Information Circular 9233

A Personal Miner's Carbon Monoxide Alarm

By J. E. Chilton and C. R. Carpenter

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

A	ampere	μF	microfarad
°C	degree Celsius	mg/kg	milligram per kilogram
ft	foot	min	minute
ft^3	cubic foot	mL/min	milliliter per minute
g	gram	Mohm	megohm
h	hour	pct	percent
in	inch	ppm	part per million
kohm	kilohm	ppm/min	part per million per minute
lb	pound	s	second
mA	milliampere	V	volt
mA-h	milliampere-hour		

A PERSONAL MINER'S CARBON MONOXIDE ALARM

By J. E. Chilton[1] and C. R. Carpenter[2]

ABSTRACT

Underground miners may be exposed to hazardous quantities of toxic gases, such as carbon monoxide (CO), generated from mine fires or explosions. Every underground miner is required to carry a filter self-rescuer (FSR), which when operated will remove CO from the miner's breathing air. In addition, every underground miner must have a self-contained self-rescuer (SCSR) near the worksite that will supply breathing oxygen. In many situations, miners do not know when to don either rescuer since they do not know if there is a fire in the mine, nor do they carry instrumentation necessary for the detection of the toxic, colorless, and odorless fire product CO. If each miner carried a personal CO alarm, which would respond to high concentrations of CO, the miner would then be alerted when to don either the FSR or SCSR and exit the mine. A prototype personal miner's CO alarm called PEMCOAL was developed by the U.S. Bureau of Mines. The PEMCOAL unit is small enough to be carried on a miner's belt, has a flash lamp visual alarm, requires no calibration for use, and uses a chemical sensor that changes color by reaction with trace quantities of CO. The chemical sensor was tested at concentrations of CO from 10 to 1,000 ppm, at temperatures from 5° to 40° C, and with several potential mine gas interferents. The PEMCOAL alarm times were sufficiently fast to warn miners before they are exposed to hazardous quantities of CO.

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INTRODUCTION

Miners could be exposed to significant quantities of CO during their work experience. Coal mines may contain endogenous CO, which is produced by air oxidation of pyrophoric coal. Fires in mines involving coal, wood, and belting materials will produce CO as one of the principle components in the initial fire stage. Diesel-powered engines produce CO as one constituent of the exhaust, and explosive fumes from blasting also contain substantial quantities of CO.

This universality of potential exposure to CO was recognized by the Mine Safety and Health Administration (MSHA) in promulgating rules that require every underground miner to carry a belt-mounted self-rescuer. This FSR is intended to be used in case of a mine fire or explosion to remove CO from breathing air. The FSR catalytically oxidizes the CO to form relatively innocuous carbon dioxide (CO_2). Thus, by timely use of the FSR, the miner can breath air purified of CO while leaving the mine. This use of the FSR tacitly assumes that the contaminated air still contains sufficient oxygen for the miner to breathe. Recognizing that substantial amounts of oxygen may be consumed in large mine fires, and that the fire may produce large quantities of toxic products so that the miner cannot breath the air filtered by the FSR, MSHA now requires, in addition, that all miners have a SCSR stored in close proximity to their workplaces. This SCSR contains either a pressurized oxygen supply or an oxygen-generating chemical to provide a 1-h supply of breathing oxygen for the miner to use while leaving a contaminated area in the mine.

Although a miner may have an FSR and an SCSR on hand, the miner will not be protected from exposure to CO unless the devices are actually used. Obviously, if miners can see the active mine fire or survive a mine explosion, they will be prompted to use the breathing units and leave the area. If, however, the miners are not within sight of the fire, they will have to rely on receiving that information from others. Usually after a fire is discovered, a fire alarm is actuated and the mine supervisor is notified. The supervisor will verify that there is a fire and, based on the size and intensity of the fire, will have the miners exit the mine or stay and fight the fire. This decision will be sent to the affected miners at various work locations. This may be the first time that some miners are aware that there is a fire and that breathing devices should be donned. The problems inherent in this complicated supervisory process and the likelihood of breaking this chain of logical steps was, unfortunately and tragically, illustrated by the Wilberg Mine fire near Orangeville, UT, in December 1984, when 27 miners and management observers died when some of them failed to don their SCSR's in time or could not activate them to escape from the mine fire.

As a direct result of this mine accident, MSHA has issued rules requiring hands-on training of underground coal miners in the use of SCSR's. Through this training miners will know how to quickly don their SCSR's; however, in addition, they will still need to know when to use them. One technique of insuring the timely use of the FSR's or SCSR's is to have all miners carry a personal CO alarm to inform them that they are exposed to high concentrations of CO and thus, prompt the miners to don their breathing apparatus. This U.S. Bureau of Mines report will examine the characteristics of PEMCOAL, which will help the miner to know when the FSR or SCSR should be used.

