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Carbon Monoxide Monitor for Automobile Passenger Compartment

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16. Abstract

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The approach followed in this study was first, to define the physical and chemical characteristics of the vehicle's compartment and the surrounding environment; second, to evaluate the effects of these environments on the MOS sensor performance in terms of sensitivity, selectivity and stability.

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PREFACE

This document reports the results of the study conducted by the Carnegie Mellon Research Institute (CMRI) to evaluate its recently developed metal oxide semiconductor (MOS) gas sensor technology for applications in the automobile environment. The specific use of this technology is for a low-cost carbon monoxide (CO) monitor to be placed in the automobile compartment to protect the driver and passengers.

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METRIC / ENGLISH CONVERSION FACTORS

ENGLISH TO METRIC

LENGTH (APPROXIMATE)

1 inch (in) = 2.5 centimeters (cm)
1 foot (ft) = 30 centimeters (cm)
1 yard (yd) = 0.9 meter (m)
1 mile (mi) = 1.6 kilometers (km)

AREA (APPROXIMATE)

1 square inch (sq in, in^2) = 6.5 square centimeters (cm^2)
1 square foot (sq ft, ft^2) = 0.09 square meter (m^2)
1 square yard (sq yd, yd^2) = 0.8 square meter (m^2)
1 square mile (sq mi, mi^2) = 2.6 square kilometers (km^2)
1 acre = 0.4 hectares (he) = 4,000 square meters (m^2)

MASS - WEIGHT (APPROXIMATE)

1 ounce (oz) = 28 grams (gr)
1 pound (lb) = .45 kilogram (kg)
1 short ton = 2,000 pounds (lb) = 0.9 tonne (t)

VOLUME (APPROXIMATE)

1 teaspoon (tsp) = 5 milliliters (ml)
1 tablespoon (tbsp) = 15 milliliters (ml)
1 fluid ounce (fl oz) = 30 milliliters (ml)
1 cup (c) = 0.24 liter (l)
1 pint (pt) = 0.47 liter (l)
1 quart (qt) = 0.96 liter (l)
1 gallon (gal) = 3.8 liters (l)
1 cubic foot (cu ft, ft^3) = 0.03 cubic meter (m^3)
1 cubic yard (cu yd, yd^3) = 0.76 cubic meter (m^3)

TEMPERATURE (EXACT)

[(x - 32) (5/9)] °F = y °C

METRIC TO ENGLISH

LENGTH (APPROXIMATE)

1 millimeter (mm) = 0.04 inch (in)
1 centimeter (cm) = 0.4 inch (in)
1 meter (m) = 3.3 feet (ft)
1 meter (m) = 1.1 yards (yd)
1 kilometer (km) = 0.6 mile (mi)

AREA (APPROXIMATE)

1 square centimeter (cm^2) = 0.16 square inch (sq in, in^2)
1 square meter (m^2) = 1.2 square yards (sq yd, yd^2)
1 square kilometer (km^2) = 0.4 square mile (sq mi, mi^2)
1 hectare (he) = 10,000 square meters (m^2) = 2.5 acres

MASS - WEIGHT (APPROXIMATE)

1 gram (gr) = 0.036 ounce (oz)
1 kilogram (kg) = 2.2 pounds (lb)
1 tonne (t) = 1,000 kilograms (kg) = 1.1 short tons

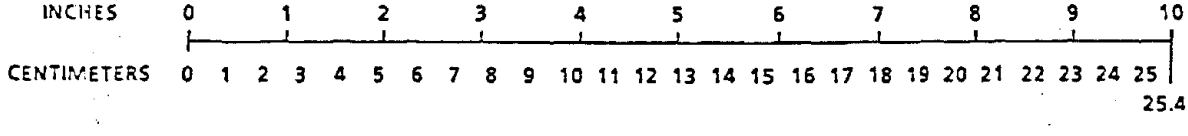
VOLUME (APPROXIMATE)

1 milliliter (ml) = 0.03 fluid ounce (fl oz)
1 liter (l) = 2.1 pints (pt)
1 liter (l) = 1.06 quarts (qt)
1 liter (l) = 0.26 gallon (gal)
1 cubic meter (m^3) = 36 cubic feet (cu ft, ft^3)
1 cubic meter (m^3) = 1.3 cubic yards (cu yd, yd^3)

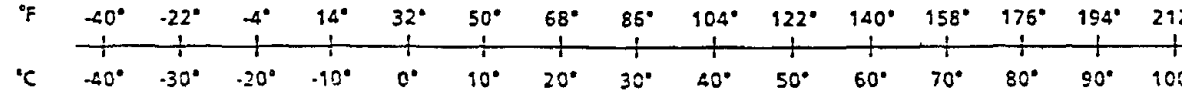
TEMPERATURE (EXACT)

[(9/5) y + 32] °C = x °F

QUICK INCH-CENTIMETER LENGTH CONVERSION



QUICK FAHRENHEIT-CELCIUS TEMPERATURE CONVERSION



For more exact and/or other conversion factors, see NBS Miscellaneous Publication 286, Units of Weights and Measures. Price $2.50. SD Catalog No. C13 10 286.

Table of Contents

List of Figures

List of Tables

Executive Summary

This document reports the results fo the study conducted by the Carnegie Mellon Rsearch Institute (CMRI) to evaluate its recently developed metal oxide semiconductor (MOS) gas sensor technology for applications in the automobile environment. The specific use of this technology is for a low-cost carbon monoxide (CO) monitor to be placed in the automobile compartment to protect the driver and passengers.

The problem that initiated this sutdy is the potential danger presented by the CO produced by motor vehicles that might accumulate in the automobile's compartment impairing the health of the driver and passengers. Accidental CO poisoning in automobiles is estimated to cause 500 deaths each year. Most of these accidental deaths and many of the estimated 2300 suicides, might have been prevented if the automobile passenger compartment were equipped with an appropriate CO monitor and alarm system.

The danger of CO is that low levels of exposure can cause illness or death. Exposure to CO at levels above 1800 parts per million (ppm) can lead to asphyxiation in minutes. At a level of 400 ppm for 2 to 4 hours, exposure to CO can produce headaches, nausea and general disorientation. Even at lower levels of exposure, the neurobehavioral effects of CO in individuals may lead to the reduction of visual perception, manual dexterity and performance in sensory motor tasks.

The exposure of individuals to CO results in an increase of the carboxyhemoblobin (COHb) level in the bloodstream and a decrease of the ability of red blood cells to transport oxygen. This effect is dose dependent, i.e., related to the product of the CO concentration and the time of exposure. Based on this information, an assumption was made that the CO montior must perform as a dosimeter for the duration of the trip. An alarm signal will be activiated by the monitor when any CO dose would induce a COHb level of 4% in average healthy individuals traveling in the vehicles's compartment. The choice of 4% was made based upon the combination of two factors: no negative neurobehavioral effects and no nuisance alarms. The estimated exposure levels corresponding to 4% COHb indicate a range from 302 ppm for 0.25 hour to 30 pm for 4 hours.

The approach followed in this study was first, to define the physical and chemical characteristics of the vehicle's compartment and the surrounding environment; second, to evaluate the effects of these environments on the MOS sensor performance in terms of sensitivity, selectivity and stability. The problems of potential false alarms caused by undesirable gaseous contaminants was also addressed in the context of the sensor chemical environment.

The study of the chemical environment of the vehicle's compartment revealed that contaminants such as organic solvents, that might accidentally or purposely be introduced in the automobile, may induce false alarms in unfiltered MOS sensors. The analysis of reported data on chemicals resulting form the outgassing of manufacturing materials used in the vehicle's compartment, indicated a potential small contribution to the total contamination (a CO equivalent of less than 2 ppm in the worst case).

The study also assessed the CO background levels that might be found in congested traffic conditions. In general, reported data collected during this work indicated that street and highway CO concentrations around 35 ppm are found occasionally in very heavy traffic. Higher levels may be present in road tunnels where CO concentrations exceeding 250 ppm have been measured. A variety of concentrations and distributions of CO even larger than these may occur due to particular meteorological conditions, terrain configuration and air flow patterns. Although substantial reductions in the emission of CO have been achieved by the use of catalytic converters, motor vehicles are still responsible for almost all of the CO encountered in the cities and roadways.

These chemical data were used to evaluate the expected MOS gas sensor performance in a car's compartment worst case scenario. The comparison of this chemical environment with MOS sensor data previously collected by CMRI, revealed the feasibility of this technology for CO monitoring in cars and other highway vehicles. Potential interferences by gaseous contaminants that may lead to false alarms might be eliminated by placing an appropriate filter on the sensing element. Preliminary designs of the sensor chip filter and electronics are presented in this report.

Recommendations for a follow-up program to develop and install CO prototype monitors in highway vehicles with the objective of proving the concept and collecting data during actual field testing conditions, are also included in this document.

Introduction

Carbon monoxide (CO) is an extremely toxic gas that is generated at a high level in automobile exhaust. Undetected, this odorless and tasteless gas can readily accumulate in the passenger compartment of a vehicle. CO can enter the passenger compartment due to a malfunction in a car's exhaust system, or through the open back window of a station wagon. Running a vehicle in an enclosed area, such as a garage, can also lead to dangerous situations.

The danger of CO is that low levels of exposure can cause illness or death. Exposure to CO at levels above 1800 parts per million (ppm) can lead to asphyxiation in minutes. At a level of 400 ppm for 2 to 4 hours, exposure to CO can produce headaches, nausea and general disorientation. These numbers are guidelines for the general population. However, many segments of the population such as children, pregnant women and people with heart conditions are more susceptible to CO poisoning than the general population.

Accidental CO poisoning in automobiles is estimated to cause 500 deaths each year. Most of these accidental deaths, and many of the estimated 2,300 suicides, [National Center for Health Statistics (NCHS), 1985)], could have been prevented if the automobile passenger compartment were equipped with an appropriate CO monitor. The ideal monitor must be rugged, reliable, low cost and sufficiently accurate to identify potentially hazardous levels of CO.

Metal Oxide Semiconductor (MOS) gas sensor technology represents a good candidate for this application. MOS gas sensors are inherently rugged and long lived. The problem with commercially available gas sensors is that they are not selective for the detection of CO, and they are not stable over the desired time scale. The technology developed at Carnegie Mellon Research Institute (CMRI)* has improved the state of MOS gas sensor technology to the point where a stable selective CO monitor is within reach.

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* The effort to develop this sensor technology was funded by American Intell-Sensors Corp.

The purpose of this program is to evaluate the CMRI MOS technology. The items of work for this program are given below:

Item #1 - Definition of operating environment

Item #2 - Sensor and signal processing characteristics of CMRI MOS based CO sensing devices

Item #3 - Projection of cost

Item #4 - Documentation

Items 1 through 3 will be discussed in detail in the following sections.

Item 1 Definition of Operating Environment

The passenger compartment of an automobile is a unique and harsh environment. Many conditions exist in this environment that can potentially interfere with the proper operation of a CO monitor. For example, extreme swings in temperature and relative humidity occur from winter to summer. In addition, many solvents ranging from alcohols to acetone to chlorinated hydrocarbons are contained in products that are commonly carried in automobiles such as rubbing alcohol, fingernail polish remover, spot removers and gasoline. Other environmental considerations include mechanical shock due to bumpy roads, sudden stop engine induced vibrations, and large electrical impulses.

A variety of sources [Thi, 1978, SAE, 1978, Aus, 1984, Num, 1987] were reviewed and found in agreement with regard to mechanical and electrical specifications for the automobile, Table 1.1.

The Society of Automotive Engineers (SAE) standards J211, 1978, listed the environmental specifications for electronics for the automobile passenger compartment. Basically, automotive electronics need to be packaged to withstand the variety of conditions listed in Table 1.2.

Table 1.3 lists the automotive lubricants and chemicals by product and constituent chemical classification.

1.a/b Temperature and Humidity Range

The SAE J211 standard specified temperature and humidity ranges are listed in Table 1.2. The ranges in Table 1.2 correspond to extreme conditions. These extremes occur while the automobile is unoccupied. Clearly a human cannot survive in a car at temperatures of 85°C, and within minutes of entering a car at 0% relative humidity (RH) the humidity level would rise due to human presence. Hence, the specifications in Table 1.2 are not operating conditions, but conditions for which the monitor must survive.

Table 1.1: Automotive Environment for Electronics Passenger Compartment

Mechanical

Shock
Anticipate drops of 4 feet in transit and component shocks during bench mishandling.

Operational the worst shock other than a crash would be becoming airborne after a bump, the acceleration, up and down, ranges from +18 G's to -14 G's within 1 millisecond.

Vibration
Under hood and chassis 6 G's peak at up to 1000 Hz
Subsystem 20 G's peak at up to 2000 Hz.

Electrical

Operating Voltage
9 to 16 volts, 14.2 volts nominal

Voltage Transient:
Periodic Pulse 75 volts - 90 ms
Inductive Pulse -125 to -300 volts rise time = 100 ms
fall time=100 ms to 4.5 s

Noise: 1.5 volts (accessory), 75 volts (abnormal ignition). The ignition EMI characteristic waveform is relatively well understood and exists up to approximately 7 MHz.

Life Expectancy

Integrated circuits 6 to 10 years.

Table 1.2: Automotive Environment for Electronics Passenger Compartment

Temperature	Minimum	-40 °C (- 40 °F)
	Maximum	+85 °C (+185 °F)
	Top of Dash and Rear Window Deck	+115 °C (224 °F)
Humidity	Minimum	0% relative humidity - Frost
	Maximum	98% relative humidity at 38°C (100°F). Equivalent to 64,000 ppm absolute humidity
Frost, Salt Spray, Immersion		Damp and cold conditions, salted winter roads, ocean mists, and water immersion must be anticipated.
Sand, Dust, Automotive Lubricants, Automotive Chemicals		Contact with alkaline dust, battery fumes and acid, washer solvents, gasoline, antifreeze, degreasers, brake fluids, oils, steam, etc., must be anticipated.

Table 1.3: Automotive Lubricants and Chemicals

Product	Constituent Chemical Classification
Gasoline	Aromatics n-Alkanes Iso-Alkanes Cycloalkanes
Washer Solvent Degreasers Freon Spray Paint Ether Vinyl Plasticizers Anti-Freeze	Alcohols Ketones Chloro-Compounds Terpenes Aldehydes
Engine Oils & Additives Transmission Oil Rear Axle Oil Power Steering Fluid Brake Fluid Axle Grease Waxes Undercoating Material	Non-Volatile Lubricating Oils Long chains attached to aromatics

The precise temperature operating range is of little importance, since the CMRI sensors are temperature controlled. Of more importance is the precise operating humidity range. If the practical lower limit of the humidity range can be shown to be substantially greater than 0% RH, the effective humidity interference can be reduced.

1.c The Chemical Environment

To define the passenger compartment's chemical environment, an extended literature search was performed. The objective of this search was to determine the variety of chemicals present in the automotive environment and their respective concentrations. The search was directed to combustible and toxic chemicals that in the gas phase would have the potential to react with the CMRI MOS sensor, including chemicals given off by construction materials, household products, cigarette smoke, and automobile exhaust.

1.c.1 Outgassing of Automobile Construction Materials

Materials used in the construction of automobiles are composed of a variety of plastics, glues, epoxies, and paints. Several articles [Hed, 1976, Zwe, 1977] detail that the level of outgassing (the release of compounds into the ambient air) is on the level of the ppb to ppm. Several cars were heated to 38°C, and samples were collected to determine worst case numbers. These studies identified 147 chemicals at concentrations between 2 ppb and 50 ppb. It is estimated, based on this information, that these chemical products at these concentrations would not significantly interfere with the CO MOS sensor. It is estimated that the total of all these compounds from the outgassing of construction materials would produce an equivalent reading of less than 1 ppm CO.

1.c.2 Consumer Products

A likely source of potential interfering compounds would be leaky household products carried in the passenger compartment. For example, a bottle of spilled nail polish remover (acetone) or an open can of gasoline (hydrocarbons, aromatics, etc.) could easily produce

100 or 1000 ppm of these combustible compounds within the passenger compartment.

