber containing activated MOGS. The vapor was collected and analyzed as recommended in the NIOSH sampling and analysis method for phosgene. None was found.

### 3.3.2 Catalytic Detection

#### 3.3.2.1 Sensitivity and Stability

A commercial hot wire detector, manufactured by the Mine Safety Appliances Corp., was tested using the apparatus described in section 3.3.1.1. As the highest sensitivity scale of the detector circuit was 0-10% LEL, it was necessary to tap the output from the bridge circuit and feed it into a potentiometric recorder with a full scale sensitivity of 1 mv. Figure 12 shows the output obtained for various scale readings in the 0-10% range.

Two of the materials listed in Table 2 were examined, namely n-butanol and trichloroethylene, which were representative of materials to which the MOGS detector was most sensitive and least sensitive, respectively.

Figure 13 shows the response obtained at vapor concentrations ranging from about 100 ppm to 900 ppm. The response of the catalytic detector was approximately linear over the range studied. It appears that the device should be able to detect oxidizable vapors in the range 100 ppm to 200 ppm. However, for application as an ESLI device, it would be advantageous to amplify the output signal at least a thousandfold.

The most serious problem with the hot wire detector tested was the observation of a continuously drifting baseline. Typically, the baseline would drift by about 0.25 mv over a period of 6 hours when the detector was exposed to clean dry air. When one considers that the

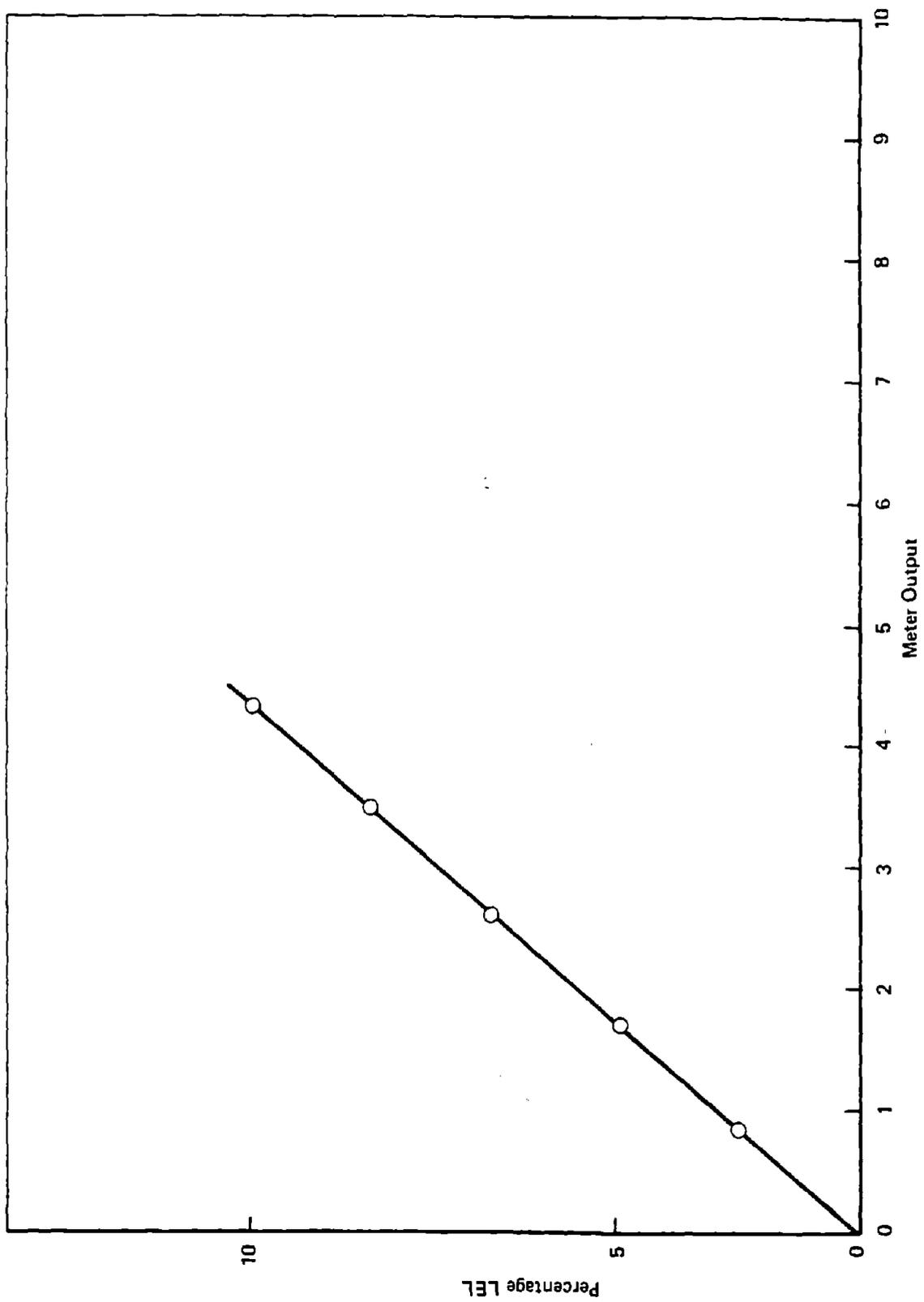


FIGURE 12  
OUTPUT OF MSA DETECTOR.