EXPOSURE TO CARBON MONOXIDE

The concentrations of CO to which an underground coal miner is normally exposed during the work-shift ranges from 2 to 4 ppm for West Virginia and Pennsylvania mines, to 8 to 10 ppm for Illinois and western Colorado mines. The sources for this CO include air oxidation of coal and CO in the mine ventilation intake air from surface sources. Undiluted mine diesel engine exhaust CO concentrations can range from 200 ppm for well maintained equipment to an MSHA limit of 2,500 ppm (1).[3] The ventilation air-diluted CO concentrations measured in several mines range up to 20 ppm; the MSHA limit for diluted diesel exhaust gas is 100 ppm CO. Coal mines using explosives may typically fire 30 lb of explosives per round, which generate an average of 9 ft³ of CO (2).

If this were mixed with air in a typical heading with dimensions of 5 by 20 by 20 ft, a concentration of 4,500 ppm CO would be formed. This CO must be diluted to a safe working level by fresh air ventilation before the miners reenter the section to remove the loose coal. CO produced by coal fires may reach concentrations of up to 3.0 pct (30,000 ppm) or 4.0 pct (40,000 ppm) in mines sealed to extinguish the fire.

Miners may not work in air containing harmful quantities of noxious gases, and the concentration of any gas shall not exceed the current threshold limit value (TLV) for the gas (3). For CO, the TLV is an average concentration of 50 ppm taken over an 8-h work-shift for a 40-h workweek. There is also a short-term exposure limit (STEL) for excursions of CO concentrations, which is 400 ppm CO average concentration over a 15-min period. These periods should not be repeated more than four times per work-shift (4). The TLV of 50 ppm CO or

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[3]Italic numbers in parentheses refer to items in the list of references preceding the appendix at the end of this report.

STEL of 400 ppm CO are concentrations to which nearly all miners may be repeatedly exposed without adverse health effects (5). In addition, the Occupational Safety and Health Administration (OSHA) lists an immediate danger to life or health (IDLH) concentration which is a maximum level from which one could escape within 30 min without any escape-impairing symptoms. The IDLH limit for CO is 1,500 ppm (6).

To summarize, there can be potentially lethal amounts of CO generated in mines by many sources, such as fires, as well as ever-present small amounts of CO to which miners may be exposed without adverse effects. The mission of PEMCOAL is to alert the miner only when potentially harmful amounts of CO are present so that the miner can take appropriate action. This action should take place before the miner has been exposed to a sufficient amount of CO that would prevent escape.

CO is absorbed by hemoglobin in the blood to form a carboxy-hemoglobin (COHb) compound, which is more stable than the oxygen-hemoglobin complex. Thus, the ability of the hemoglobin in the blood to supply oxygen to vital parts of the body, such as the brain and heart, is impaired. The symptoms or response of humans is dependent on the amount of COHb in the blood as shown in figure 1 (7). Generally, no symptoms appear in healthy humans at concentrations of COHb less than 10 pct. Slight to severe headaches, impairment of judgment, dizziness, and shortness of breath occur between 20 to 50 pct COHb, unconsciousness from 50 to 60 pct COHb, and

eventually death at 80 pct COHb. The amounts of COHb are correlated to the CO exposure in ppm CO-hours where at exposure of 600 ppm-hours and below there are no perceptible effects (8). Obviously the exact amount of COHb formed in a human at a given concentration of CO for a given exposure time is dependent on (1) the breathing rate and thus the work being performed, (2) the size of the human and thus the blood volume, (3) the oxygen pressure in air and thus the altitude, and (4) the ambient temperature. The differences in exposure conditions and in human response account for some of the data variability. Another way of showing the effects of CO on adult health as a function of exposure time is given in figure 2 (9). The MSHA limits for the TLV average concentration of 50 ppm CO over a 480 min duration is well below the two areas showing adverse symptoms. At the upper range of 10,000 ppm CO within 3 to 5 min of exposure, a miner could collapse and be in danger of death. The CO alarm should operate at a level below the point where any of the symptoms of headache, impairment of judgment, dizziness, or nausea occur and thus, give an alarm at a level that can be located on this graph below and to the left of the curves showing these effects. The alarm times determined experimentally by this work using the prototype PEMCOAL 1 unit from early data are shown on figure 2. With 1,000 ppm CO concentration, the alarm occurred in an average time of 8 min. Thus, the PEMCOAL unit would provide an alarm before onset of the first symptoms of CO poisoning.
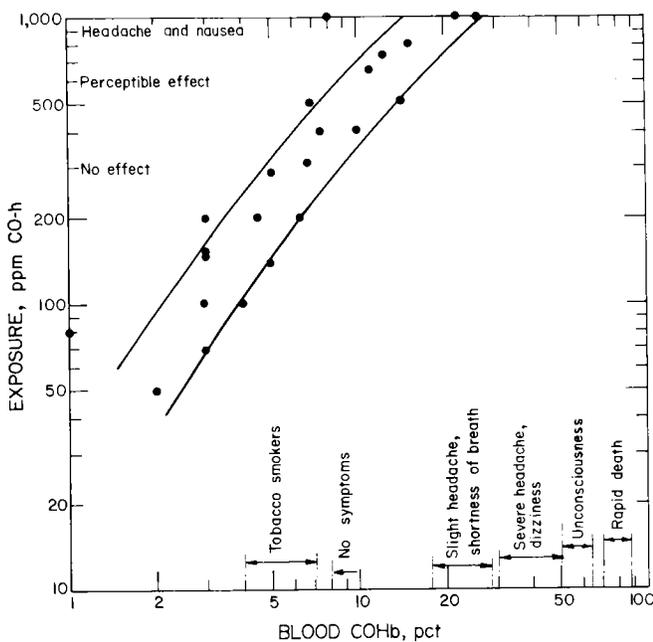