A review of household compounds [Tic, 1988, Kno 1989] indicates that household products can be classified by the family of chemicals listed in Table 1.4 This table lists the chemical families and some of their members. It should be noted that this list includes all the chemicals listed in Table 1.3. The worst-case concentrations were not available from the literature.

During this project, CMRI estimated some worst-case exposure events from consumer products. Figure 1.1 shows a plot estimating levels of organic vapors generated from organic solvents sealed in a compact car. This plot was generated using calculations detailed in equation 1. This plot shows that the lower the molecular weight of the compounds the more readily it will evaporate into the ambient air.

eqn #1 $C = [1{,}000{,}000 \times (G \div Mw)] \div [V \div Ml]$

where

C = concentration in parts per million (ppm)
G = weight of solvent (grams)
Mw = molecular weight of solvent (gram/mole)
V = volume of car interior (liters)
Ml = gas constant (22.414 moles/liter)

For the case of 2 grams of acetone evaporating into a sealed compact car:

G = 20 grams of acetone
Mw = 58.08 gram/mole
V = 2550 liters
Ml = 22.414 moles/liter

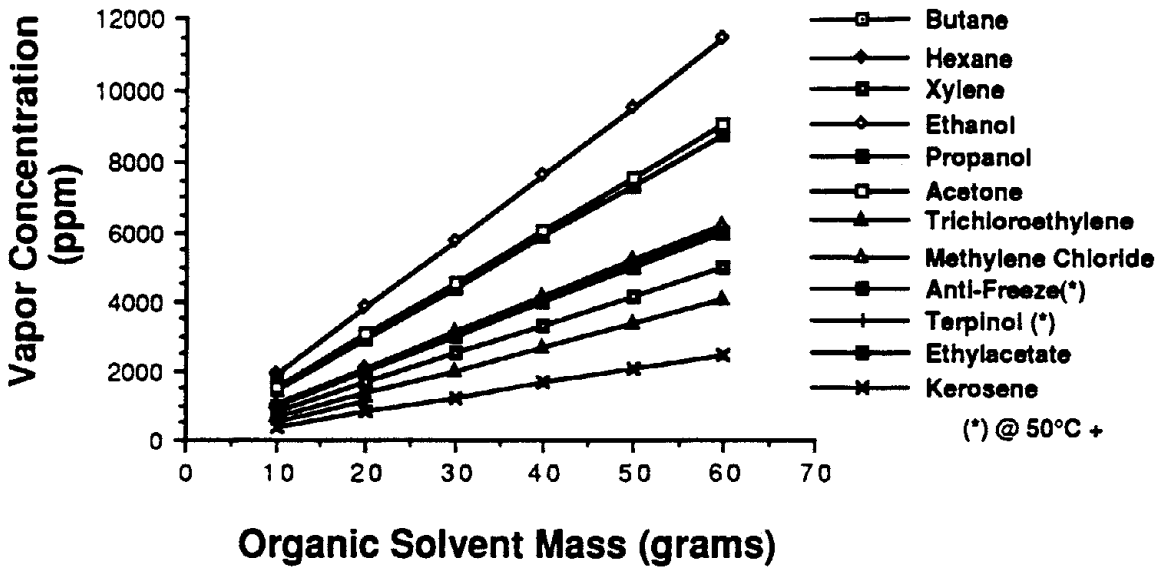
Equation 1 yields:

C = 3027 ppm Acetone

Worst-case exposure for each chemical family has been estimated and listed in Table 1.5. They are based on a substantial evaporation of the solvents in a sealed car. As the car door is opened, these levels would rapidly decrease. The level to which the vapor concentration decreases is dependent upon how long the car door is allowed to remain open before the car is started. With the exception of butane, each chemical is readily detected by the driver by its strong odor. The driver would likely air out the car before driving upon detecting a strong solvent odor.

Table 1.4: Household Chemicals

Product	Constituent Chemical Classification
Gasoline	Aromatics
Kerosene	n-Alkanes
Butane	Iso-Alkanes
Propane	Cycloalkane
Paints (spray)	Alcohols
Paint Thinner	Ketones
Paint Remover	Chloro-Compounds
Caulk	Terpenes
Window Cleaner	Aldehydes
Bleach	Ammonia
Hair Sprays	Chlorine
Nail Polish Remover	



Compact Car Volume = 90 cubic feet
Assumes complete evaporation of solvent at 38°C

Figure 1.1: Estimate of Organic Vapors (ppm) Generated from Organic Solvents (grams) in a Sealed Compact Car

Table 1.5: Order of Magnitude Estimates of Possible Interferences Worst Case Scenarios Assuming a Sealed Compact Car.

Alkanes

A butane lighter leaks its contents (10 grams) generating 1500 ppm of butane

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Aromatics, Alkanes

A soaked rag of gasoline (10 grams) is allowed to evaporate generating 1000 ppm of mostly butane, hexane and xylene in the vapor phase.

Alcohols

The equivalent of a shot (23 grams) of 200 proof alcohol is allowed to evaporate generating 4400 ppm of ethanol in the vapor phase.

Ketones

A bottle of nail polish remover (2 grams of acetone) is allowed to evaporate generating 300 ppm of acetone in the vapor phase.

Chloro-Compounds

A container of paint remover is left open overnight allowing 5 grams of methylene chloride to evaporated 500 ppm of methylene chloride.

Ammonia

1/3 of a bottle of window cleaner spills generating 350 ppm ammonia.

1.c.3 Cigarette Smoke

The most important constituents found in cigarette smoke are shown in Table 1.6. The only gas present in greater abundance than CO is carbon dioxide (CO_2), CO_2 is not a toxic gas and will not interfere with the sensing of CO. The remaining gases other than CO are potential contaminants but are present in relatively small quantities with respect to CO. In terms of interacting with the monitor, smoking is a source of CO. This is a local source, under the control of the driver, and it should be considered a potential threat to health.

The CO level for various cigarettes is given in Table 1.7. This information was used to generate a worst-case estimate of CO levels produced from cigarette smoke. The worst case considered is 1 cigarette being smoked in a compact car with no air exchange. A level of 105 mg CO/cigarette is used in this estimate. For a 2000 liter volume, the CO concentration will approach 50 ppm.

This is clearly a worst-case event, and the actual CO level from smoking is considerably less than 50 ppm. The CO from this source is likely by itself to be below the federal standard of 35 ppm for 1 hour. [NAAQS, Federal Register, 1985]

1.d Congested Traffic, Tunnels and Parking Garages

There are a variety of every day driving situations that can expose a vehicle occupant to relatively high levels of CO. As part of this work, the worse case CO exposure events that are likely to be experienced while driving have been estimated. The situations considered are:

- Driving in congested traffic.
- Passing through a tunnel.
- Using an underground parking garage.

Table 1.6: Prominent Constituents of Cigarette Emissions

Compound	Concentration (µg/cig.)
Carbon dioxide	10,000 - 80,000
Carbon monoxide	500 - 26,000
Nitrogen oxides	16 - 600
Ammonia	10 - 130
Hydrogen Cyanide	280 - 550
Formaldehyde	20 - 90

Table 1.7: Cigarette Smoke CO Emission Rate

Reference	CO Emission Rate µg/cigarette
National Research Council 1983	105
Woods 1983	51.6
Girman et al. 1981	78
Health and Welfare Canada 1971	.5-21
Richert et al. 1984	53-65
Boleij and Bruenkreef 1982	100

A study by Flachsbart and Yo [Fla 1986] has directly measured the average CO exposure for a driver in congested traffic. The study was conducted in the Washington DC area. The routes considered are shown in bold on the map in Figure 1.2. The thrust of this study was to develop a mathematical model of the CO concentration in the passenger compartment. As part of the work a number of vehicles were equipped with CO monitors. The windows of the vehicles were kept up and the ventilation was set to a specified level for passenger comfort.

The results of the Washington study are shown in Figure 1.3. This is a plot of measured average CO levels versus average CO levels calculated using the authors' model. The relevant information for use in the present study is the measured CO level. A total of 150 measurements are represented in Figure 1.3 All but 1 event were below the 1 hour exposure limit of 35 ppm, and 95% of the events were below 22 ppm.

The time of the average trip in the Washington study was not given but it is likely to be under 1 hour, and therefore the exposure would be below the federal limits.

The CO levels in a tunnel can at times of highly congested traffic reach levels of 100 to 200 ppm CO. For example, The Fort Pitt Tunnel in Pittsburgh operated by the Pennsylvania Department of Transportation (Penn DOT), is monitored continuously for CO. The policy for this tunnel is to take action when CO levels reach 125 ppm. This action usually involves increasing the speed of the ventilation fan. If the CO level reaches 250 ppm the tunnel is closed.

According to the tunnel manager for the Fort Pitt Tunnel levels of 125 ppm are reached only in traffic jams that slow traffic to a crawl. Levels of 200 to 250 are very rare and are observed only for cases of stopped traffic in the tunnel due to an accident in or near the tunnel.

The CO concentration at the Fort Pitt tunnel is recorded as a function of time using a chart recorder. The charts for a 7 week period were scanned for the worst case events. Figure 1.4 is a tracing of a 5 hour period on December 1, 1990. The CO level was

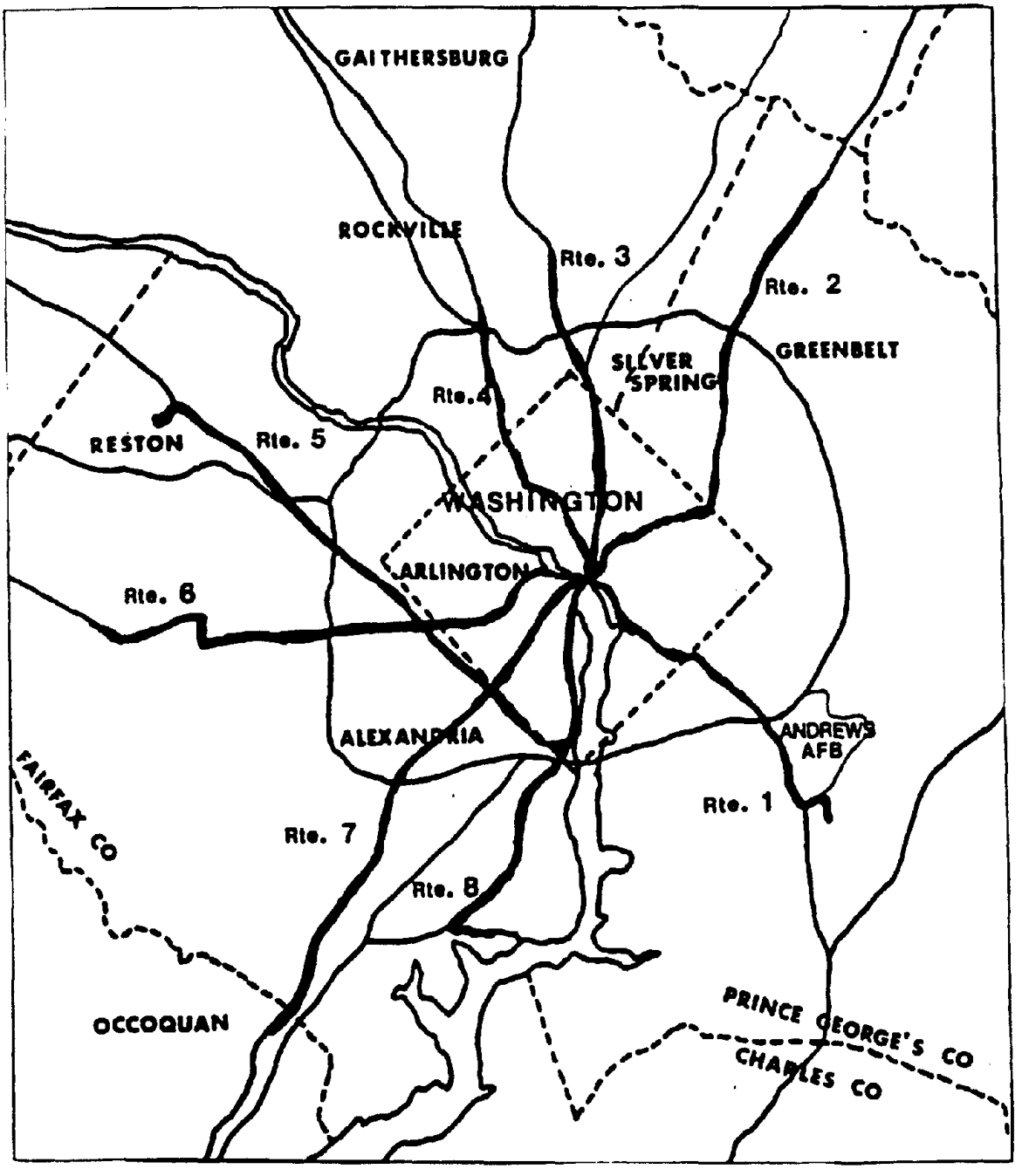


Figure 1.2: Eight hypothetical automobile commuter routes surveyed in the Washington metropolitan area [Fla, 1986].

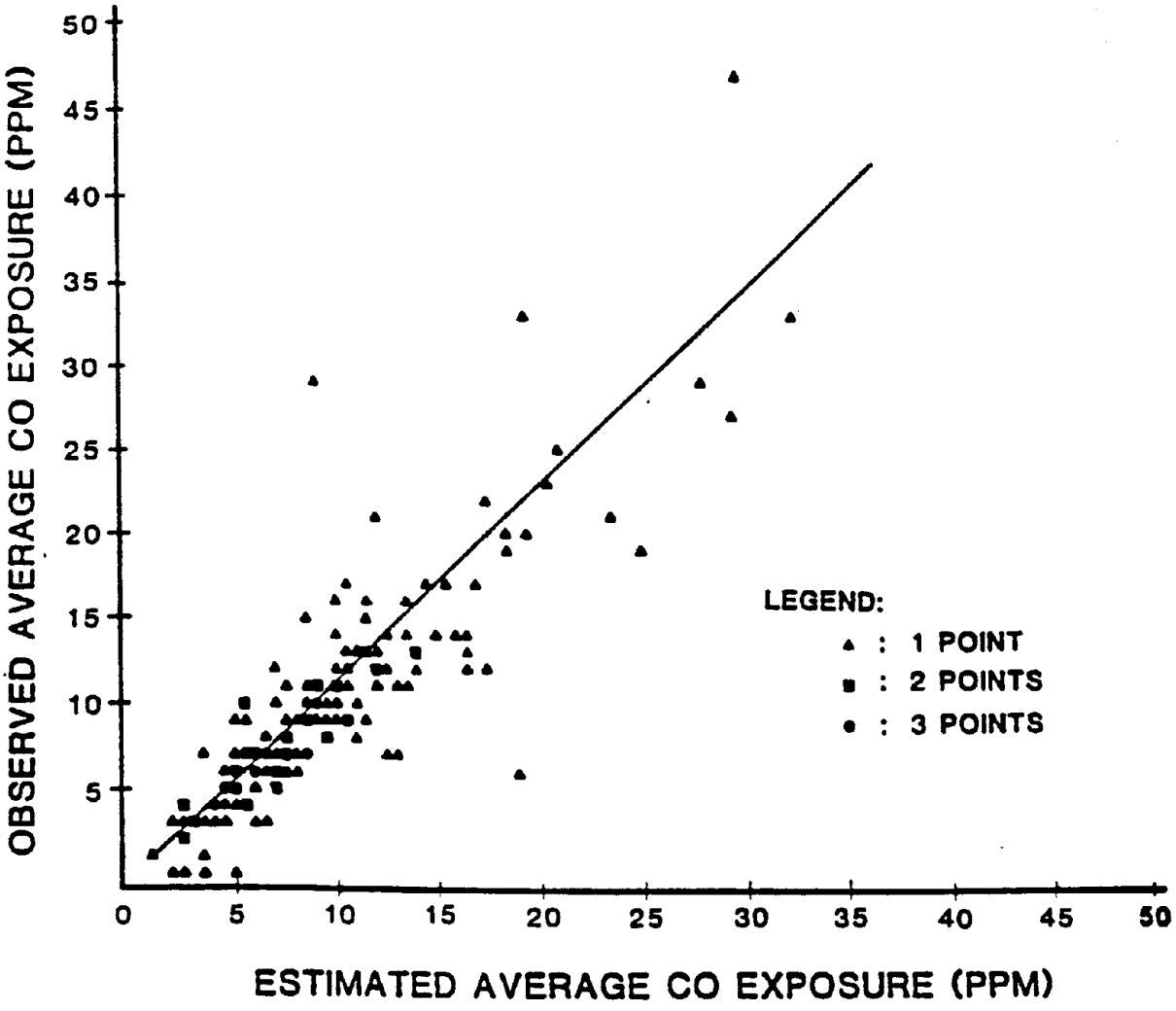


Figure 1.3: Plot of observed average CO exposures as a function of calculated average CO exposures [Fla, 1986].

seen to approach 70 to 120 ppm for a period of 30 minutes. Figure 1.5 is a tracing of a 5 hour period on November 6, 1990. The CO concentration was measured between 200 to 300 ppm during a period of approximately 1 hour. Upon examining the tunnel log, this event was identified as a diesel powered sewer cleaning truck working in the tunnel. This same effect could probably be caused by a truck or a bus blocked in the tunnel by an accident.