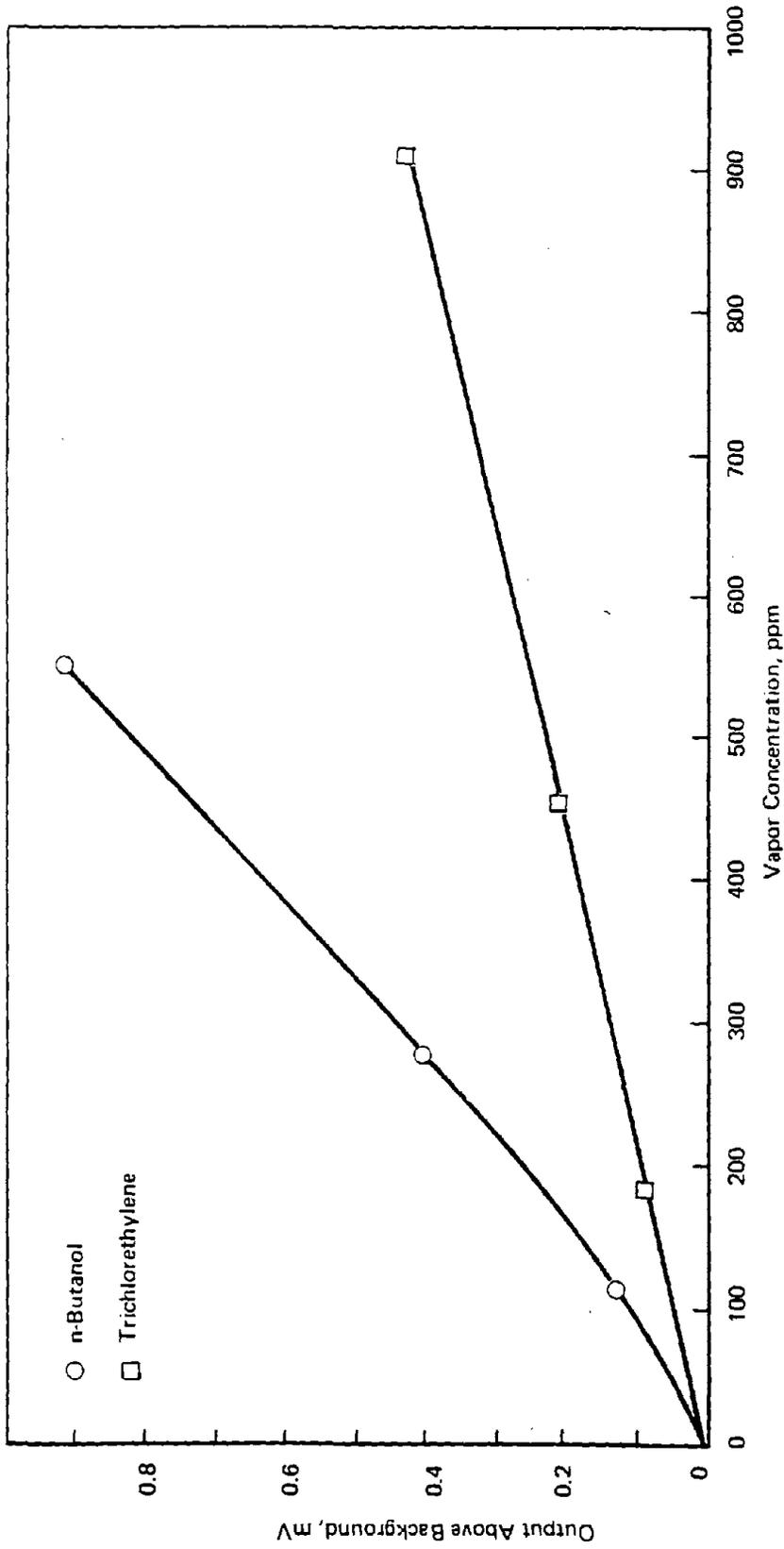


FIGURE 13  
RESPONSE OF MSA DETECTOR.

output for 100 ppm of n-butanol was only 0.1 mv above the baseline, the observed drift is obviously unacceptable for an ESLI. Despite the use of a second detector (isolated in a clean atmosphere) as a temperature compensator, baseline drift was not eliminated. It is conceivable that by amplifying the signal sufficiently at the earliest possible opportunity, the observed instability might be controlled, but since this type of detector was being considered only as an alternative to the MOGS, further efforts to improve its performance were not felt to be justified at this time.