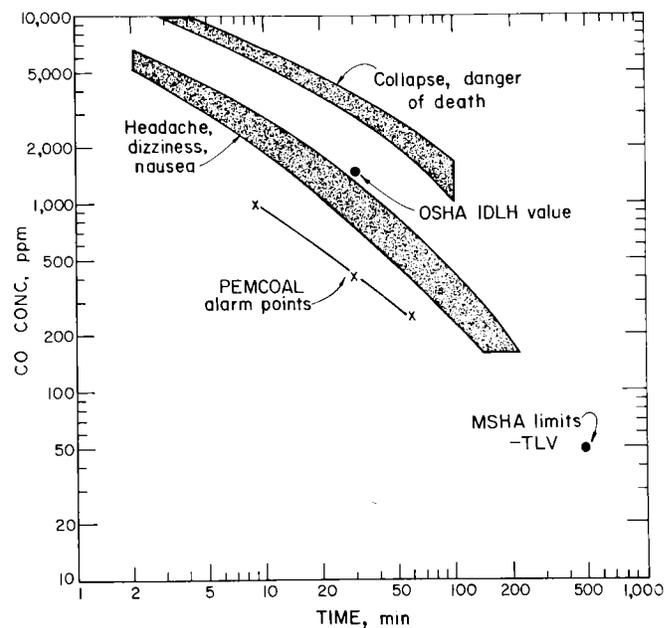Figure 1.-Formation of carboxy-hemoglobin by carbon monoxide exposure.

Figure 2.-Effect on health by exposure to carbon monoxide.

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MEASUREMENT OF CARBON MONOXIDE

Several techniques are available for measuring CO in the concentration range of 10 to 1,000 ppm. These include (1) chemical stain tubes and disks that change color upon reaction with CO, (2) electrochemical sensors that measure the CO oxidation current, (3) solid-state semiconductors, such as tin oxide, which change resistance when reacted with CO, and (4) infrared (IR) detectors that measure light absorption by the CO. The CO stain tubes and disks normally rely upon visual examination to warn of high levels of CO. However, an automatic alarm is preferred to relying on haphazard visual detection of the CO indication. Handheld electrochemical CO monitors with audible and visual [usually light emitting diode (LED)] alarms, which are certified by MSHA for intrinsic safety, are available from seven manufacturers at an average price of $850. In addition to the initial purchase price, each monitor will have an annual maintenance cost of $250 to $300 for the replacement CO sensor, battery, and gas calibration supplies. Although these electrochemical monitors may now be used for this application by the more affluent mining companies, the CO alarm discussed in this report will be much less expensive and will not require continual calibration during use. Present IR gas monitors require large electrical power for operation, are not readily portable, and cost $1,500 or more. Semiconductor CO detectors require high electrical current for operation, and are very sensitive to humidity. To date, none of the electrochemical, IR, or semiconductor sensors have proven applicable to this personal monitor concept because of cost or sensitivity. New developments now occurring in microsized solid-state sensors may, however, have future applications for this CO alarm type.

The CO alarm discussed in this Bureau report will use an optocoupler consisting of an IR LED and a photosensitive silicon transistor to detect the change in color of a chemical disk that reacts with CO.

PROTOTYPE CO ALARM CHARACTERISTICS

The PEMCOAL objective is to warn the miners of exposure to potentially hazardous quantities of CO. Therefore, the alarm must activate before the miner's health or judgment is impaired. One goal for this alert or alarm level is the OSHA IDLH standard: alarm at a concentration of CO of 1,500 ppm before 30 min have elapsed (6). Thus, the most critical objective can be met if the alarm activates at concentrations of CO lower than 1,500 ppm of less than 30 min duration. The ability of the disk to trigger an alarm at a given time and at a given concentration of CO depends entirely upon the properties of the chemical reaction of the solid compound with CO. These properties include the speed of the overall reaction, the arrangement of the reactive chemicals on the substrate for rapid interaction of the gas phase CO with the solid phase, and the ultimate reaction color change. The test program, which is described below, was implemented to see if this objective can be met with one type of a commercially available palladium salt-silica gel system.

On the other hand, the alarm should not be too sensitive, causing the miners to needlessly don their breathing equipment. Tests were run at background concentrations of CO, which are normally encountered in mines to verify that false alarms will not be triggered.

Based on the premise that the PEMCOAL should be carried by all miners, (attached to their belt or rescue equipment) and that each unit should be inexpensive (cost less than $50), the following criteria were used in the unit's design:

Size—Smaller in size than a self-rescuer—5 by 3.5 by 2.5 in.

Weight—Less than 0.5 lb.