In congested traffic, the time to travel through the Fort Pitt Tunnel can approach 10 to 15 minutes. Even at 250 ppm, this is a smaller equivalent CO dose than the federal standard of 35 ppm for 1 hour.

An underground parking garage is in many ways like a tunnel. It is enclosed and dependent on ventilation fans to keep the CO level down. However, most of the garages are not monitored for CO. The case of interest in a parking garage is that of a large number of cars lined up to exit the garage. These cars are initially running cold and will produce larger quantities of CO. It is estimated that under these conditions CO levels could reach 100 to 200 ppm for a period of 10 to 20 minutes.

1.e Potential Sensor Contaminants and Other factors

1.e.1 Potential Sensor Contaminants

Potential sensor contaminants refer to gases present that can permanently damage the sensor or alter the sensor's properties for extended periods of time. The CMRI sensors are quite rugged in this regard. The sensors are able to withstand exposure to a wide variety of gases at high levels without exhibiting any long term detrimental effects. The list of gases that CMRI sensors have been exposed to with no detrimental effects is shown in Table 1.8.

The only class of compounds that has been identified as possible contaminants are the sulphur bearing compounds, such as SO_2, H_2S, and CS_2, etc. When sensors are exposed to significant levels of these compounds, the sensors immediately respond, but recover very slowly. The time scale for recovery can be as much as several hours.

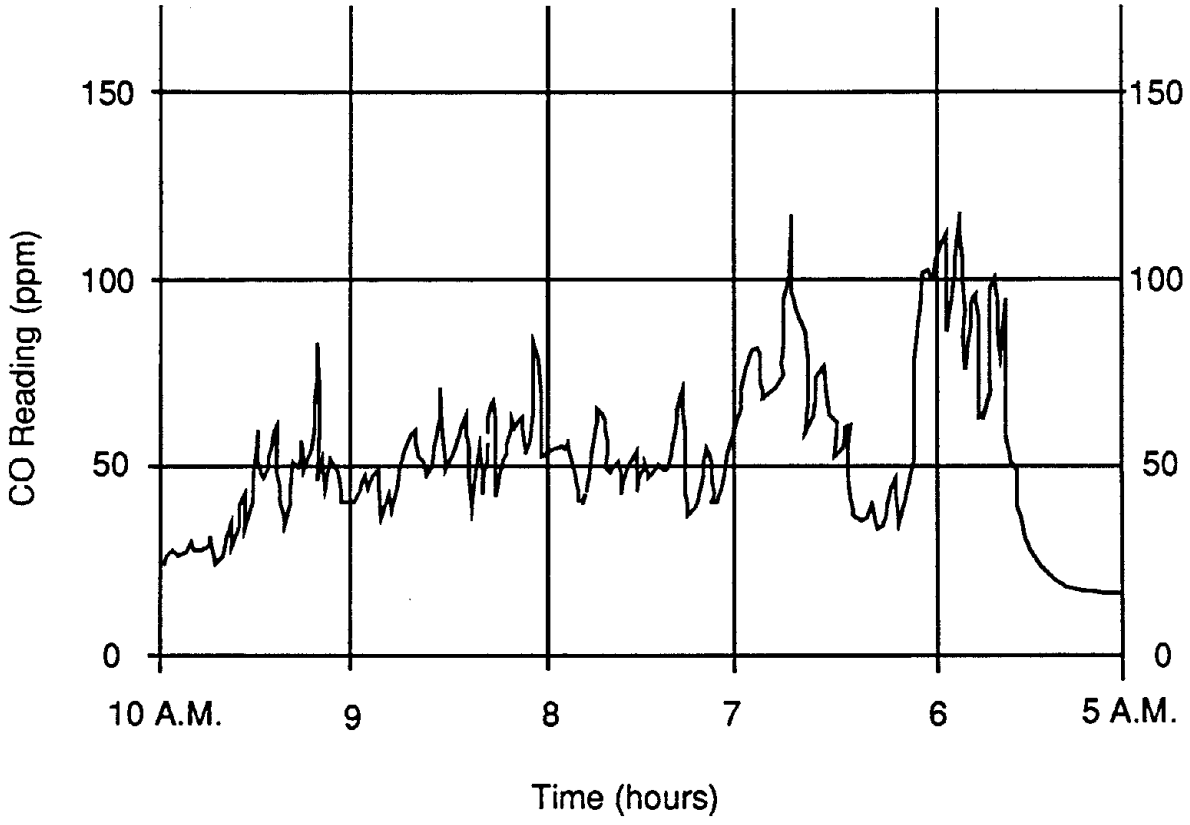


Figure 1.4: Measured CO levels in the Fort Pitt Tunnels, on December 1, 1990. (Hand traced)

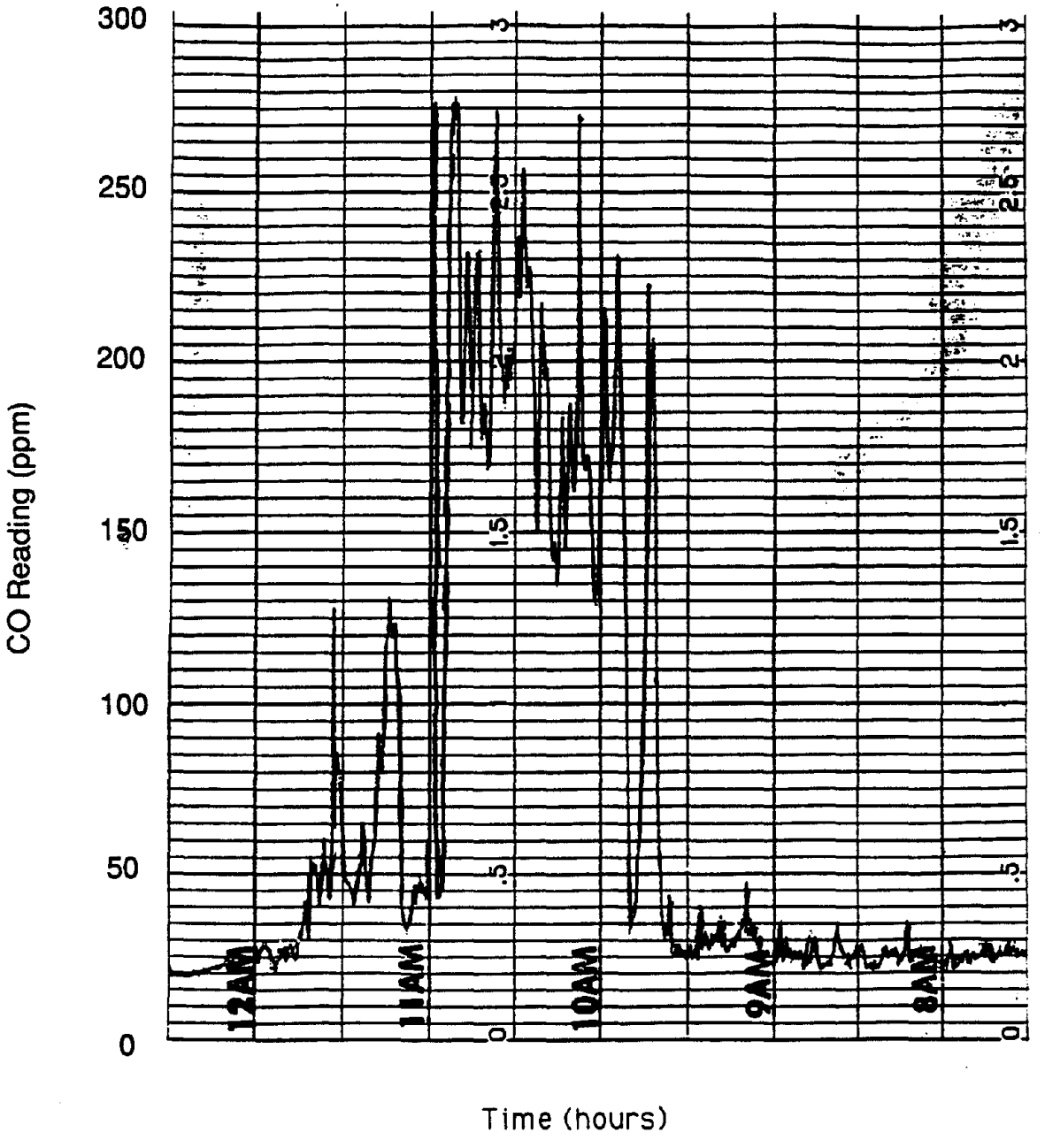


Figure 1.5: Measured CO levels in the Fort Pitt Tunnels, on November 6, 1990. (Photocopy of actual chart)

Table 1.8: List of chemicals that the CMRI sensors chips have been exposed to.

Test Gas	Concentration (ppm)
Methane	5000
Ethane	3000
Propane	2120
Butane	1860
Pentane	1400
Hexane	1180
Gasoline	1000
Hydrogen	2000
Ethylene	2750
Methanol	6720
Ethanol	3280
Acetone	2550
Acetylene	2500
Isopropanol	2000
Methylene Chloride	1000
Freon-12	1000

The most prevalent of all these gases is SO_2. The levels of SO_2 found in the atmosphere are typically below 1 ppm. In Los Angeles during 1988 the highest level observed [CAR 1989] was less than 1 ppm. At this level the detrimental effect of sulphur bearing compounds is minimal and can be totally eliminated by the use of an appropriate filter material. A common filter material used for this purpose is potassium permanganate, $KMnO_4$. This material is found in many electrochemical type CO sensors presently on the market, and has been shown to be quite effective in eliminating unwanted effects from these acid gases.

A $KMnO_4$ filter was tested in the CMRI laboratory. This filter was intended for use in the stack of a coal fired boiler, where high levels of SO_2 are present. The SO_2 level, 1000 ppm, used for these tests was much larger than the levels likely to be present in the atmosphere. The effectiveness of this filter is shown in Figure 1.6. Even for these extreme levels of SO_2 an appropriate filter has be constructed to eliminate the access of these compounds to the sensor.

1.e.2 CO Exposure Issues

The effects of CO exposure have been extensively studied over the past 20 years. The body of knowledge pertaining to physiological effects, health effects, and possible exposure situations is extensive. The interaction of CO with the human circulatory system is quite well understood. Accurate mathematical models have been devised [Cob 1965] and tested [Doe 1985, Pet 1970 Doh,1972] that relate the CO concentration and exposure time to the level of CO in the blood. The safe exposure limits for the most sensitive segment of the population, namely people suffering from chronic angina, have been carefully determined. However, the remaining information concerning a safe exposure level for a healthy person or for other sensitive groups of the population has not been determined as thoroughly. For example, a consensus has not been reached concerning the safe exposure level for a pregnant woman.

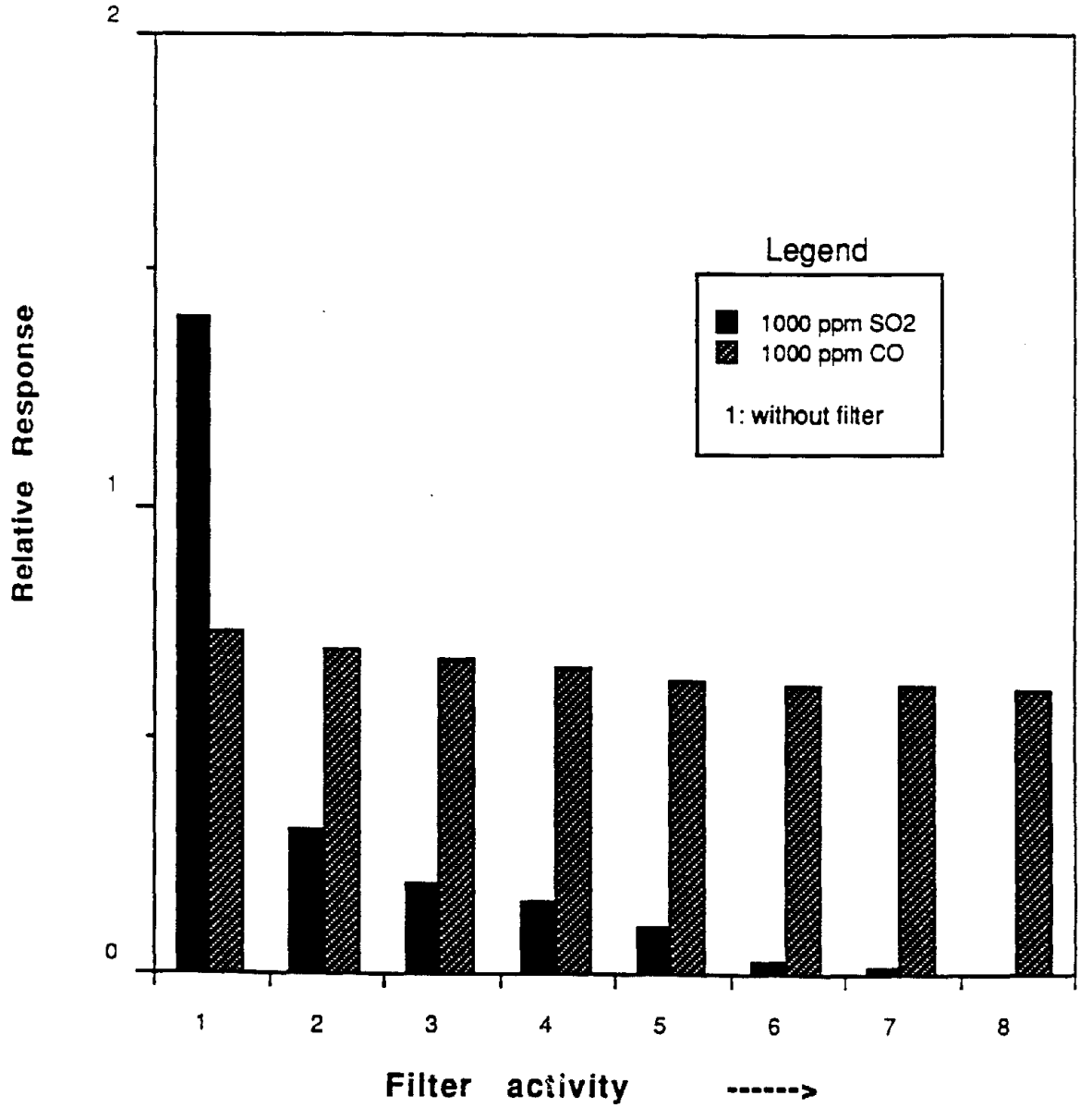


Figure 1.6: Effects of Physical Filters on CO and SO2

1.e.2.1 Physiological Effects

CO reduces the blood's ability to transport oxygen by binding with blood hemoglobin to form Carboxyhemoglobin (COHb). CO has in excess of 200 times the affinity for binding to hemoglobin than oxygen. Hence, CO present in the atmosphere in small quantities can produce a significant fraction of COHb in the blood.