### 3.4 Development of Prototype Units

Based upon the superior performance of the MOGS system in experimental evaluation, that detector was chosen for incorporation into a prototype ESLI.

The physical assembly is based upon the concept of locating the detector and indicator light on the face mask of a chemical cartridge respirator,\* with the associated electronics and power supply placed in a pack suitable for belt mounting.

The electronic circuitry is designed to provide one signal indicating the presence of vapor, and another distinctive signal indicating a low power through on-off cycling.

Details of the ESLI prototype design are provided in the following sections.

#### 3.4.1 Electronic Circuitry

##### 3.4.1.1 Power Supply

The power supply consists of a battery of five Eveready CH1.2T rechargeable Nicad cells. This battery weighs 247 grams (.54 pound) and has a nominal rating of 1.2 ampere-hours. The design of the power supply is very conservative in that the battery is sufficient to operate the detector circuitry for more than six hours without the power-saving duty cycle feature. Through the use of cycled operation, operating time is extended approximately threefold, with the result that there will be only small changes in battery voltage during normal operation and performance will be optimum.

##### 3.4.1.2 Duty Cycle

The electronic circuit was designed to operate the metal oxide gas sensor (MOGS) detector on a 25 percent duty cycle to save power. The MOGS takes two minutes after application of heater power to warm up and equilibrate. The operating cycle, therefore, consists of a 2-minute

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\* For chest-mounted gas mask applications, the detector is located on the canister, with the light on the face mask.

interval during which power is supplied to the MOGS heater, followed by a 6-minute "off" time. The actual measurement of the concentration of vapor is made during the last part of the "heater on" interval.

The battery drains are about 180 and 20 milliamperes during the "on" and "off" time periods, respectively. The alarm indicator light draws 8 milliamperes when on, but since it is usually off or flashing (average flashing load is 4 milliamperes), it is not a significant drain on the battery. The nominal operating time per charge is 20 hours.

#### 3.4.1.3 Alarm Indication

When excessive vapor is detected during the measurement (toward the end of the "heater on" interval), a latch is set which gates a flashing on-off signal to the LED driver amplifier. The resultant flashing indication persists throughout the 6-minute "heater off" period. At the start of the "heater on" interval the latch is reset, which stops the flashing indication until another measurement of excessive vapor is made.

A separate circuit monitors the battery voltage and turns the LED driver on if this voltage should fall below the level for proper circuit operation (about 5.5 volts). The low voltage indication, since it is a "full on" signal, overrides the flashing excessive vapor indication. The circuit was designed this way to eliminate false alarms caused by low battery voltage.

#### 3.4.1.4 Circuit Description

A circuit diagram is shown in Figure 14. An oscillator, consisting of  $R_1$ ,  $R_2$ ,  $C_2$ , and two gates from  $U_1$ , drives  $U_2$ , a 14-stage counter, whose lowest output frequency is the 8-minute cycle. Outputs from this counter are combined to produce the 2-minute "on" interval, the "reset" pulse which occurs during the first half minute of the "on" interval, and the "measure" pulse which occurs during the last half minute of the "on" interval.

One section of  $U_5$ , an operational amplifier quad, together with transistors  $Q_1$  and  $Q_2$  form a voltage regulator maintaining five volts across the heater of the MOGS. The reference for the voltage regulator is Zener diode CR2. The voltage regulator also serves as the switch for the heater power; a high level output from pin 10 of  $U_3$  turns the voltage regulator off.

The resistance of the MOGS is measured in a bridge circuit consisting of  $R_6$ ,  $R_7$ ,  $R_{10}$ ,  $R_{11}$ ,  $R_{12}$ , and the temperature compensation thermistor, JA41J1. The output from this bridge is amplified by one section of  $U_5$ , gated by the "measure" pulse through the "nor" gate,  $U_4$ , and sets the latch formed from two more "nor" gates in  $U_4$ . When the latch is set, its output gates the flashing signal from pin 5 of  $U_2$  through an "and"



gate, U3, to pin 11 of the driver amplifier U5, causing the LED to flash. The low voltage signal from pin 9 of U5 will override the flashing signal and keep the LED on continuously when the battery voltage is low.

The "reset" pulse from pin 9 of U1 resets the latch at the start of the heater on time interval.

The circuit board layout is shown in Figures 15 and 16.