Calibration—Not required if each disk is identical, containing the same amount of the reactive chemical. This requirement means that the disk manufacturer should have the production system under good quality control.

Power—9-V low-current alkaline battery, available in any mine locality, such as NEDA[4] 1604-A.

Alarm Mode—Strobe light with pulsed operation, effective in dark, noisy mines.

Sensing Principle—A chemically treated disk that changes color by reaction with CO. The disk is obtained from commercial, readily available sources. One type of disk uses a palladium salt on a silica gel substrate, which is initially a straw yellow color and reacts with CO to form a gray color.

Electronic Design—Sense the disk color change with a reflective-type optocoupler containing an IR emitting LED and a silicon photo detector. Minimize electrical current drain by pulsing or intermittently operating both the optocoupler sensor and the alarm light.

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[4]Reference to specific products does not imply endorsement by the U.S. Bureau of Mines.

PROTOTYPE PERSONAL MINER'S CO ALARM

The electronic circuitry and a CO sensing disk were assembled into a plastic case suitable for wearing on a miner's belt. The electrical function diagram is given in figure 3 showing the relationship between the IR diode, the CO sensitive disk, and the photosensitive transistor. The complete electrical schematic for the most recent prototype, PEMCOAL 2, is figure A-1 in the appendix. In this unit, a reflective optocoupler (TRW OPB 703A) is positioned to view the disk during the color change caused by reaction with CO. The measured voltage was 2.6 V for unreacted disks, and the final voltage was 4.2 V for the completely CO reacted disks (dark gray). An alarm threshold voltage was chosen at 3.5 V for this application, which is almost one-half of the total voltage change. The 703A reflective device is powered by a pulse generator with periods of 0.1 s on and 1.5 s off. The voltage output from the silicon phototransistor is compared with the reference voltage (3.5 V), and when this voltage is exceeded, the alarm is latched on until the next pulse sequence starts. The prototype unit PEMCOAL 1 alarm is a visible red LED and the PEMCOAL 2 alarm is a strobe light with greater visual impact. The PEMCOAL 2 strobe light and all of the high-voltage components were encapsulated in a transparent flexible silicon polymer. This will render flash components intrinsically safe for operation in potentially flammable gas mixtures. The alarm is pulsed with a time period of 0.05 s on and 0.5 s off, two flashes per second, to conserve the battery power. The battery is a 9-V transistor type with a useful capacity of 100 mA-h at the 10 h rate of discharge. The average current drain is 3.1 mA, and it is recommended that a new battery be used each week. A secondary Ni-Cd 7.2 V battery may be used also with a projected service life over one year.

To check the operation of the alarm, a plastic holder carrying the CO sensitive disk is inserted part of the way into the unit until the closing of the spring-loaded turn-on switch can be felt. The optical sensor will then view the dark inner case wall. With the holder in this position, the alarm lamp will flash, thus checking the operating status of the electrical circuitry and the battery. The holder with the disk is then pushed all of the way into the unit to position the fresh unreacted disk in front of the optocoupler. The alarm will then stop flashing as the sensor views a fresh unreacted disk and the unit will then be ready for use. The prototype unit in figure 4 shows the disk on the holder before insertion into the unit.
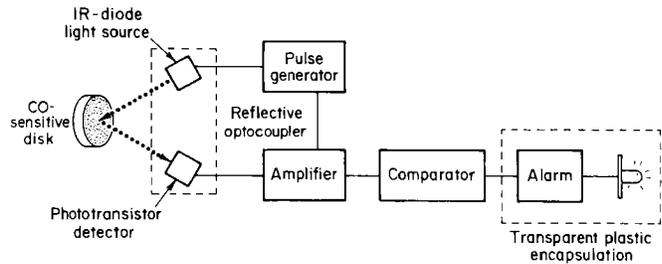

Figure 3.-PEMCOAL 2 electrical function diagram.

Figure 4.-PEMCOAL 2.

TEST METHOD

All of the following data were obtained by the PEM-COAL 1 unit which was tested in the experimental setup shown in figure 5. An environmental chamber was used for ambient temperature control. The gas mixtures were prepared using compressed cylinders of standard gases diluted by air in a dynamic gas mixing system regulated by mass flow controllers (10). The test gas mixture was humidified using water in a gas washing bottle with a fritted disk for bubble dispersion. For tests with water soluble gas constituents, only the air diluent was humidified. The test gas was fed into the CO alarm using a plastic hood with gas flow set usually at 400 mL/min. Times to alarm were measured with an electronic timer containing an optical sensor that stopped the timing cycle when the alarm LED was turned on. For all of this work, commercially available CO sensitive chemical disks were purchased from the American Gas & Chemical Co., Northvale, NJ, as Leak-tec CO-50-R CO indicators.

TEST RESULTS

Initial experiments with the prototype CO alarm were run at 24° C using fresh disks and immediately exposing them to a CO test gas. Generally, three test gas concentrations were used: 250, 400, and 1,000 ppm CO mixtures in air with 84 pct relative humidity. Alarm times measured with the fresh disks are shown in the lower curve in figure 6. Average alarm times of 10.94 min were obtained with standard deviation of 3.88 min for 250 ppm gas challenge. At higher concentrations of CO, the disks responded faster with an average alarm time of 2.58 min and a standard deviation of 0.98 min for the 1,000 ppm CO challenge.