A hemoglobin molecule contains 4 oxygen bonding sites. The oxygen molecules in these 4 sites are available consecutively, and each consecutive oxygen molecule is bound more tightly. Normal muscles generally remove a single oxygen from the first bonding site to satisfy its oxygen demand. The heart and the brain have a greater need for oxygen and often remove oxygen from the second and third bonding site.

This effect is very important when one considers the effect on the human body. Since CO bound to the first site of a hemoglobin molecule blocks access to the remaining 3 oxygen molecules, the effects of oxygen starvation to the heart and brain are doubled or tripled. In the case of the heart the situation is worse yet. When a significant fraction of COHb is present, the body demands more oxygen and the volume of blood flow is increased to satisfy this demand. This places an additional burden on the heart which in turn demands more oxygen be delivered to the heart muscle.

1.e.2.2 Health Effects

The health effects related to CO exposure are cardiovascular and neurobehavioral in nature.

The cardiovascular effects include a decreased work or exercise capacity in healthy adults, and an increase in angina attacks at a given exercise rate for people with chronic angina. The neurobehavioral effects include reduced visual perception, manual dexterity and performance in sensory motor tasks (e.g. driving). The cardiovascular and neurobehavioral effects and the levels of COHb associated with the onset of these effects are given in Table 1.9.

Table 1.9 Human Heath Effects to CO Exposure

COHb Concentration Percent	Cardiovascular Effects,	Neurobehavioral Effects
2.3-4.3	3 to 7% decrease in work time for young healthy men	
2.9-4.5	Reduced exercise time before the onset of pain for angina patients	
<5%		No measurable decrease in vigilance
5- 17%		Measurable decrease in visual perception, manual dexterity and and performance in sensory motor tasks

In the case of cardiovascular impairment, work capacity is observed to decrease by 3% to 7% in young healthy individuals at levels of 2.3 to 4.3% COHb [EPA 1980, Hor 1975, Dri 1974]. In the case of angina patients a decrease in exercise capacity before the onset of pain was observed [DOE 1985] at levels of 2.9% to 4.5% COHb.

In the case of neurobehavioral effects, several studies [Put 1976, Win 1974, Hai 1976] have shown that, at levels of 5% COHb, and below there is no measurable decrement in vigilance. At levels above 5%, there is a great deal of contradiction among the various studies. The onset of vision impairment and other neurological effects is observed to start at levels ranging from 5% to 17% COHb.

The studies up to now have focused on the 2 ends of the sensitivity spectrum, an angina sufferer being the most sensitive and a healthy adult being the least sensitive. There are other sensitive groups in the population but these groups have not been studied as thoroughly. These groups are:

- People with heart and respiratory problems are more sensitive to CO exposure. This group as a whole cannot be easily studied. Intentionally exposing members of this group to CO as part of a study could pose serious health problems. The 1 exception to this rule is the group of patients suffering from chronic stable angina. Extensive studies have been performed on this group. This information is the basis for the present federal CO exposure guidelines.

- People taking depressant medication or under the influence of alcohol will be more susceptible to neurological symptoms from CO exposure [EPA 1979].

- Fetuses and newborns are more susceptible to CO exposure. It is stated [DOE 1985] that potential fetal damage can occur at 4% to 6% COHb levels. However, nothing is stated as to the period of time this level must be maintained for damage to occur. It is clear that a pregnant woman who smokes maintains a level of COHb of 3% to 8% [DOE 1985], and that the children born to these women have a reduced birth weight, are subject to certain birth defects, and are likely to develop more slowly than other children. Unborn children are exposed to these levels of COHb continuously for 9 months causing these effects. Information pertaining to short term fetal exposure is not available.

- Persons not adapted to lower oxygen levels at high altitudes produce higher natural levels of CO, and are therefore more susceptible to CO exposure.

A person who is identified with more than 1 of the above conditions is likely to be very susceptible to CO exposure.

1.e.2.3 CO Exposure Limits

The National Air Quality Standard (NAAQS) for CO exposure has been determined by considering an angina patient undergoing moderate exercise. A measured decrease in the duration of exercise before the onset of pain was observed at levels as low as 2.9% COHb [DOE 1985]. Based on this observation the CO exposure levels have been set at 2% COHb. For a person undergoing moderate exercise this corresponds to exposure of CO at 9 ppm for 8 hours or to 35 ppm for 1 hour.

Based on the above discussion it is clear that a CO monitor must be considered as a dosimeter, and not a simple threshold alarm device. A discussion of possible alarm conditions and their implementation with the proposed monitor will be given in Item 2.e.

Item 2 Sensor and Signal Processing Characteristics of CMRI's MOS based CO Sensing Device

The CMRI CO monitor consists of 3 main components: the sensor chip, the physical filter and the signal processor. Each of these components is an important part of a sensitive, selective, stable, and long lived sensor [Por 1990]. The following sections describe some of the characteristics of the elements.

2.a Overview of CMRI Sensor Technology

2.a.1 The Sensor Chip

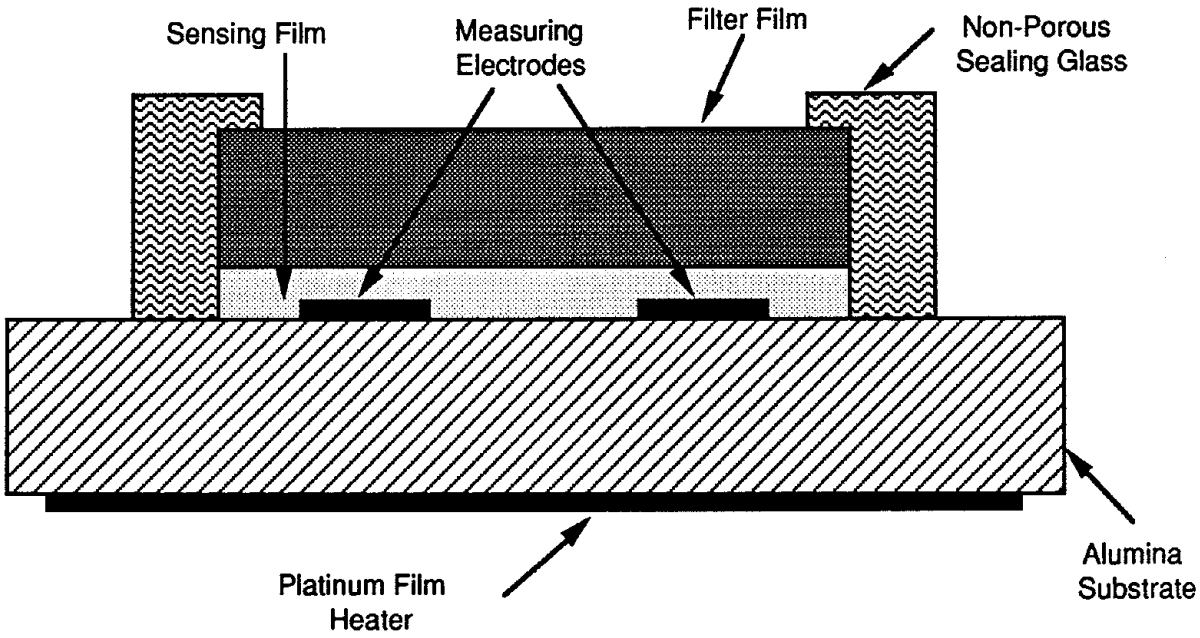
An illustration of the basic components for a typical sensor CMRI used in this work is shown in Figure 2.1. (see appendix 2 for further discussion) The basic components are:

- Platinum Heater
- Sensor Electrodes
- Sensing Material
- Filter Layers
- Alumina Substrate

With the exception of the alumina substrate, which is simply a vehicle for mounting the sensor, each sensor element is a tool for adjusting sensor properties. In addition to these tools, conditioning the sensors with high concentrations of various gases at elevated temperatures is an important method for obtaining improved sensor properties. Selectivity in the final instrument can be further improved by the use of computational enhancement techniques. The use of these tools is outlined below.

- Platinum Heater

The platinum heater is used in conjunction with appropriate electronic controls to precisely set the temperature of the sensor. The temperature is an important tool for varying the sensitivity and the selectivity of the sensor. The sensors operate in the temperature range from 350°C to 550°C. Over this range the sensitivity to a given compound can vary greatly. Hence, the choice of operating temperature is an important design parameter.



Cross Sectional View

Figure #2.1: CMRI MOS Sensor Chip Structure

Since the sensitivity of a given sensor is highly dependent on temperature, the precise control of the sensor temperature is necessary for stable operation. The active control method used here is capable of maintaining the set temperature to within 1% of the designated value independent of ambient temperature.

- Sensor Electrodes

The materials used for the sensing electrodes also have an effect on the sensor sensitivity for a given compound. For example, a sensor with platinum electrodes is more than 5 times more sensitive to methane than a sensor with gold electrodes.

- Sensing Material

The sensing material composition can also be used to alter the sensitivity and selectivity of a sensor; however care must be taken in doping these materials since these procedures quite often lead to instability of the sensing properties of the material. A set of stable sensitive materials has been produced by CMRI that is suitable for most sensor designs. Some inadequacies of the sensing materials in terms of selectivity can usually be compensated for by other means.

- On-Chip Filter Layers

The filter layers, incorporated in the sensor structure, are used to prevent certain undesired vapors from reaching the sensing element. A variety of filter materials have been successfully employed for enhancing sensor selectivity. Many of these filters are catalytic in nature, and combust the unwanted compounds on the surface of the sensor away from the active layer. Other materials used are based on the diffusion of gases through the filter medium. These filter layers can be used separately or in combinations of 2 or more to limit the access of unwanted compounds to the active sensing material.

2.a.2 Off-Chip Physical Filter

The physical filter envisioned for this monitor will be placed in the sensor enclosure and will contain 3 distinct sections (Figure 2.2). Section 1 will be a zeolite molecular sieve that discriminates by molecular size. The second filter will be a $KMnO_4$ filter for

suppressing the effect of sulphur bearing compounds. The third filter component will be activated charcoal, which will adsorb ammonia and prevent it from reaching the sensor chip. The activated charcoal and the $KMnO_4$ filters are often used and well understood. Although zeolite materials have been extensively studied and are regularly used in oil refining, coal gasification and coal liquefaction, the use of these materials as filters for sensors is relatively new.

The molecular sieve will ideally be made of 3Å to 4Å pore size zeolite. This material will allow small molecules to pass but will not allow larger molecules to pass. Muller and Lang [Mul 1986] have successfully employed zeolite filters in conjunction with MOS sensors. The sensor constructed utilized a 40 mm thick zeolite filter applied directly onto an MOS sensor chip. Zeolites of 3 different pore sizes were employed, 3Å type A, 4Å type A, and 9Å type X. The sensors were tested for response to 6 different gases: hydrogen ammonia, methanol, acetone, benzene, and toluene. The test results are shown in Figure 2.3. The response of the sensor to the small molecular species of hydrogen and ammonia is seen to be independent of pore size. The responses to the methanol and acetone are seen to fall off sharply with the reduction in pore size. The responses to benzene and toluene are low in all cases.

The above description is only 1 example of what can be done. Several things must be considered before designing the zeolite filter. A 3Å pore size zeolite will block many large molecules from passing. However, depending on the nature of the cation site in the zeolite, CO could possibly dissociate at this catalytic site.

Many different types of zeolite exist with a variety of pore sizes, structure and catalysts. The A type zeolites used in the above example have a single long pore with a cation site in the pore. The normal zeolite contains a sodium (Na) cation site. A type zeolite can be prepared with a number of cation sites including iron and potassium. It may be possible to attach a $KMnO_4$ molecule at these internal catalytic sites to combine the 2 types of filter action.