### 3.4.2 Physical Design

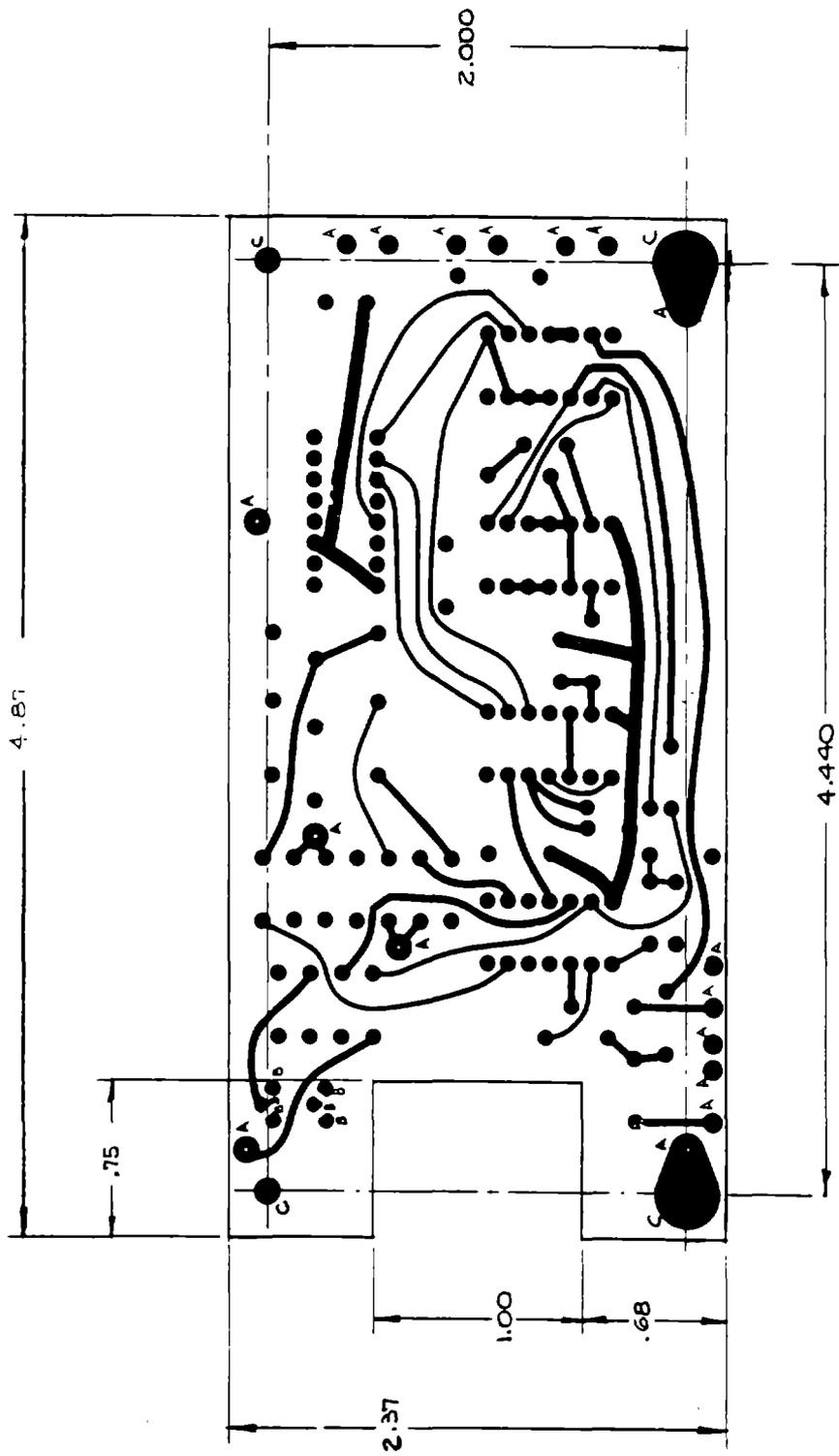
The ESLI has two major physical elements: a detector mounted in the respirator mask and an electronics box.

Air-purifying respirators intended for use in organic vapor atmospheres have one or more cartridges of sorbent material. Check valves are arranged so that upon inhalation, air passes through the cartridge and the inhalation valve. On exhalation, air is prevented from flowing out through the cartridge by the inhalation valve, and it flows out through the exhalation valve. It was decided that the most favorable place to mount the detector was between the cartridge and the inhalation valve. This assures that freshly filtered air passes over the detector, giving the earliest possible warning of vapor breakthrough. Furthermore, the detector is protected from exhaled air which could contain alcohol or other organic vapor. In the prototype ESLI, the plastic adapter into which the cartridge is threaded has a passageway terminating with the inhalation valve. This had sufficient space to mount the detector, after adding a second rubber gasket to space the cartridge further out.

The warning light that indicates the presence of vapor could most easily be mounted on the electronics box, but that configuration could permit a signal to go unnoticed for a time. It was concluded that the light could not remain unnoticed if it was mounted within the wearer's range of peripheral vision. Both the half- and full-face respirators have the cartridges in this range; therefore, the warning LED was mounted in a small bracket on the plastic housing, with leads connected at the detector mounting screws. In this way, the connector cable goes into the airtight housing through a seal, and all the connections are inside.