HUMIDITY EFFECTS

The disks were found to have a slower response if they were initially exposed to air containing water and then challenged with CO, simulating their use in wet mines. Tests were run for 2 h with humid air (84 pct RH), and then the disks were challenged by test gases containing CO. The results of these tests are plotted on the upper curve in figure 6. The alarm times at 250 ppm CO were an average of 49.5 min with a standard deviation of 12.03 min. At 1,000 ppm CO gas challenge, the alarm times were an average of 8.4 min or over 3 times as long as the alarm times obtained with the fresh disks.

Several tests were run with the initial CO test concentration at 10 ppm CO in humid air for 6-h duration, simulating typical mine background levels of CO. The PEMCOAL unit did not alarm at the 10 ppm CO concentration level during the 6-h exposure. At the end of each test, the unit was then challenged with a higher concentration of CO. Alarm times of 12 and 16 min were measured at 1,000 ppm CO, alarm times of 30 and 36 min at 400 ppm CO, and alarm times of 78 min at 250 ppm CO challenge gas. This test simulated the use of the CO alarm by coal miners working in a mine with high humidity (84 pct RH) with a background concentration of CO of 10 ppm, and having a fire occur after they had been working for 6 h. The units would still respond before the miner was adversely affected by the ambient CO at concentration levels from 250 to 1,000 ppm CO.

GAS INTERFERENTS TO DISK REACTION

Several gas interferents to the reaction of CO with the chemical disks were examined. The interferent gases included hydrogen sulfide (H_2S) formed in mines by reaction of sulfide minerals with acid mine water, sulfur dioxide (SO_2) generated in mine fires from burning of sulfur-containing materials and present in diesel engine exhaust from sulfur in the fuel, and nitric oxide (NO) and nitrogen dioxide (NO_2) both formed in diesel engine exhaust and in gas fumes from explosive blasting.

The PEMCOAL 1 unit was run in air with 50 ppm SO_2 for 3 h; no alarm was obtained. This exposed disk was then challenged with 1,000 ppm CO and an alarm time of 7 min was measured. This alarm time for the 1,000 ppm CO measured after the 3-h exposure to SO_2 was equivalent to the average alarm time of 8 min previously found in runs at 1,000 ppm CO after a 2 h exposure to moist air. With additional tests at 25 ppm SO_2 and 243 ppm CO, alarm time of 18 min was measured. With 5 ppm SO_2 and 255 ppm CO, alarm times of 7 min and 6.3 min were measured. With tests at 255 ppm CO alone, alarm times of 9.5 and 8.7 min were obtained. Thus, at a concentration of 5 ppm SO_2 there is very little effect on the CO disk reaction. The TLV for SO_2 is 2 ppm, and if the mine is operating under compliance for allowable toxic gases (3), no effect of SO_2 is expected on the CO alarm.
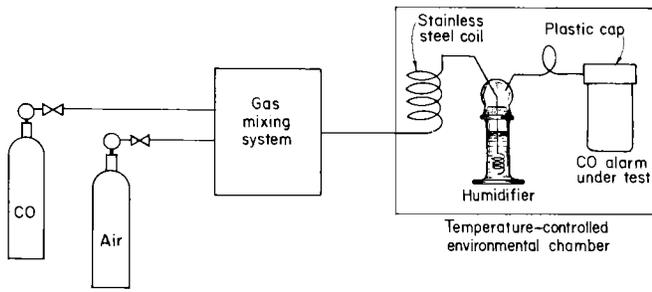
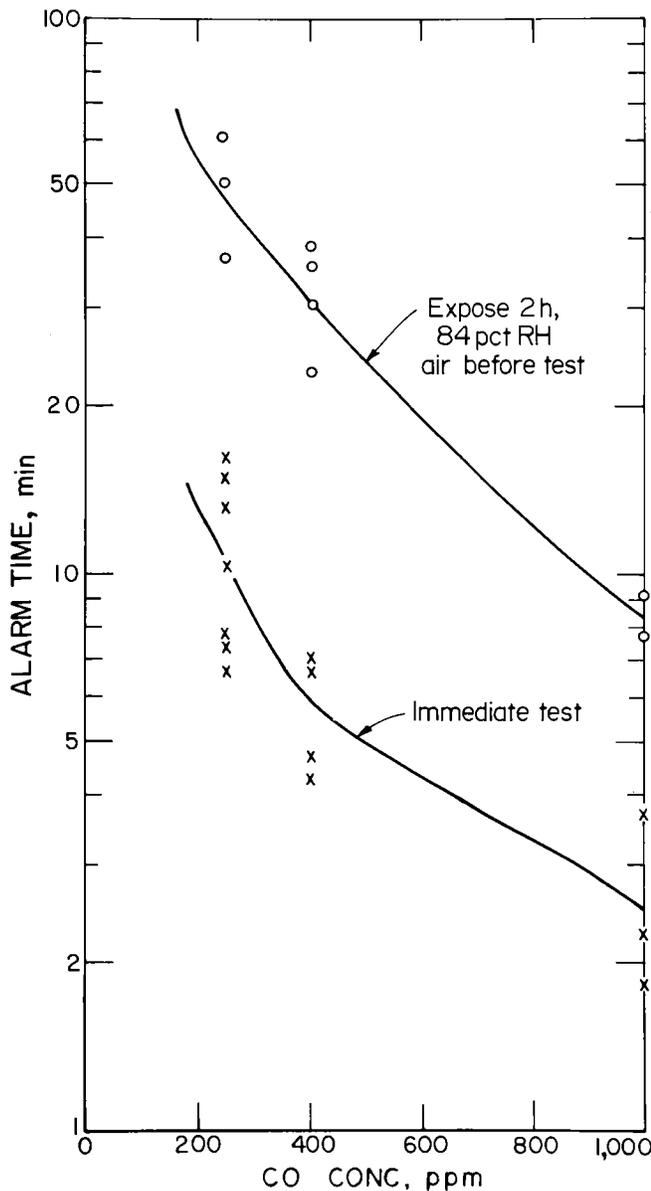Figure 5.-Apparatus for test of carbon monoxide alarm.