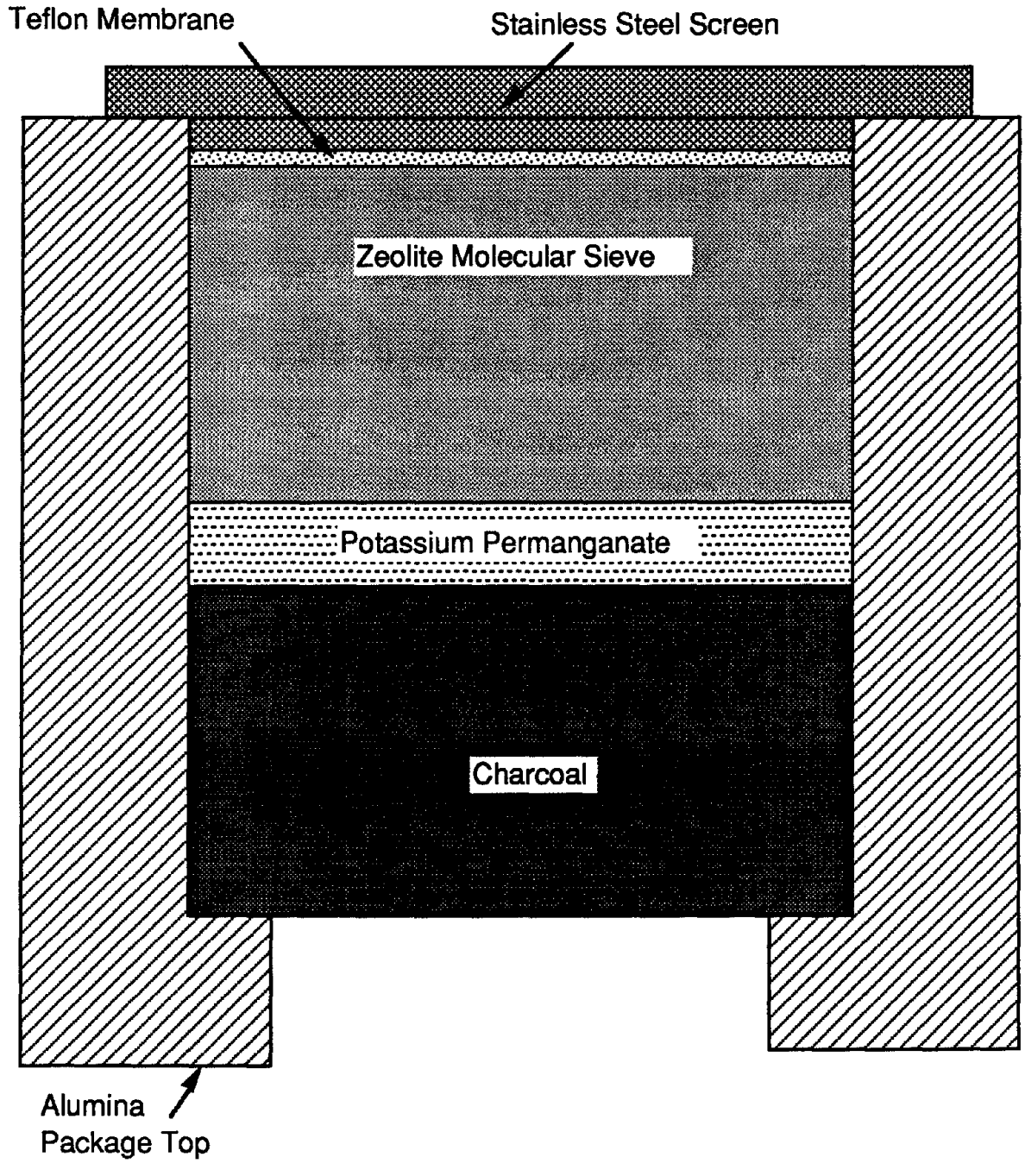


Figure #2.2: Physical Filter Pack

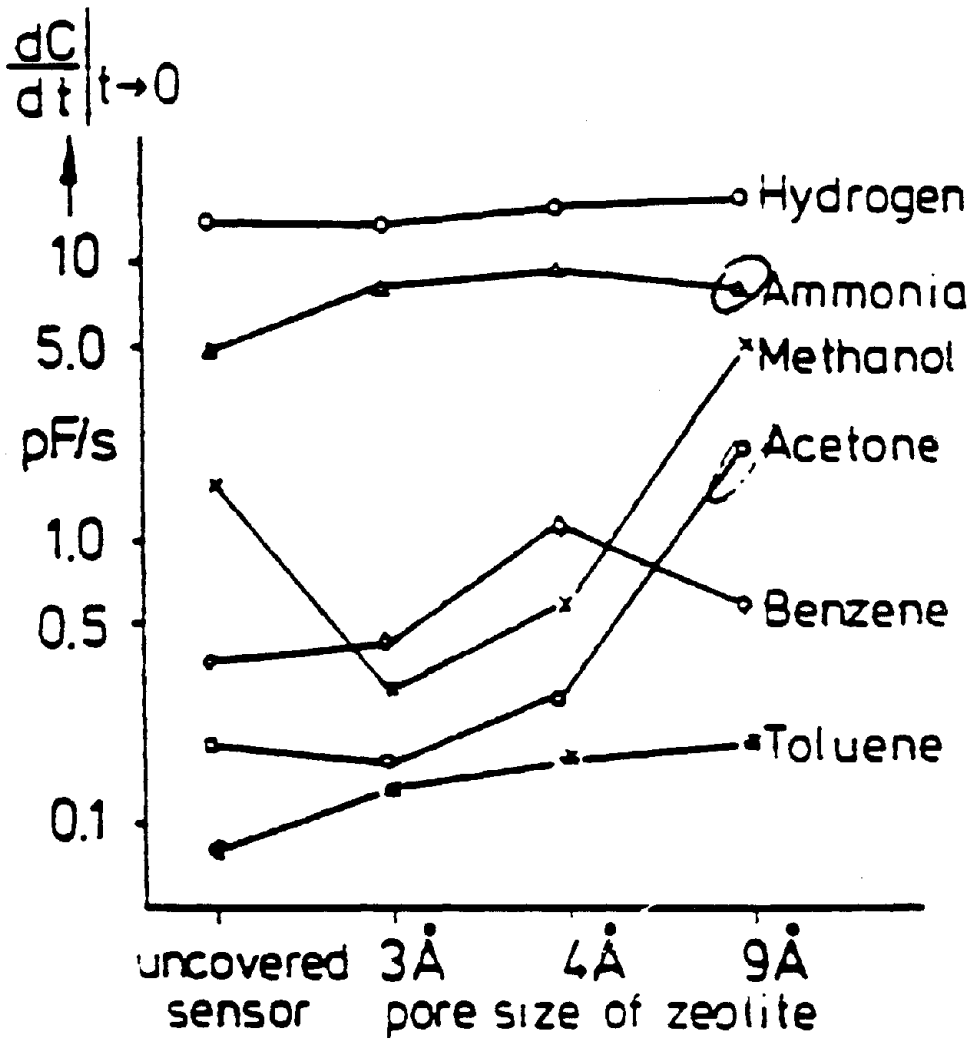


Figure 2.3: Sensor response as a function of zeolite pore size [Mul 1986].

Certain compounds can be occluded by the zeolite permanently clogging the pores. This effect can be minimized by a number of means, including wisely choosing the zeolite types and the associated cation sites. A layered filter of several zeolite types could prove very effective in this regard.

2.a.3 Processor/Computational Enhancement of Selectivity

The primary purpose of the processor is to translate the sensor signal into a CO reading. Another important use for the processor is computational enhancement of selectivity. If a perfectly selective sensor is not available, an array of partially selective sensors can be used to determine the individual gas concentrations.

For example consider the case of 2 gases, and a 2 sensor array. Sensor #1 is very sensitive to gas #1 and somewhat sensitive to gas #2, and sensor #2 is very sensitive to gas #2 and somewhat sensitive to gas #1. The two sensor signals are calibrated to a known equation as a function of gas #1 and gas #2. These equations are stored in the processor and are solved to determine the concentrations of the two gases given the two signals.

The heart of selectivity enhancement, as applied to MOS sensors, is the sensor response model equation [Gra 1990]. The application of this equation allows one to characterize an array of nonselective sensors with respect to the gases simultaneously present in the environment in question. This knowledge is then used to determine the specific gas concentrations represented by the response of the sensor signals, by "simply" inverting this set of equations. In order for this approach to work the sensors in the array must be chosen such that each sensor responds differently from each of the remaining sensors with respect to at least 1 gas.

This work has been successfully applied to the case of methane and ethane (see appendix 1). The drawback of this approach is that a greater demand is put on the accuracy of a single sensor. For a given specified accuracy this effect manifests itself as a more frequent calibration interval. The better the selectivity of the sensor the smaller the correction needed, and the smaller the effect on accuracy and calibration interval.

For the vehicles interior CO monitor it is envisioned to use a very simple processing scheme to avoid excessive cost. It is possible

that a small correction will have to be made at the processor with regard to humidity. This correction is slight and should not considerably reduce the calibration interval of the device.

2.b. Potential Life of the Device

Commercially available MOS sensors have exceeded lifetimes of 10 years. CMRI sensors have been continuously powered since December of 1986 with great success.

It is expected that the sensor lifetime will exceed 3 years. Testing will need to be undertaken to determine the effects of intermittently powered operation on the sensor lifetime as well as the effect of shock and vibration on the mechanical integrity of the sensor.

The lifetime of the filter pack is not well known yet, but efforts will be devoted to design for long life (3 years) under normal operating conditions.

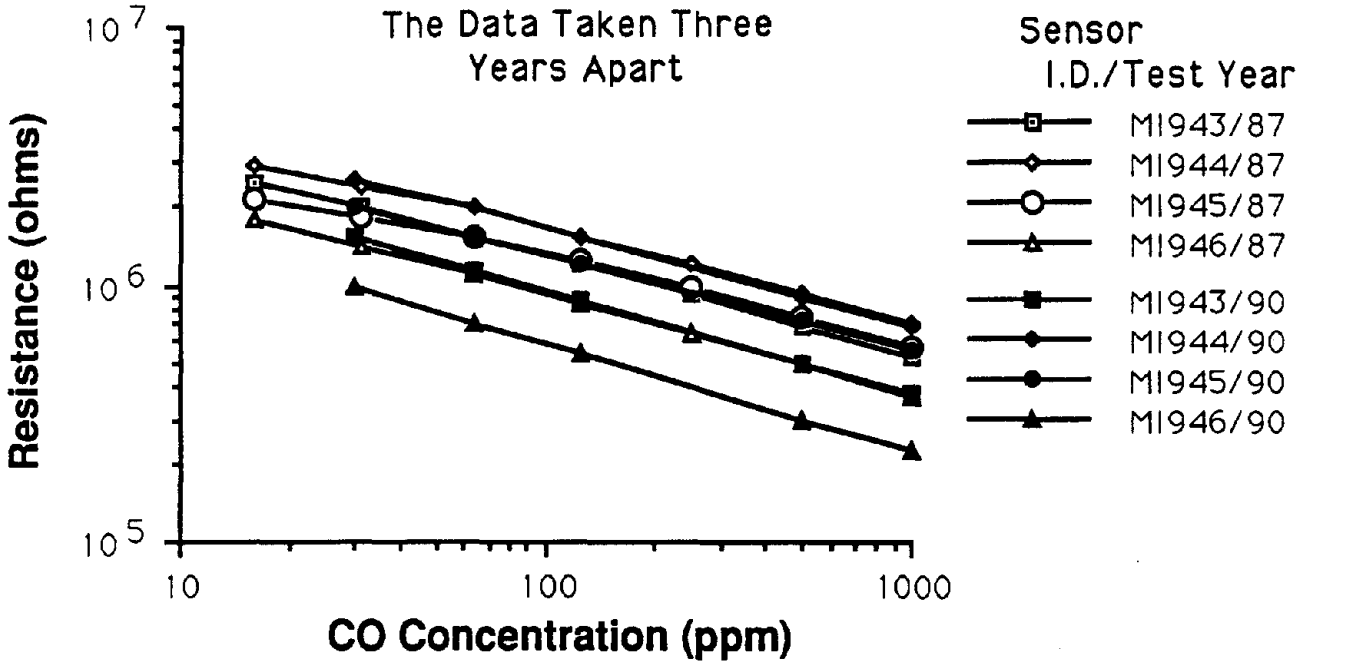
The lifetime for the monitor driving electronics is expected to exceed 6 years.

2.c. Required Calibration Intervals

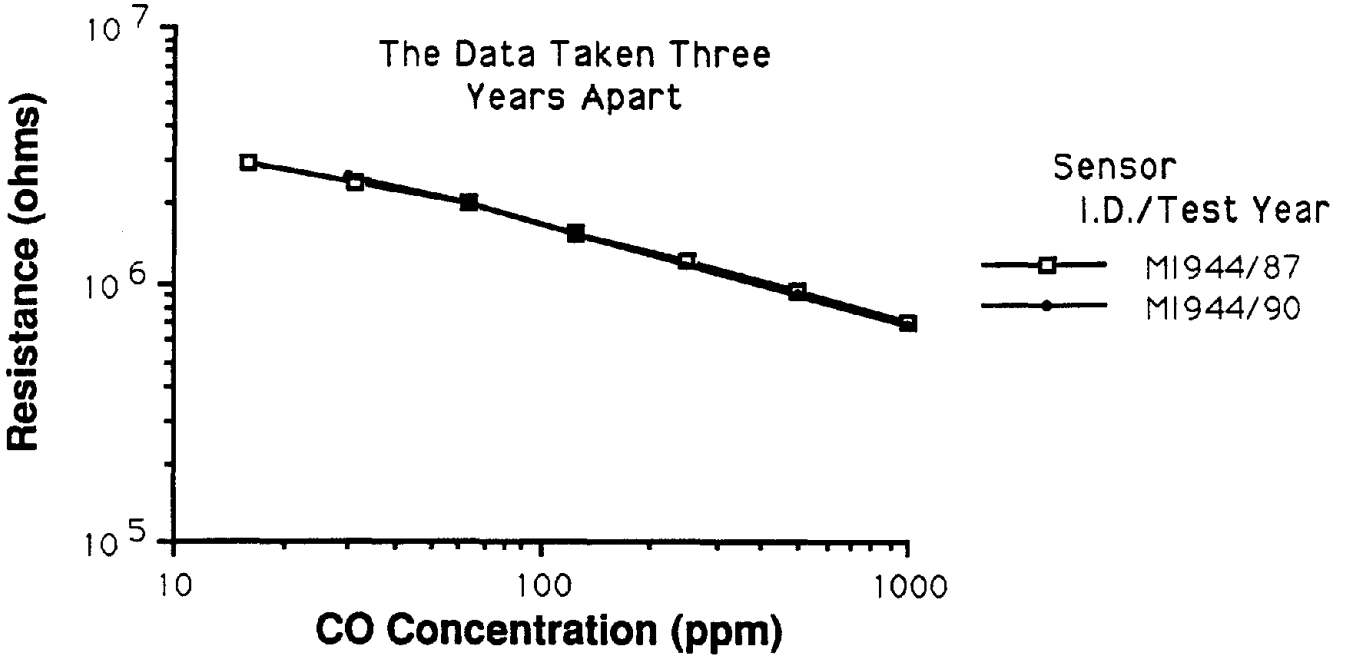
CMRI CO sensors have been tested for long term stability. These tests were geared towards a continuously powered monitor for the home market. Thus, these tests were conducted on sensors in stationary positions free of shocks, vibrations. Figure 2.4 shows that CMRI sensors have a stable response to CO. The data plotted was collected over a 3 year interval. This data indicates that at 125 ppm CO, 2 out of 4 sensors have remained stable within 5%, and 3 out of 4 sensors within 15%, over the 3 year period. The characteristic sensor response has remained stable for all 4 sensors indicating that 1 point calibration is sufficient to correct for any sensor drift.

At 500 ppm CO levels, several different types of CMRI sensor types have demonstrated to maintain calibration to better than 15% over the course of a year.

Tests for intermittently powered sensors would have to be undertaken to verify the effects on sensor stability.



a) Four CMRI sensor Chips



b) One CMRI sensor Chips

Figure #2.4: Stability Plots
CO Sensor Resistance vs. CO Concentration Curves for a) four sensors chips and b) one sensor chip. The data was taken three years apart.

2.d. Potential Threshold, Selectivity Stability, and Speed of Response and Recovery

The gas sensor properties important to the automobile CO monitor include sensitivity, speed of response and recovery, stability and selectivity. CMRI has collected volumes of data pertaining to the use of MOS CO sensors in the home. During the course of this Department of Transportation contract, selected sensors were tested to determine properties with regard to the automobile specifications listed in Table 2.1.

The sensitivity of a CMRI sensor to CO is demonstrated in Figure 2.4b. This figure shows the changes in sensor resistance with respect to changes in CO concentrations. By modeling this data, sensor resistance can be converted into measured readings or equivalent readings for the CO concentration.

The speed of response and recovery to CO can be seen in Figures 2.5 and 2.6. These plots compare the known CO concentrations (solid line) with the CO concentration calculated from the sensor's response (square boxes). Figure 2.6 expands on a portion of the data presented in Figure 2.5. During this test, the CO level is changed abruptly every 20 minutes. The CO concentration changes through the following CO steps: 0, 100, 25, 200, 50, 800, 12, 50, 100, 0 ppm CO. The data shows the sensor tracking the delivered CO concentration with good precision and speed. It should be noted that the delivered CO does not take into account the time necessary for the sensor test chamber concentration to change from 1 level to the next. The test chamber 95% time constant is on the order of 3 minutes. Thus, this sensor speed of response is on the order of 3 minute and speed of recovery is approximately 5 minutes.

It can also be seen that the sensor's steady state response is excellent holding to within the $\pm$ 3.5% that the gas delivery system maintains the CO concentration.

Figure 2.7 shows the effects of changes in humidity and interference gases on sensor CO readings. 3 types of sensors are presented which were calibrated for CO at a level of 18,000 ppm water vapor (60°F, 100% relative humidity). The test atmosphere was then changed to 6,000 ppm water vapor (60°F, 30% RH) holding the CO

Table 2.1: CO Monitor Specification

CO Response Range:	10-2000 ppm
Calibration Interval	1 Year
95% Response Time	5 min.
Temperature Range	
Minimum	- 40°C (- 40°F)
Maximum	85°C (185°F)
Absolute Humidity Range (ppm H_2O)	
Minimum	2,000
Maximum	64,000
Powered	Intermittent
Potential Interference (Worst Case)	
Butane	1000 ppm
Gasoline	1000 ppm
Ethanol	1000 ppm
Acetone	300 ppm
Methylene Chloride	300 ppm
Ammonia	100 ppm