All the remaining parts are enclosed in an electronics box, meant to be worn on the user's belt (see photographs in the Appendix of this report). External elements include a power switch, a test button, connector cable, and a charging jack, all mounted on the top surface. The batteries consume the most space, and a commercially available plastic box was selected that was slightly larger in every dimension than a row of batteries, and the controls were accommodated in the remaining space.

The packaging approach taken was expedient for prototype construction, but production units could be more compact and attractive. By placing the circuit board beside, rather than over the batteries, the case

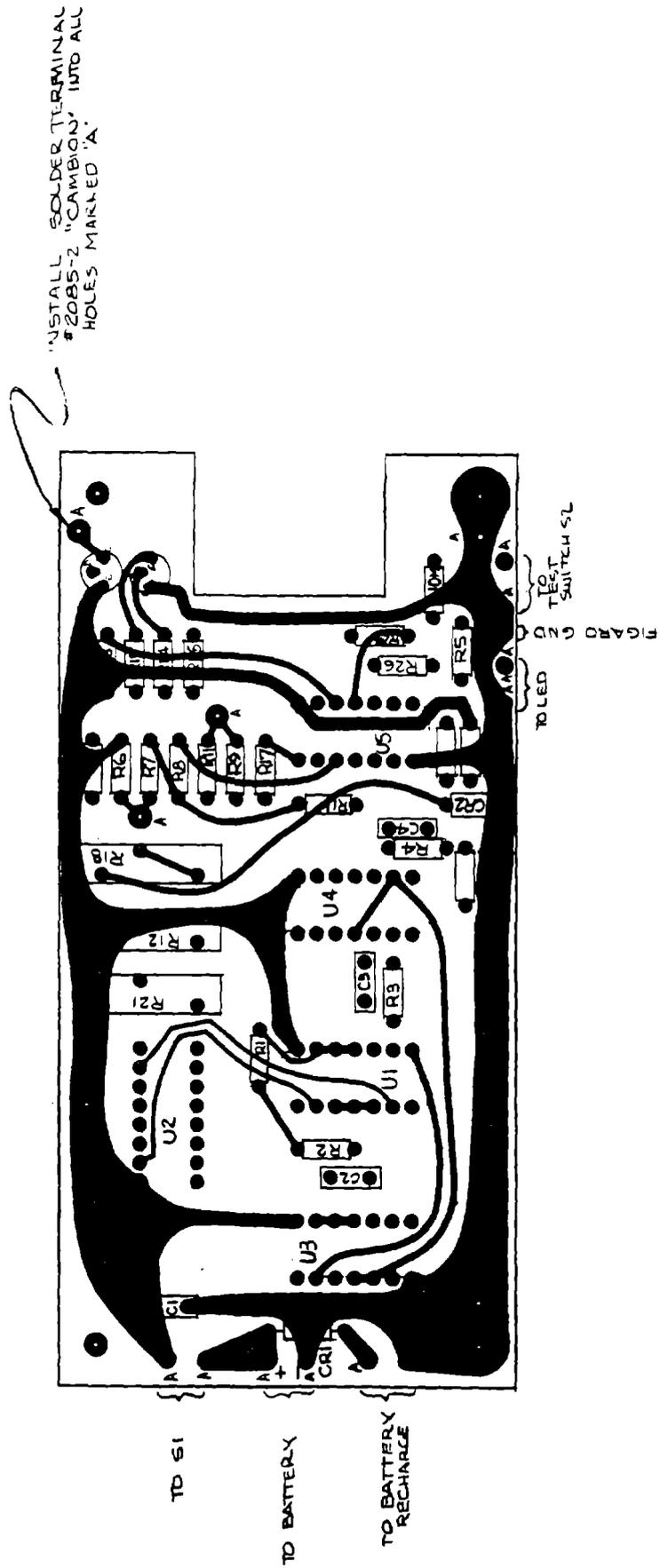


HOLE LEGEND		
HOLE PH	SIZE	QTY
-	.030 DIA. .037	140
A	.047 DIA .049	17
B	.023 DIA .028	6
C	.154 DIA.	4

REF DRAWINGS:  
 C-79677-02  
 MASTER PATTERN  
 B-79677-01  
 SCHEMATIC  
 C-79677-03  
 ASSEMBLY

PH - PLATED THRU HOLES  
 NPH - NON PLATED THRU HOLES  
 MATERIAL: PLASTIC SHEET LAMINATED, COPPER CLAD  
 FL - 6E062C1/1B118 PER MIL - P - 13949

FIGURE 15  
 ORGANIC VAPOR DETECTOR PRINTED CIRCUIT BOARD DRILLING AND ROUTING.



REF. DRAWINGS:  
 SCHEMATIC B-79677-01  
 MASTER PATTERN - C-79677-02  
 DRILLING DWG C-79677-04

FIGURE 16  
 ORGANIC VAPOR DETECTOR CIRCUIT BOARD ASSEMBLY.

could be reduced from 1-1/2" thick to 1" thick, without increasing other dimensions. This would also permit the use of board-mounted switches and jack, eliminating some wiring. The prototype connector cable is relatively stiff and bulky, and would, therefore, be replaced by a more appropriate cable.