The PEMCOAL 1 unit was run in 7 ppm NO for 3 h and no alarm was obtained. This unit was then challenged with 7 ppm NO and 250 ppm CO, and an alarm time of 10.5 min was obtained. When a fresh disk was run in a mixture of 7 ppm NO and 242 ppm CO, an alarm time of 6.2 min was measured. For comparison, a run in 241 ppm CO alone had an alarm time of 8.7 min. Thus, the presence of NO did not significantly effect the response of the CO chemical disk. The TLV for NO is 25 ppm and typical concentrations measured in several coal mines with diesel-powered equipment are less than 8 ppm NO.

The PEMCOAL 1 unit was run in 8.9 ppm NO_2 with 254 ppm CO, and an alarm time of 90 min was measured. With 3.6 ppm NO_2 in 248 ppm CO, an alarm time of 29.7 min was measured. The alarm time for the unit exposed to 276 ppm CO alone was 7 min. Thus, NO_2 in these tests is an interferent to the reaction of the CO chemical disk. The PEMCOAL 2 unit has a dust filter composed of open cell porous polyurethane placed over the gas inlet ports. This unit had alarm times of 2.9 and 5.7 min when tested in 3.6 ppm NO_2 with 248 ppm CO, and when tested with 3.6 ppm NO_2 with 908 ppm CO had an alarm time of 2.3 min. Thus, no effect was found on the PEMCOAL 2 unit from the NO_2. In these tests, the foamed plastic filter adequately removed the NO_2 from the CO mixture. The TLV for NO_2 is 3 ppm and measurements in mines with diesel-powered equipment have found concentrations of 1 ppm or less.

Tests of the PEMCOAL 1 unit with H_2S showed a strong positive interference to the CO chemical reaction (fig. 7), which shows the alarm times obtained at various gas concentrations. CO reacts with the sensor disk to
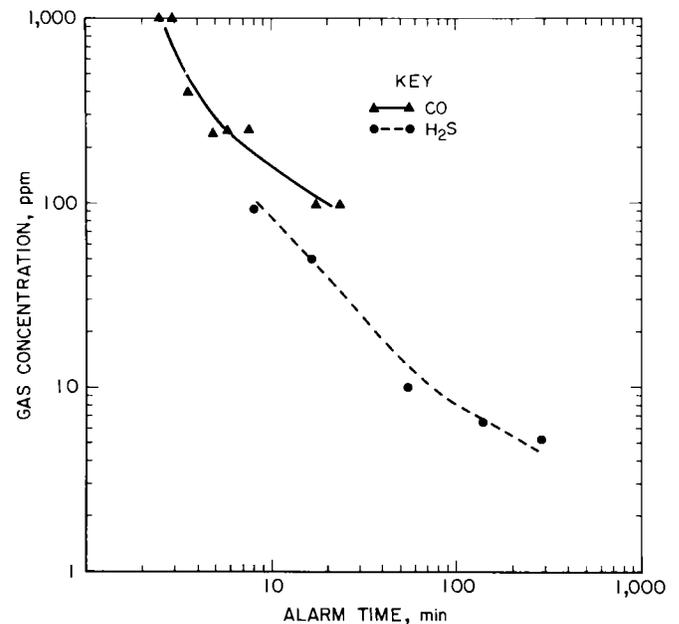

Figure 6.-Effect of CO concentration and humidity on the PEMCOAL alarm time.

Figure 7.-Effect of hydrogen sulfide and carbon monoxide on PEMCOAL 1 alarm times.

form gray palladium metal. H_2S reacts with the sensor disk to form black colored palladium sulfide. The disk is more sensitive to H_2S by a factor of 2 over the CO. If a mine atmosphere contained H_2S, a chemical filter containing zinc, lead, or mercury salts would be added to the unit to remove the interferent. The TLV for H_2S is 10 ppm and at this concentration an alarm time of 55 min would be obtained with the CO reactive disk.