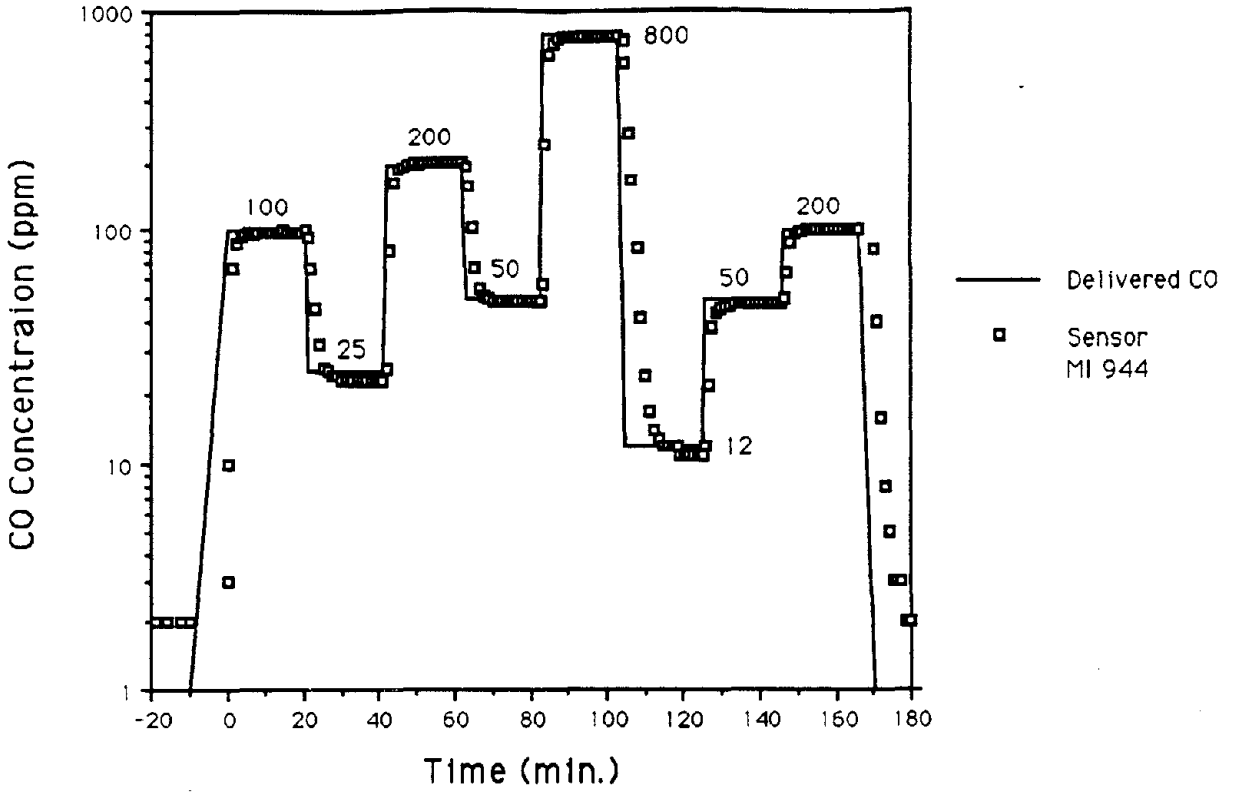


Figure 2.5: Sensor Chip Response to Changing CO Conditions

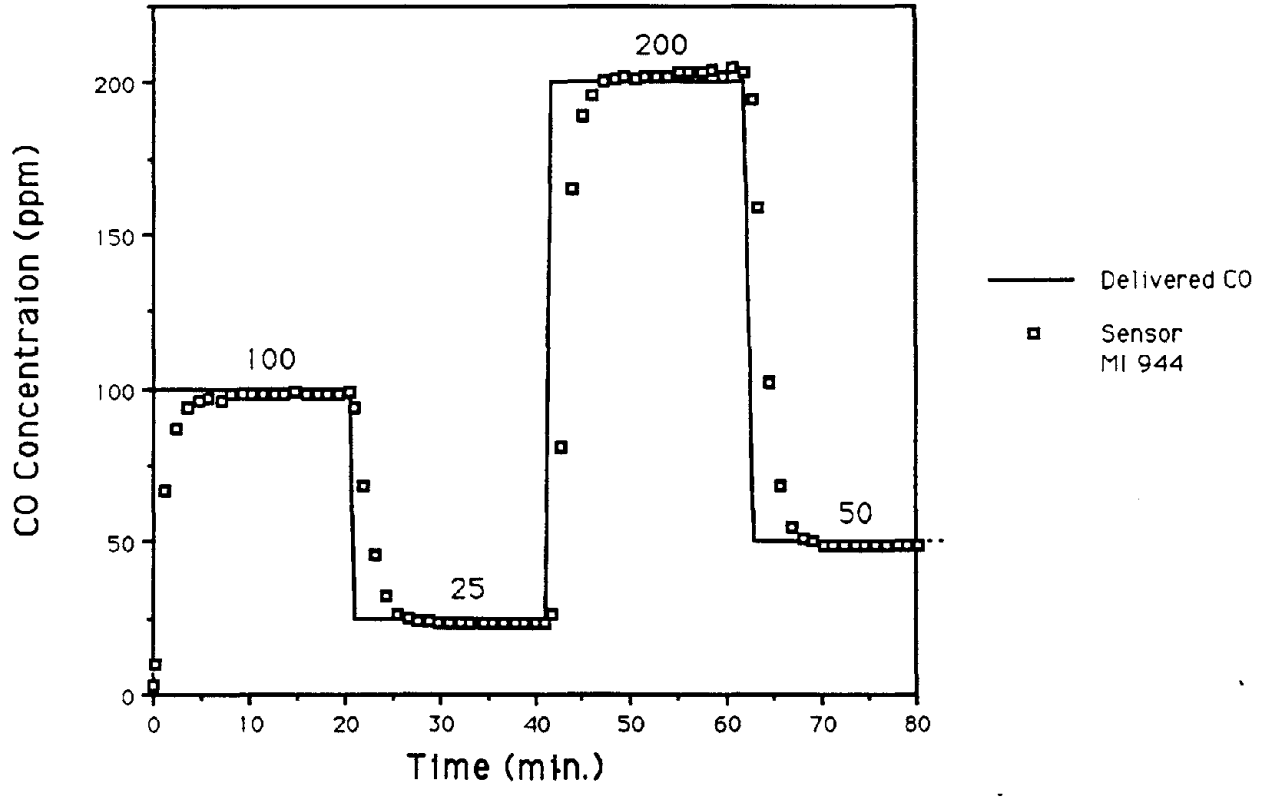


Figure 2.6: Sensor Chip Response to Changing CO Conditions
(Expanded section from Figure 2.5)

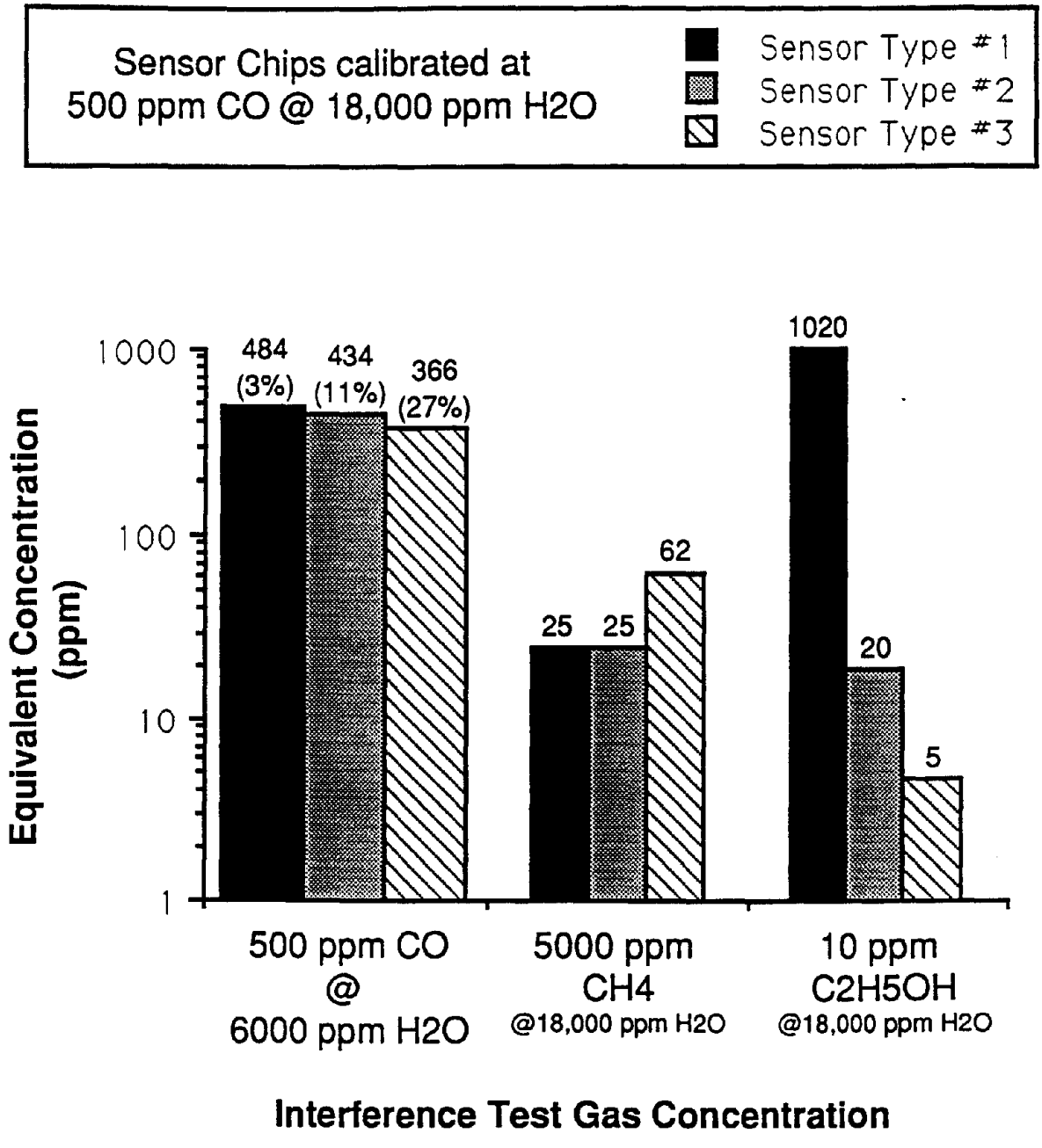


Figure 2.7: The Effects of Humidity and Interference Gases on Sensor Chip CO Reading

concentration steady and a CO reading was taken. Next, the sensors were exposed to 5000 ppm methane (CH_4) (1/10 the explosive limit) and 10 ppm ethanol (C_2H_5OH), with respective CO readings taken. The data presents a picture where the effects of changes in humidity and possible interference from ethanol are linked. Sensors with a smaller humidity response (type #1) are more sensitive to solvents like ethanol. Sensors with a larger humidity response (type #3) are less sensitive to ethanol. By using the CMRI patented sensor fabrication techniques, CMRI is able to manipulate response to balance these 2 extremes as seen in the case of sensor type #2. In all these cases, small chain hydrocarbons such as methane, which will be able to pass through the proposed sensor physical filter, will hardly effect the CO readings.

2.e. Alarm Conditions

In considering the alarm conditions for this monitor, it is important to consider the purpose and functionality of the monitor. Simply stated, a monitor should identify conditions of CO exposure that are potentially hazardous to the health of the driver and passengers. However, the situation is not this simple. People in every day life are confronted with exposure to CO at moderate levels that can be interpreted as hazardous based on federal guidelines. However, the source of the CO is often not under the control of the individual being exposed. For example, in major metropolitan areas levels can exceed the federal 8 hour exposure limit of 9 ppm CO [EPA 1989].

Clearly it is not beneficial for all the cars in a major metropolitan area to alarm a hazardous CO situation caused by an atmospheric inversion or other global CO source. Hence, as part of this program, alarm specifications must be clearly identified that will minimize the health risk due to a faulty exhaust system or other local CO source, while eliminating nuisance alarms from external sources beyond the operator's control. In order to wisely balance these 2 concerns, a knowledge of how CO affects the health of the passenger population must be compared with estimates of worst-case CO exposure incidents.

An additional consideration with respect to the CO alarm condition is the potential inaccuracy of the monitor. To account for these potential inaccuracies one must consider the alarm condition to cover a region of CO exposure rather than a point. This region should be chosen such that the lower part of the region does not overlap with the likely global CO exposure events, and such that the higher

part of this region is low enough to protect as many people as possible.

If the worst-case error in the monitor is taken as ±25%, it is recommended that the targeted alarm level be set at 4% COHb. Including the potential monitor error, this will cover the region from 3% to 5% COHb.

These levels of COHb are low enough to eliminate all neurobehavioral effects shown in Table 1.9. The cardiovascular risk in this region is not totally eliminated. People with cardiovascular illness are more susceptible to exercise related heart attacks. One can argue that these people will not be exercising while driving a vehicle, but the effects of CO exposure linger for several hours. Young children and fetuses are also sensitive to these levels.

This monitor will not protect the entire population from all possible health effects. It will, however, prevent serious exposure that can lead to reduced motor skills and other neurobehavioral effects. It will also prevent very serious accidental exposures that lead to death from asphyxiation.

The next step is to implement a method for relating the CO reading obtained from the monitor to the COHb levels of the occupants of the vehicle. The COHb level is dependent on the CO concentration, exposure time, and physiological parameters such as respiration rate, etc. A useful model has been developed [Coburn 1965] to relate these parameters to the COHb.

Using the Coburn model directly in the processor to determine the COHb levels was considered, but rejected as too complicated. A 5 point approximation of this model has been chosen for use with this monitor.

The Coburn model has been used to calculate the CO exposure levels for a person at rest corresponding to 4% COHb for several time intervals. This information is shown in Table 2.2. The times chosen were 0.25 hr, 0.5 hr, 1 hr, 2 hr and 4 hr. The processor will store a sliding time average of the CO concentration for each of the time periods. If any of these averages rises over the value in Table 2.2, an alarm will be activated.

Table 2.2 Exposure levels corresponding to 4% COHb

Time period (Hours)	0.25	0.5	1	2	4
Average carbon monoxide conc. (ppm)	302	156	84	48	30

Once an alarm condition is reached, several possible actions to the alarm can be considered. A visual or audible alarm is appropriate for warning a driver of a case of accidental CO exposure. However, a more direct approach must be taken to prevent a suicide attempt. In this case, a signal can be passed to the main processor of the automobile to communicate that a dangerous CO level has been detected. The main processor can then turn off the engine providing the vehicle is not moving.

Item 3 Projection of Costs

The cost of the monitor including sensor chip, off-chip filter, processor and associated electronics has been estimated for lots of 250,000 units. The sensor chip, the sensor package, and off-chip filter are considered as a single package. The processor and associated electronics are considered separately.

3.a Projection of Packaged MOS CO Sensor Costs

The CMRI MOS sensor technology lends itself to state-of-the-art electronic mass production technologies. The discussion of the fabrication steps and costs are divided into 4 areas:

- Fabrication of the Sensor Chip
- Testing of the Sensor Chip
- Packaging of the Sensor Chip with Physical Filter
- Final Testing of Packaged Sensor

The design of the CO monitor sensor chip takes into account the stringent environment in which such a sensor will operate. Also, the design is directed to minimize manufacturing costs.

As stated previously and shown in Figure 2.7, changes in humidity can cause inaccurate CO measurements using a single CO sensor. To accommodate for the extremes in humidity expected in the automobile environment a second sensor to monitor humidity is planned. This sensor will be used to correct for inaccuracies caused by humidity changes.

The proposed CO monitor sensor chip will incorporate 2 sensors, 1 for CO and 1 for humidity. These 2 MOS sensors and the platinum film heater are planned to be screen printed on the same side of 1 sensor chip substrate to reduce manufacturing costs.

The CMRI sensor chips operate at elevated temperatures (350°C-550°C). Since operating power is not a limiting conditioning in this application, the sensors and heater will be screen printed onto a substrate designed to provide the benefits of increased mechanical strength and lower costs. The substrate will be ordered as a snapstrate (pre-scribed alumina), so that many sensors can be screen printed simultaneously.

Figure 3.1 outlines the manufacturing tasks and estimated costs for the packaged cantilever type sensor. The steps involved in the screen printing and firing of the heater and sensor films are estimated to cost $1.04/sensor in lots of 250,000.

The snapstrate with sensors and heater in place will then be subjected to quality control testing (approximately $0.30/sensor) to discard those sensors that do not meet production specifications.

The sensor packaging design includes the use of automated equipment to attach lead frame electrical connectors to the sensor substrate and sandwiching it between an alumina package bottom and a top package containing the physical filter. These 3 substrates will be held together with screen printable epoxy capable of meeting automobile specifications and maintaining a hermetic seal. The costs for packaging the sensor substrate are projected at $1.22/sensor.

The packaged sensors will then undergo stringent testing to determine gas sensor, heater, and physical filter parameters at a cost of $0.60/sensor.

The projected cost of a packaged sensor, Figure 3.1, is $3.16/sensor in lots of 250,000. This cost does not include the amortization of capital equipment needed for manufacturing and testing.