Although there is some opportunity for improvement in subsequent generations, the present prototype should provide a realistic impression of the final physical characteristics of an ESLI.

### 3.5 Recommended Use Conditions

The prototype ESLI that has been developed in the present program was designed to have as wide a range of applicability as possible, while preserving a satisfactory level of accuracy in detecting failure of the air-purifying sorbent module. Inevitably this device, and probably any device intended for this purpose, will represent a number of compromises between ideal but unrealizable goals and a practical product. Thus, any service-life indicator system will be usable only in strictly defined and limited situations. Recommended use conditions, along with approval criteria, will have to be specified for each detector, and probably for each detector-sorbent combination.

The metal oxide gas sensor (MOGS) detector is sensitive to concentrations in the range of 20-100 mg/m<sup>3</sup> of a wide variety of moderately volatile organic substances. As we have shown, it is also sensitive to water vapor and to some other oxidizable vapors, and is essentially incapable of distinguishing qualitatively among any of these substances. Some substances to which the sensor is most sensitive may have a high OSHA permissible exposure level (e.g., 500 mg/m<sup>3</sup> or more) while others, like water vapor, may be quite harmless to human health. The presence of large quantities of such harmless substances in mixtures with more toxic compounds will inevitably cause confusion and ambiguity unless the capabilities and responses of the sorbent indicator system to each particular mixture are well understood and specified. Additionally, differences in the ability of any given sorbent to retain different volatile substances to which the MOGS is sensitive may result in a further complication, the possibility of false alarm signals.

Probably the most severe limitation on the reliable performance of the MOGS system as an ESLI is imposed by its sensitivity to water vapor. Under conditions of reasonable stable water vapor concentration, the MOGS may be quite effective as an ESLI for specific organic vapors, since "breakthrough" for those vapors will produce a signal that is clearly distinguishable above the steady-state "background" signal due to the water vapor. If, however, the humidity of the air changes substantially during periods of continuous use, then the pre-set alarm level will have to be adjusted, either up or down, to compensate for the change. The same procedure would also apply to any other low-toxicity substance that is less strongly sorbed than the component of

concern, and which represents a normally constant "background" constituent. Detectable, poorly sorbed "background" substances whose concentrations fluctuate widely and unpredictably could render the ESLI virtually useless.

In general, false-negative signals are likely to be the most serious type of error, since they could subject the wearer of the respirator to excessive exposure to toxic substances. Provided that sufficient care is exercised in identifying the components of any occupational environment in which the ESLI-equipped respirator is to be used, and in establishing the concentrations in which contaminants will be present, the likelihood of a false negative condition occurring in practice can be virtually eliminated. Obviously, the set of conditions to be avoided is that in which the sensitivity of the MOGS to the substance of concern is marginally close to the OSHA permissible exposure limit for that substance, while the "background" signal is high and variable. Under these circumstances, the concentration of a toxic constituent that only slightly exceeds its OSHA limit may go undetected indefinitely because the necessary sensitivity has been sacrificed in order to compensate for the high and variable background.

One may state as a general rule the following requirements for use of this type of ESLI (the MOGS), which may be applicable to ESLI's in general:

1. For any proposed industrial use, identify the toxic substance(s) of concern for which the respirator is to be used, and the expected concentration levels.
2. Identify any other components of the specific occupational environment to which the ESLI will respond, and the expected concentration levels.
3. Determine from (1) and (2) whether an adequate signal (e.g.,  $\Delta V = 1.0$  V DC) will be produced by the OSHA permissible exposure limit concentration of toxic components, once a suitable correction has been made for inconsequential background substances.
4. If an adequate specific signal is anticipated, test the ESLI in actual use (note that, for respirators equipped with two sorbent cartridges, both units should have ESLI's) to assure that the background-nulling correction in the output signal is sufficient to prevent false alarms. (This will presumably require a screwdriver adjustment.) Then remove the sorbent cartridge and check to see that the ESLI responds to the "challenge" concentration of the toxic vapors in the unpurified air.

### 3.6 Suggested Performance Criteria for Approval

The use of air-purifying respirators by individual workers is presumably limited to instances in which the workplace air is or may be contaminated by one or more toxic substances at levels above the appropriate OSHA standard. The conditions under which a device for respiratory protection against toxic gases might be used are described in 30 CFR 11, Subparts A, I, and J. A fundamental assumption that must be made in granting approval for the use of respirators is that the devices may fail in use, and the wearer should be warned of such failure in time for him to avoid excessive exposure to a toxic substance. The present regulations stipulate that such air-purifying respirators may be used to protect against only those toxic vapors that have "adequate (sensory) warning properties," a condition that is now recognized to be so poorly defined as to create confusion over the acceptability of these devices. The purpose of the ESLI is to provide the necessary warning for as many as possible of the toxic vapors that have no intrinsic sensory warning property, such as a characteristic odor, that is perceptible just at (or slightly below) the OSHA permissible exposure concentration.