To summarize the effect of gaseous interferents on the CO disk reaction, significant quantities of NO_2 would increase the alarm times and H_2S would shorten the alarm times for the CO detection, while both SO_2 and NO would give minimal effects at the low concentrations expected in mines.

TEMPERATURE EFFECTS

The effect of ambient temperature on the alarm times was measured from 5° to 40° C as presented in figure 8.

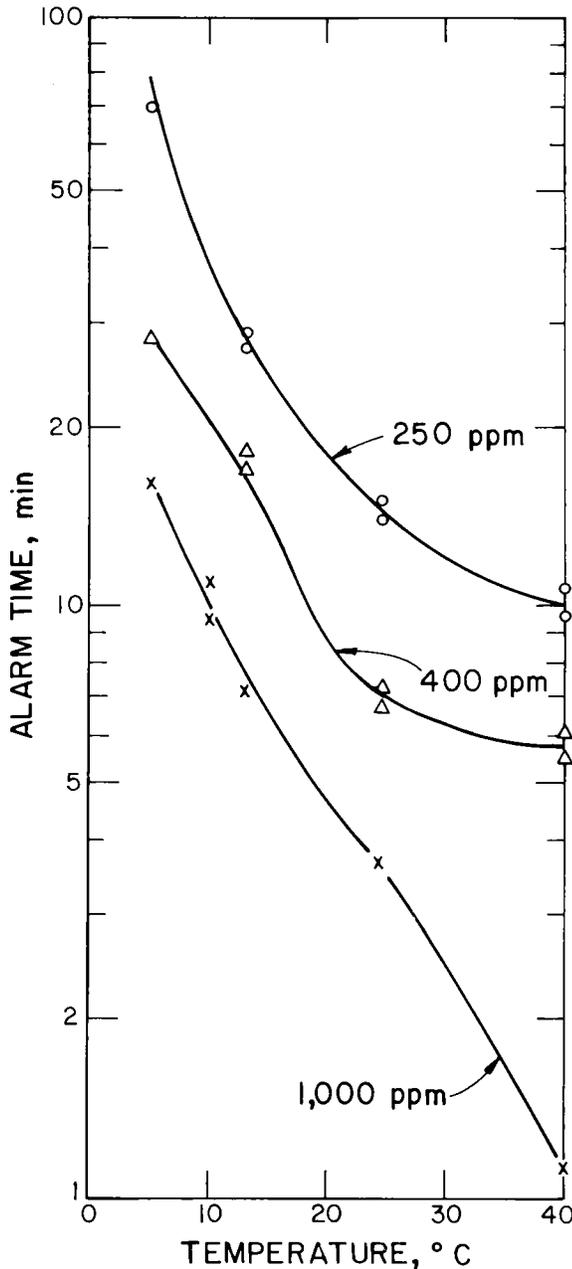Figure 8.-Effect of temperature on PEMCOAL alarm times.

The alarm times were quicker at the higher temperatures for all three gas concentrations. At 5° C and with 250 ppm CO challenge gas, several of the tests did not alarm in 100 min. When the disks were removed from the test fixture, the disks were still the original light straw yellow color, but turned dark gray as the disks were warmed in air. This observation leads to the conclusion that the disks adsorb the CO at the low temperature, but the subsequent reaction of the adsorbed CO with palladium ion to produce the metallic palladium is slow at low temperatures.

The slow reaction of CO with palladium salts at low temperature, and the slow reaction in the presence of excess water may be explained by the hypothesized reaction sequences presented in figure 9. The interaction of a palladium chloride coordinated complex with water and CO is indicated. The equilibrium constant for the formation of the palladium-water complex is probably greater than the equilibrium constant for the palladium CO-water
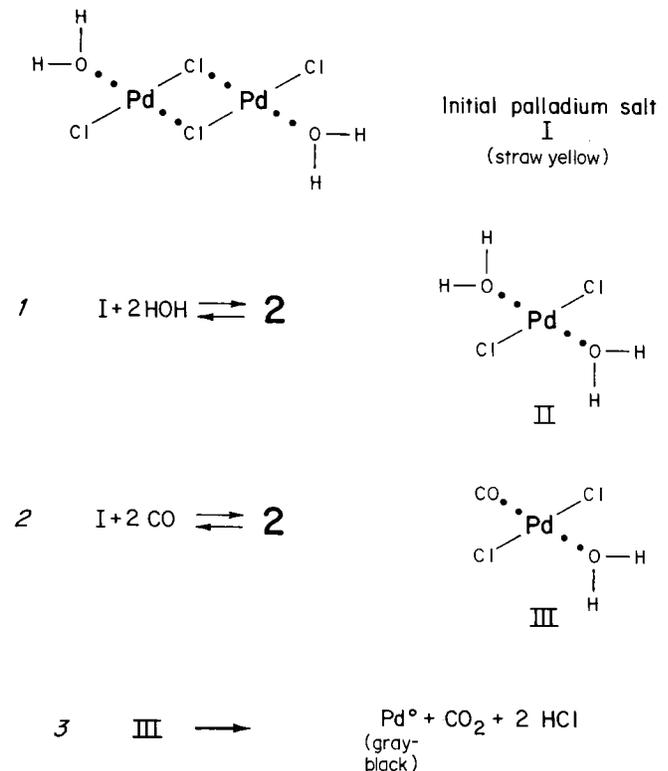