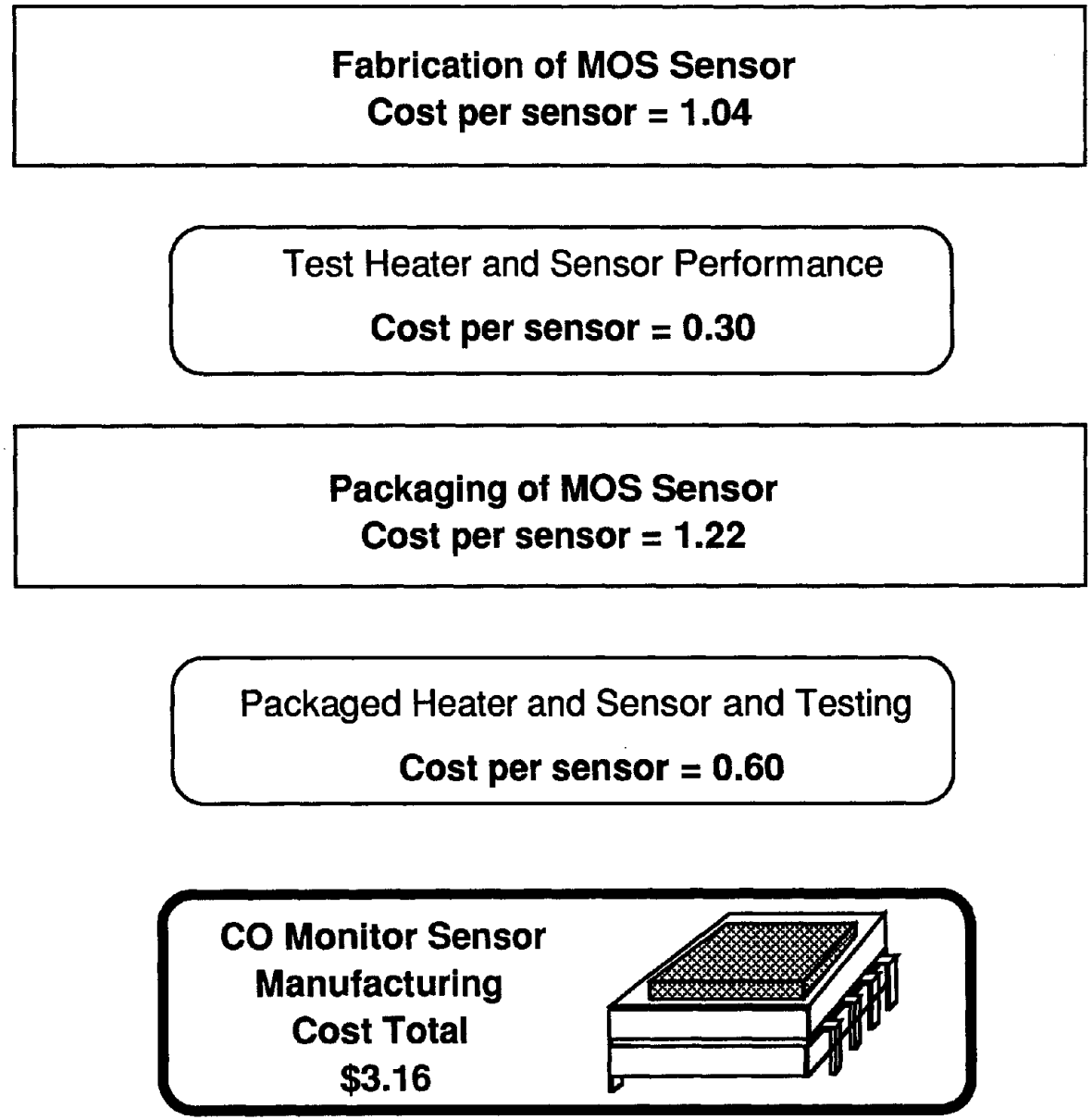


Figure # 3.1 : MOS CO Sensor Manufacturing Task and Cost Flow Chart

3.b. Electronics Design and Costing

The CO monitor electronics consists of 4 basic elements:

1. Temperature Controller for the Sensor
2. Resistance Measurement of the Sensor
3. Alarm Circuitry
4. Microcontroller/Signal Processing

Design criteria of these elements consists of several factors including:

- Automobile Electronic Specifications
- Production Runs of 250,000 Units/Year
- Integration of Electronic Circuitry Elements.

A 2 chip design comprised of a custom analog interface chip and an off-the-shelf microcontroller integrated circuit is proposed.

Elements 1-3 will be manufactured as a custom analog integrated circuit. Discrete components assembled on a printed circuit board for these circuits were evaluated and found to be significantly more expensive than a custom integrated circuit (I.C.).

The custom analog interface chip will contain the analog signal conditioning and control circuitry necessary to connect a microcontroller to the MOS gas sensor chip. The temperature controller, element 1, will maintain a constant temperature of the sensing surface to within $\pm$ 1°C. The resistance measurement circuitry, element 2, measures the sensor's response to CO gas exposure. The alarm circuitry, element 3, comprises the driver circuitry necessary to power an audible transducer, or buzzer, and optionally a visual alarm dash-panel lamp. A piezo electric transducer audible alarm will be mounted and connected to the analog I/O chip on the printed circuit board. The analog interface chip can be seen in block diagram form in Figure 3.2.

Preliminary estimates for this custom IC were obtained from a U. S. supplier. The estimate is for under $2 per IC cost in 250,000 quantity. This does not include a nonrecoverable engineering setup cost of $50,000. The costs will be formally quoted by the factory upon the acceptance of the final designs.

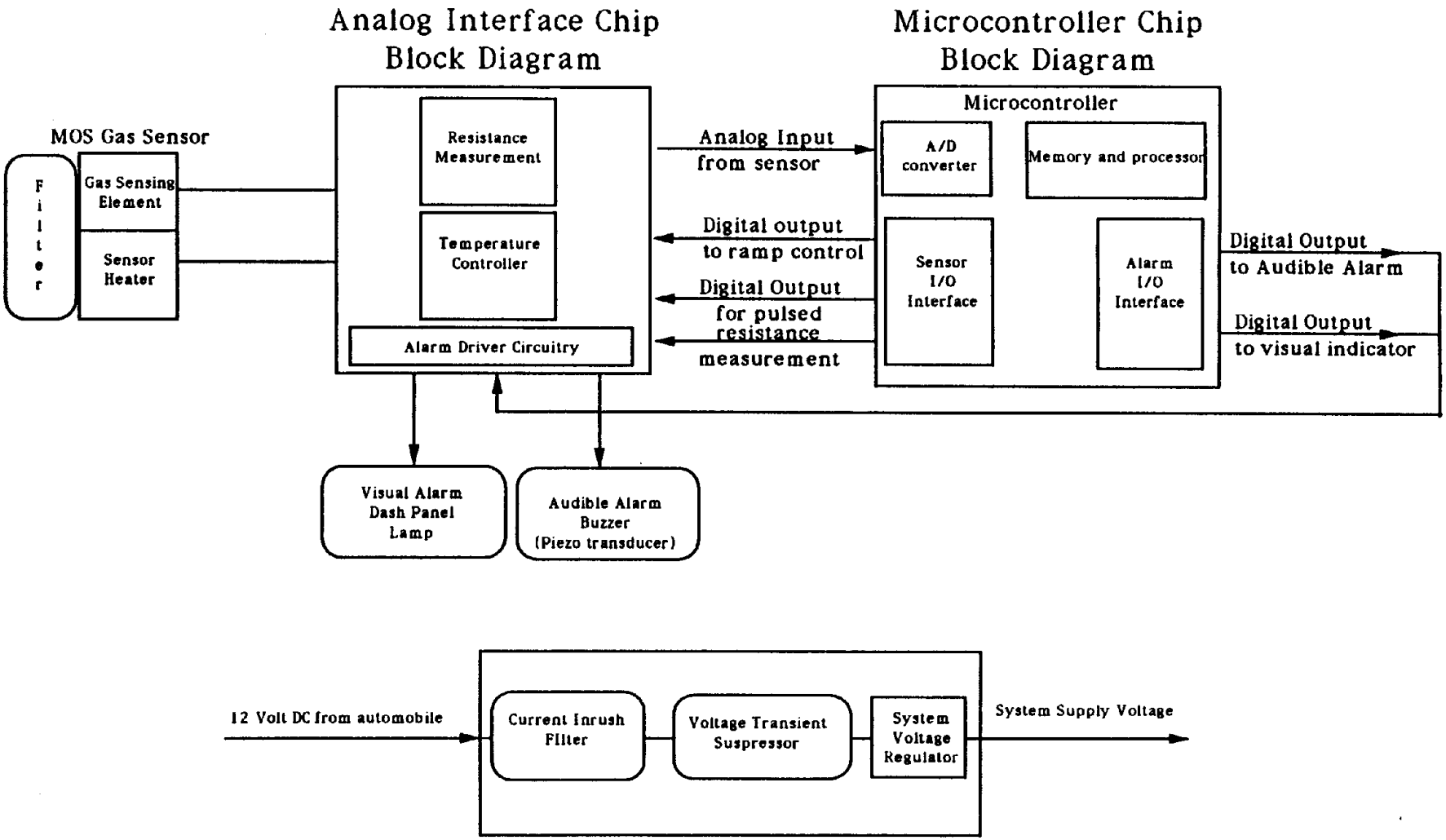


Figure 3.2: System Block Diagram for CO Gas Detection Monitor

The second major circuit group, the microcontroller, element 4, utilizes a low-cost, off-the-shelf integrated circuit selected from major manufacturers. A large variety of suitable microcontrollers are available with automotive environment specifications. 5 potential manufacturers and 10 microcontroller product lines were evaluated. The single chip microcontroller integrated circuits have functional I/O (input/output) optimally chosen for the application. The microcontroller contains analog input, digital input and output lines, memory, signal processing and algorithm software. At this time the selected microcontroller is low cost, about $3 in 250,000, and has suitable functional specifications. The microcontroller has 2 kilobytes factory mask programmable ROM, 112 bytes of RAM, and an 8 bit A/D converter.

Additionally there are 3 other circuit design considerations. They are:

a. Power Source Filtering
b. Automotive System Interface/Special Wiring Considerations
c. SAE Recommended Environmental Practices for Electronic Equipment

The power source for the MOS CO gas sensor system will be the 12 VDC supply within the automobile. Standard circuit components on the printed circuit board will protect the sensor circuitry from voltage and current transients, and other noise or abnormal conditions as per SAE J1211 recommended practices. The CO sensor system will be switched on and off from standard power wiring harness connections.

The CO sensor system printed circuit board will have an audible alarm. CMRI recommends that provisions be made via the wiring harness to activate a colored **CO/EXHAUST GAS WARNING** indicator lamp on the dashboard, or similar visual indicator, in order that the audible alarm sound can be identified as to the nature of the warning condition. Also, provisions should be made to help prevent suicide attempts. This can be accomplished by transmitting the alarm signal to the main processor of the automobile. This processor will contain information regarding the status of the automobile that can be used to determine if conditions warrant turning off the engine.

The estimated costs for the electronics for the CO monitor are $11.39/unit. These costs are listed in the Table 3.1 . These costs do not include the $ 54,300 in setup costs.

Table 3.1: ESTIMATED MANUFACTURING COST DETAIL ELECTRONICS PLUS SENSOR

THE UNIT COSTS BELOW ARE BASED UPON 250K/YEAR UNIT PRODUCTION.

UNIT COST	DESCRIPTION	COMMENTS
$3.16	MOS CO gas sensor assembled & tested.	
$3.08	Microcontroller	$3,500 1 time Mask Charge 1.6K unit minimum order.
$2.00	Custom analog interface I.C.	$50,000 NRE 1 time setup cost estimated.
$1.25	12VDC power filter, transient suppressor and voltage regulator	
$0.35	Blank printed circuit board costs.	$800 PCB Setup costs
$0.55	Estimated board assembly costs. Based upon $40/hr. automated equipment usage rate, 10 components at 5 sec./component insertion rates	
$1.00	100% final PCB calibration & testing charge.	
$11.39	Estimated Unit Cost Total of Electronics and Packaged Sensor	

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Conclusions

The results of this study show that the gas sensor technology developed at Carnegie Mellon Research Institute (CMRI) under the sponsorship of American Intell-Sensors Corporation (AIS), provides a good basis for the development of a low cost device for detecting hazardous levels of carbon monoxide in the space occupied by the driver and passengers in highway vehicles.

The sensor chip technology developed at CMRI has been tested in the laboratory showing substantial improvements in terms of long term stability and lower humidity response compared to commercial sensors. However, the CMRI/AIS sensors have not been tested in a simulated or actual car environment.

Analysis of reported data on chemicals that may be present in the highway vehicle compartment due to outgassing of manufacturing materials indicates that the total potential level of contaminants will yield a CO equivalent of less than 2 ppm in the worst case.

Contaminants introduced in the automobile compartment by the driver or passengers, accidentally or purposely, may induce false alarms if they are not properly treated. This random type of exposure to contaminant sources will require the use of a filter that by its physical and/or chemical activity will minimize or eliminate the contaminant's effect on the selective detection of CO.

The main sources of carbon monoxide in the vehicle compartment are its own internal combustion engine and exhaust fumes from other vehicles in the surrounding space. In general, reported data collected during this study indicate that street and highway background levels of CO around 35 ppm are found occasionally in very heavy traffic conditions. Higher levels may be present in road tunnels where CO concentrations exceeding 250 ppm have been detected. Although substantial reductions in the emission of CO have been achieved by the use of catalytic converters, motor vehicles are still responsible for almost all the CO encountered in the cities and roadways. Microscale situations may produce a variety of concentrations and distributions of CO depending on meteorological conditions, terrain configuration, air flow patterns and traffic volumes, among others. In addition, faulty exhaust

systems may generate potentially dangerous levels of CO in the vehicle's interior.

Protection of individuals against exposure to excessive doses of CO that may result in the impairment of their driving capabilities as well as the wellness of accompanying passengers could be achieved by placing a CO monitor in the motor vehicle's interior. Since the effect of the exposure to CO is to increase the carboxyhemoglobin (COHb) level in the bloodstream, an effect that is dose dependent (concentration x time), the monitor must perform as a dosimeter for the duration of the trip. An alarm signal will be activated by the monitor when any combination of CO concentration times the exposure period would induce a COHb level of 4% in average healthy individuals traveling inside the vehicle's compartment. The development of such monitor seems to be feasible based on the current status of the gas sensor technology existing at CMRI, and provided that an adequate filter is added to the sensing element. The manufacturing cost analysis shows that the price of this monitor would be below the guideline price of $25 per unit in quantities of 250,000.

Recommendations

The implementation of a program to equip highway vehicles with an instrument to monitor the amount of CO in the passenger compartment would require additional work to demonstrate the feasibility of low-cost CO monitoring using a newly developed sensor technology. CMRI recommends to the U.S. Department of Transportation to assess the possibility of establishing a multi-phase program for prototype development and field testing.

The first phase of the program would address testing the MOS sensors in the laboratory under simulated vehicle's interior conditions.

The second phase of the program would focus on demonstrating feasibility in the field. A limited number of monitors will be installed in designated automobiles and their operation will be compared to that of an electrochemical cell based CO monitor placed adjacent to the MOS monitor. The main purpose of this phase is to acquire data under conditions reflecting a real environment. The field tests to be performed, as well as the test methodology and protocols, will be defined by DOT and CMRI.

Phase 3 of this program would be dedicated to the analysis of the laboratory and field test data and the implementation of potential monitor modifications dictated by the results of these tests. The analysis of these data will serve to assess the feasibility of using the newly developed MOS gas sensor technology to effect low-cost CO monitoring in the automobile environment.

It is also recommended that a parallel effort to develop an efficient and long lasting filter is initiated at the start of the second phase. This effort should be completed by the end of phase 3.

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APPENDIX 1

COMPUTATIONAL ENHANCEMENT OF MOS GAS SENSOR SELECTIVITY

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Abstract

A pair of nonselective metal oxide semiconductor sensors are used to quantitatively measure the concentrations of methane and ethane present in air. Although the sensors have been optimized for the detection of methane and ethane, they still remain unselective to these very similar compounds. The sensors are characterized using a modified Clifford model which is shown to precisely fit the sensor response characteristics. Once the sensors are characterized they are used to measure the concentration of methane and ethane simultaneously present in air by using the sensors' resistances and input to a computer program that solves the 2 model equations.