Some of the physical properties that have been used as design-and-performance criteria in the present investigation (Section 3.1) were specified with the intent of satisfying what were believed to be some basic requirements for an ESLI system. Most of these properties could well be incorporated directly into a set of standards for approval. In particular, the following items might be specified:

#### 1. Specificity

It is axiomatic that a highly selective and specific detector will offer higher reliability and freedom from false indications than one that is sensitive to a wide variety of substances. To be practical and economical, however, the indicator should be sufficiently versatile (i.e., nonselective) to permit its use for a variety of toxic vapors. Recognizing the desirability of such versatility, one should be especially careful to specify in detail what the sensitivity of any proposed device is to stated detectable substances, and what substances cause interferences, both positive and negative. Inasmuch as the possible variety of interfering substances (i.e., those that are easily detectable, but have low toxicity) may be too large to catalog, and since any given industrial environment may contain a particular mixture of them, together with one or more toxic species, the only practical solution to the problem of approval would seem to involve detailed specification of each atmospheric composition (including ranges of concentration) in which the device may be used. Approval can then be given, withheld, or limited as required on the basis of demonstrated performance of the proposed device for these conditions stated.

## 2. Indicator Characteristics

To be acceptable, an ESLI must provide an active indication of the end-of-sorbent life. It must not require any action by the user to indicate warning. ESLI indication must be given by a visual signal within the user's field of vision or by an equivalent auditory signal.

## 3. Respirator Fit

No component of the ESLI, or of the devices utilized to attach the ESLI to the respirator, shall interfere with the effectiveness of (a) the facepiece-to-skin seal or (b) the respirator's headstraps or harnesses.

## 4. Weight Distribution

The ESLI shall be supported so as not to change the weight distribution of the respirator to the detriment of facepiece fit.

## 5. Impairment of Vision

The ESLI must cause no substantive impairment of existing lines of sight.

## 6. Durability

Any ESLI component that is permanently installed in the respirator facepiece must be capable of withstanding cleaning with a detergent. Any ESLI component must be capable of withstanding dropping from a height of 6 feet.

## 7. Breathing Resistance

An ESLI system shall not increase breathing resistance through the respirator to the extent that present resistance limits are exceeded.

## 8. Temperature and Humidity

Satisfactory performance for the specified detection limits and atmospheric composition must be applicable from 0°-40° C and for 0-100% RH within that temperature range, unless narrow limits are clearly stated.

## 9. Electrical Components

Any electrical power supply and electrical components of an ESLI shall conform to the applicable provisions of the National Electrical Code. The electrical system shall be approved for use in flammable atmospheres. The electrical system of the ESLI shall include a positive mechanism to automatically warn the user of loss of power.

#### 10. Hazardous By-products

The ESLI must not generate concentrations of substances so as to add hazardous conditions to the ambient environment.

#### 11. Assembly

The ESLI wiring and connecting components (if any) shall be designed for assembly and use such that (a) the user's physical motions are not restricted and (b) any break of wiring or connecting pieces which disrupts ESLI functioning is signaled to the user.

## 4. CONCLUSIONS AND RECOMMENDATIONS

### 4.1 Conclusions

During this program, a prototype, non-specific, end-of-service life indicator (ESLI) for organic vapor respirators was developed. The device is compatible with existing respirators, gives a positive alarm of contaminant breakthrough, and detects a wide variety of organic vapors. The prototype device is capable of meeting the desired performance requirements, but has not been field-tested. This device was not designed to meet all of the practical considerations that would be important in commercialization.

Service-life indicators can be developed to supplant the reliance upon inherent warning properties as an indication of sorbent saturation. Such devices would require NIOSH certification prior to their use with approved respirators; however, due to the variety of potential design approaches available and the differences in effectiveness among them, certification of indicators for protection against specific, individual contaminants appears to be necessary.

### 4.2 Recommendations

Based upon work conducted during this study, it is recommended that the following efforts be initiated:

1. The prototype ESLI should be tested under actual industrial conditions. Such tests would help to define ESLI sensitivity, reliability, capability, stability, and acceptability to workers.
2. The MOGS detector should be subjected to further testing to more fully define the range of its capability to detect various vapors.
3. The ESLI system should be tested to determine its response to various environmental factors that have not yet been evaluated. Factors of interest include the effects of sensor aging (both in use and in storage) and possible electromagnetic interferences.
4. Other types of detectors (e.g., piezoelectric) should be explored further to determine whether they can be utilized to extend the number of contaminants for which a sorbent life indicator is effective.