Introduction

In the case of nonselective metal oxide semiconductor (MOS) sensors, the selectivity of an instrument can be enhanced over that of the individual sensors by computational means. The heart of this scheme, as applied to MOS sensors, is the model equation which must precisely reproduce the observed sensor responses. The application of such a model allows one to characterize an array of nonselective sensors with respect to the gases in question. This knowledge is then used to determine the specific gas concentrations represented by the response of the sensors' signals, by "simply" inverting this set of model equations. In order for this approach to work, the sensors in the array must be chosen such that each sensor responds differently from each of the remaining sensors with respect to at least 1 gas. An example of this method is presented for the case of 2 nonselective MOS sensors applied to the detection of methane and ethane.

The sensors

The sensor construction is described elsewhere[1,2]. For this work it is sufficient to state that the SnO_2-based sensors have been optimized for the detection of methane and ethane. The response of each sensor to the methane and ethane is shown in figure A.1. The

sensors were exposed to methane and ethane in the range from 10 to 1000 ppm, and to 3 combinations of the 2 gases. Sensor #1 is seen to be significantly more responsive to ethane than to methane, while sensor #2 is seen to be only slightly more responsive to ethane than to methane.

The model

The model used for this work is the modified Clifford model[3,4] shown below.

$$R = R_0 [1 + k_1 C_1^{e1} + k_2 C_2^{e2} \cdot \cdot \cdot]^{-b} \quad \text{Equation 1}$$

where R is the sensor resistance, C_i is the concentration of gas i, and R_0,b,K_i, and e_i are model parameters.

For the limit of a large concentration of a single gas ($kC^e >> 1$) equation 1 simplifies to

$$R = A C^n \quad \text{where} \quad A = R_0 k \quad \text{and} \quad n = be \quad \text{Equation 2}$$

Equation 2 is seen to be the usual power law model used by other investigators[5] to characterize MOS sensor response. The use of this simplified power law model will, however, lead to significant errors when 2 gases are present simultaneously. The extent of the error will depend on the extent to which b differs from unity.

Sensor Characterization

The sensors were characterized using the data shown in figure A.1. The model parameters were determined from this data set using a least squares fit method. It is important to note that data points with both gases present must be used in order to accurately determine b.

In order to demonstrate the importance of including the coefficient b, 2 sets of coefficients have been calculated. For coefficient set #1, the full model was fit, and the full set of data shown in figure A.1 was used for the fit. For coefficient set #2, b was held fixed at 1.0 and only the data with a single gas present, shown in figure A.1, were used in the fit. The value for each of the resulting parameters is shown in Table A.1. Note that for the first set of coefficients, b is considerably less than 1 for both sensors, indicating the need for the complete model equation.

Results

The ability of the computationally enhanced 2 sensor system to selectively detect methane and ethane was tested over a wide range of test gases. The data was processed for the 2 sets of model coefficients to demonstrate the importance of the coefficient b. The results of this test are listed in table A.2. Accurate measurements are obtained for both sets of coefficients when only a single gas is present. However, when the 2 gases are present simultaneously much better results are obtained with the full model.

Conclusions

To successfully apply computational techniques to enhance MOS gas sensor selectivity, it is crucial that the appropriate physical model be used. The model must precisely represent the sensors' response functions throughout the multidimensional space of n gases. This work has demonstrated the practicality of this approach in the simple case of 2 gases, and has shown the error in characterizing the sensors to gases individually. The need to characterize MOS sensors with more than 1 gas present is also necessary with other more exotic approaches such as pattern recognition and neural networks.

Work is continuing to extend this technique to a larger array of sensors and more gases.

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Figure A.1: The responses of the 2 sensors to methane and ethane are shown. The sensors were exposed to first methane and then ethane in the range from 10 to 1000 ppm, and to 3 combinations of the 2 gases. Sensor # 1 is seen to be significantly more responsive to ethane than to methane, while sensor # 2 is seen to be only slightly more responsive to ethane than to methane.

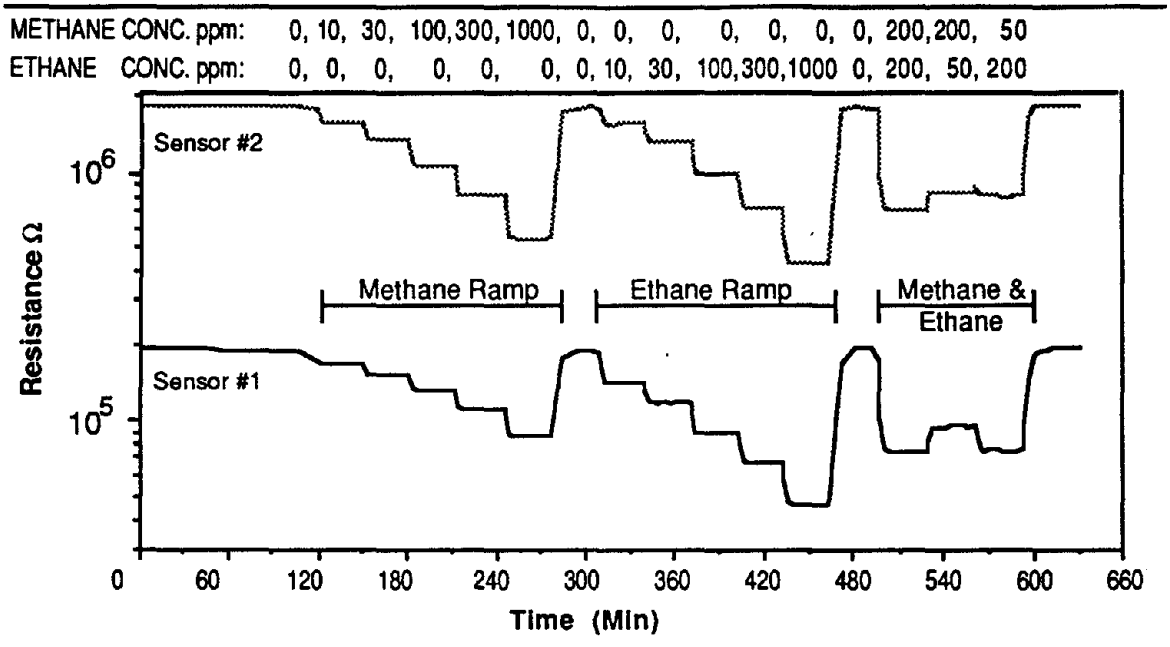

Table A.1: The model coefficients obtained from the fit of the data in figure 1 are listed for the full model fit and for β fixed at 1.0.

COEF	SENSOR #1	SENSOR #2
R_0	182111	1708953
β	0.3510	0.4028
K_1	0.0638	0.0369
ε_1	0.6895	0.8864
K_2	0.1293	0.0229
ε_2	0.8546	1.0362
R_0	189892	1826720
β	1.0 FIXED	1.0 FIXED
K_1	0.0592	0.0607
ε_1	0.4387	0.5356
K_2	0.1340	0.0516
ε_2	0.4587	0.6036

Table A.2: The actual methane/ethane(CH_4/C_2H_6) concentrations are listed together with concentrations measured using the 2 nonselective sensors plus computational enhancement. Using the full model yields better results than the model with β fixed at 1.0. All units are in ppm.

ACTUAL	MEASURED		ACTUAL	MEASURED	
CH_4/C_2H_6	FULL	β=1	CH_4/C_2H_6	FULL	β=1
10/0	11/0	8/0	100/10	107/8	100/1
30/0	34/0	29/0	100/30	107/25	89/9
100/0	107/0	105/0	100/100	103/109	62/64
300/0	298/0	307/0	100/300	99/279	51/212
1000/0	1016/0	980/0	100/1000	45/1091	83/745
0/10	0/13	0/9	1000/10	979/12	940/0
0/30	5/30	0/26	1000/30	990/31	930/3
0/100	9/104	0/109	1000/100	971/111	839/26
0/300	0/285	0/290	1000/300	957/305	712/116
0/1000	2/1060	48/767	1000/1000	908/1135	565/564

APPENDIX 2

ENHANCEMENT OF MOS GAS SENSOR SELECTIVITY BY "ON CHIP" CATALYTIC FILTERING

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Abstract

Metal oxide semiconductor gas sensors are sensitive to a variety of toxic and combustible gases but have found only limited commercial uses because they lack selectivity. Many investigators have tried to improve MOS gas sensor selectivity by altering the sensing material alone. A novel technique for fabricating practical metal oxide semiconductor gas sensors with enhanced selectivity will be presented. The discussion will focus on how, at the chip level, catalytic filtering can be employed to tailor sensor properties. Data relating to sensor sensitivity, selectivity, response time, and stability will be covered.

Introduction

Many researchers[1,2,3] have worked to enhance MOS gas sensor sensitivity and selectivity by focusing on the MOS sensing material. Their efforts have included the addition of external dopants such as Pd and Pt to the MOS sensing film, and the conditioning of the sensor film in specific gas environments. Their work also indicated that the operating temperature of the sensor film and the choice of electrode material composition have an effect on the film's response characteristics.

A new approach to enhancing MOS gas sensor selectivity, "on chip" catalytic filtering, was developed at Carnegie Mellon Research Institute (CMRI) through work sponsored by American Intell Sensors Corp. (AIS). Work at CMRI has determined that sensor chip fabrication parameters can have a strong influence in tailoring the response of a sensor chip. AIS/CMRI sensor chip structures are designed such that ambient gases must pass through a catalytic filter before reaching the active region of the MOS sensing film. Selectivity is improved for more thermochemically stable target gases with respect to less thermochemically stable interference gases by the selection and preparation of a catalytic material. This catalytic filter material should combust interference gases away from the MOS film but allow the target gas to pass through

and react with the MOS film. The appropriate filter thickness for a given application depends on such inter-related variables as the dimensions for making a mechanically stable sensor structure, the material's effective catalytic activity and surface area, and the sensor operating temperature.

Sensor Chip Construction

A goal of CMRI's research was to make practical sensor chips to be commercially produced. Thick film screen printing was selected for fabrication of the sensor chips because of the control it offers over geometry and uniformity, and its potential for low cost production. There are a variety of sensor structures that can succeed in "on chip" filtering. For this paper, a comparison of simple unfiltered and filtered sensor chip structures is presented.

Figure #1 shows a schematic cross-sectional view of 2 AIS/CMRI gas sensor chips, 1 without a filter layer (1a) and 1 with a filter layer (1b). These sensors both use tin oxide as the gas sensing material. The electrodes are made of screen printed gold, and a platinum film heater is screen printed on the opposite side of the alumina substrate. A porous glass cover layer along with a non-porous glass ring are used to provide mechanical integrity to both the tin oxide sensing film and the filter film, in this instance, made of platinum coated alumina. The non-porous glass ring also defines the path that the ambient gases must travel in order to reach the active region of the tin oxide sensing film. A more detailed description of sensor construction can be found in the U. S. patent #4,911,892(4).

Test Results

The data being presented was collected with a computer controlled gas delivery system (GDS) that creates the test atmosphere seen by the sensor chips and records the corresponding sensor responses. The GDS controls and sets proper levels for oxygen and water vapor to create a clean baseline environment. The GDS is also designed to independently set the appropriate concentrations for 5 additional contaminant gases.

Table #1 shows the response of the 2 sensors, identical except for the addition of a filter layer, made of platinum coated alumina, on sensor #2. Both sensors are operated at 500°C using a temperature control circuit to maintain the operating temperature independent of ambient conditions(5). The table lists the sensitivity ratio, response time, and water response to methane (CH4) , and carbon monoxide (CO) in humidified air. These results clearly indicate that the filtered sensor chip is no longer sensitive to CO. Also, the filtered sensor structure exhibits the same CH4 response time

and insensitivity to changes in water vapor concentration as the unfiltered structure.

Stability is a key issue in making a useful sensor. The response to CH4 and CO for a filtered sensor chip, powered continuously for over 3 years at 500 °C, is shown in Figure #2. The resistance versus concentration curves plotted for this time period confirm a stable response both for the sensing and filtering films.

Figure #3 demonstrates the selectivity of a sensor chip for fuel gases using a platinum alumina filter layer. In the resistance versus concentration curves, stable gases such as CH4 and ethane are able to diffuse through the filter layer. Less stable combustible gases such as acetone, benzene, and ethanol are largely combusted by the filter layer causing minimum changes in sensor chip resistance. This sensor calibrated for CH4, would read less than 10 ppm CH4 when exposed to 1,000 ppm ethanol.

Conclusions

"On chip" filtering is a new and powerful tool to enhance selectivity for MOS sensor chips. The simple structures shown demonstrate the concept of combusting less stable gases without compromising other important sensor properties such as sensitivity, response time, and water response to target gases. CMRI has successfully investigated several "on chip" sensor structures with selected filter and sensor materials for building stable MOS sensor chips to detect gases ranging from hydrogen to chlorocarbon compounds.

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Figure #1: AIS/CMRI MOS Sensor Chip Cross Sectional View

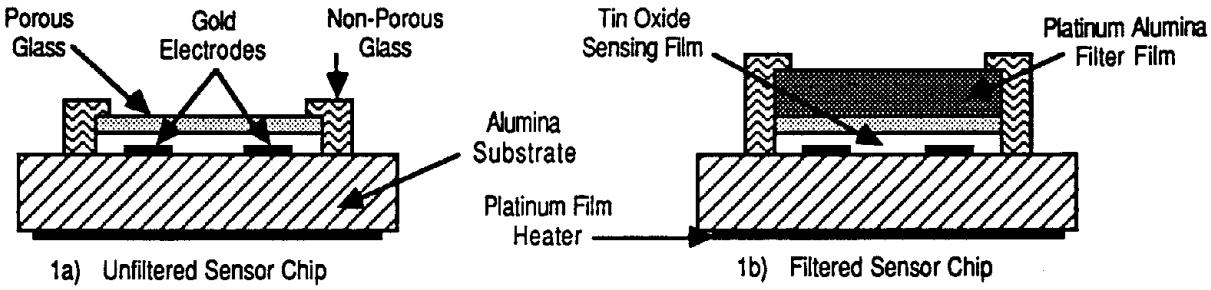

Table #1: Sensor Chip Response at 500 °C

		Unfiltered Sensor	Filtered Sensor
Sensitivity Ratio*	500 ppm CO	7.0	1.0
	5000 ppm CH4	3.1	3.1
Response Time (95%)**	500 ppm CO	less than 3 min.	not applicable
	5000 ppm CH4	less than 3 min.	less than 3 min.
Water Response(+)	500 ppm CO	1.09	not applicable
	5000 ppm CH4	0.99	0.99

* Sensitivity Ratio = (Resistance in Clean Baseline Air + Resistance in Air with Combustible Gas) both at 18 K ppm H2O

** GDS sampling rate was set for 3 minutes when this data was collected.

(+) Water Response = Resistance at 6000 ppm H2O + Resistance at 18 K ppm H2O for a given combustible gas conc.

Figure #2: Filtered Sensor @ 500 °C Response to CH4 and CO Data Taken Over a Three Year Interval

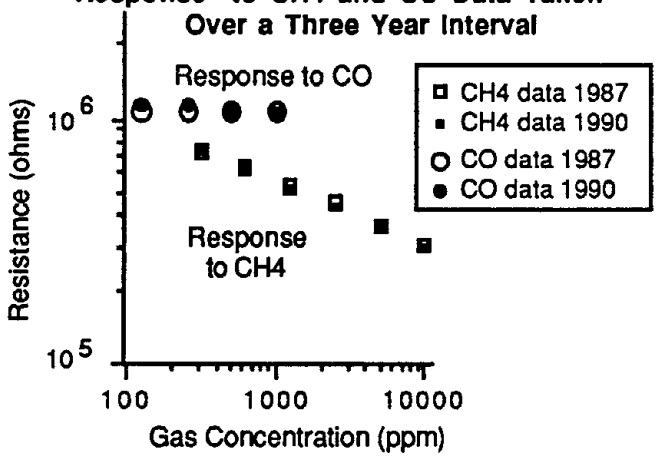

Figure #3: Filtered Sensor @ 500 °C Response to Combustible Gases