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APPENDIX  
PHOTOGRAPHS OF PROTOTYPE DEVICE

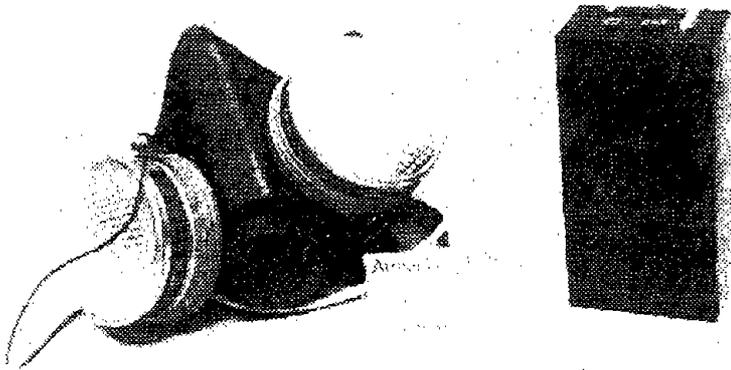


FIGURE A1  
DETECTOR INSTALLED ON  
ONE CARTRIDGE OF RESPIRATOR.

FIGURE A2  
PROTOTYPE ESLI SYSTEM.

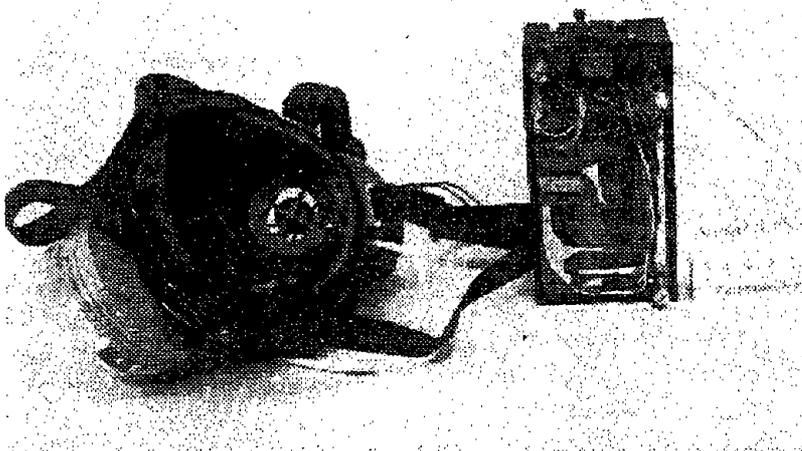
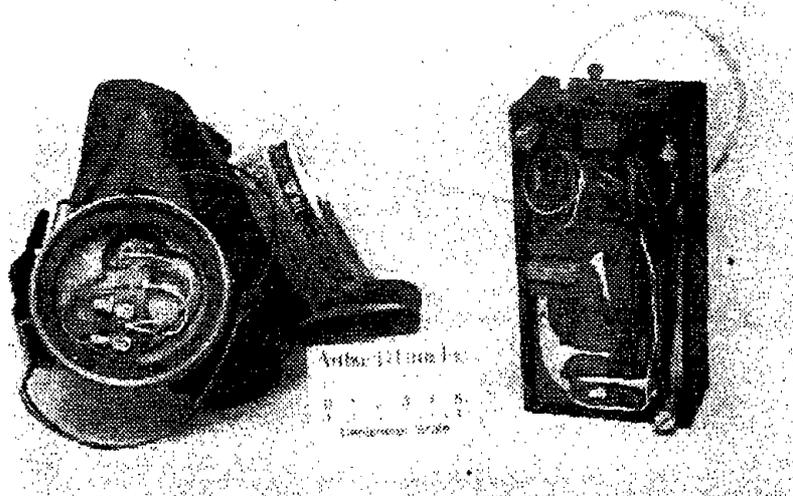
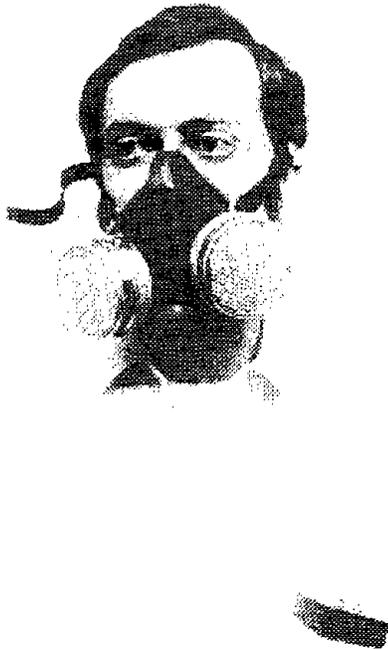


FIGURE A3  
DETECTION ELEMENT VIEWED  
THROUGH INHALATION VALVE.



**FIGURE A4**

**ESLI SYSTEM IN OPERATION (FRONT VIEW).**



**FIGURE A5**

**ESLI SYSTEM IN OPERATION (SIDE VIEW) .**