Figure 9.-Proposed reaction sequences for palladium chloride with carbon monoxide and water.

mixed complex because of the loss of reactivity of the palladium complex in the presence of excess water. By storing unreacted disks over concentrated sulfuric acid the water was removed from the disks and the disks changed color from the pale straw yellow color to a darker orange color. The dried disks did not react with dry 1,000 ppm CO during tests for an hour. Thus, some water is necessary for the reaction of the palladium compound with CO.

VARIABILITY

The CO reactive disks were purchased in lots containing 10 plastic sealed disks. To determine the alarm time variance for the disks within a lot and the alarm time variance from lot to lot, data were collected from tests of disks with 250 and 1,000 ppm CO exposure. A plot of the disk lot numbers versus the products of the CO test concentration with the measured alarm time is given in figure 10. If the reaction rate for the formation of palladium metal is a function of the CO concentration, the amount of palladium formed is proportional to the product of the CO concentration and the alarm time. If the palladium metal is uniformly spread over the disk, a given amount of palladium will form a fixed optical density change on the disk. Since the disk color density for alarm is a constant determined by the optocoupler characteristics and by the alarm set voltage, the products of the gas concentration and the alarm time should be a constant. The average value for the products measured at 250 ppm CO is 2,087 ppm min with a standard deviation of 540 ppm min or a relative standard deviation of 25.9 pct. The average value for the products measured with 1,000 ppm CO is 2,278 ppm min with a standard deviation of 498 ppm min or a relative standard deviation of 21.9 pct. These lot-to-lot relative standard deviations (coefficient of variances) are of the same magnitude as the within-lot relative standard deviations for lot 27 of 22.6 and 15.5 pct. An analysis of variance test was run on the data from the different lots, and there was no significant difference between the lot-to-lot variances and the within-lot variances. The product values for lot 27 seem to fall below the lot average values indicating that these disks may be more sensitive to CO; however, the values are within the three sigma range for normal scatter of data.

The range of data in figure 10 shows that at 1,000 ppm CO exposure the alarm times varied from 1.6 to 3.2 min. Some of the disk alarm time variation may be due to different amounts of palladium material on the disks. Chemical analysis for palladium by inductively coupled plasma emission was performed on extracts from four

disks, two from lot 17 with high sensitivity and two from lot 22 with lower sensitivity (longer alarm times). The weight of palladium plus silica material on each disk is approximately 0.1 g. For lot 17, the average amount of palladium was 1,530 mg/kg of material with a standard deviation of 99 mg/kg and for lot 22 the average was 1,385 mg/kg of material with a standard deviation of 21 mg/kg. Since the difference between these analyses are not statistically significant, other factors than total palladium content may affect the disk response times, such as the type and amount of silica gel binder and the uniformity of the metal deposits on the disk surface. Good quality control measures must be taken by the manufacturer to assure a consistent and uniform response to CO for each of the disks.
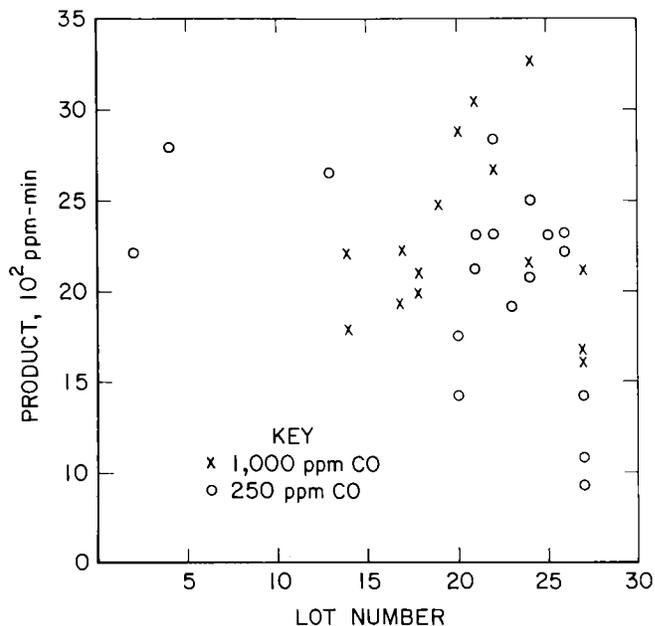

Figure 10.-Effect of lot number on response of CO reactive disk.

CONCLUSIONS

A prototype personal miner's CO alarm has been designed and fabricated using a commercial solid chemical disk, which changes color in the presence of CO. This prototype alarm is designed to warn a miner of exposure to potentially harmful amounts of CO before the miner can experience adverse health effects. Operation of two models, PEMCOAL 1 and 2, have been tested at CO concentrations to 1,000 ppm where the alarm times range from 2 to 3 min for tests at room temperature. The cost of parts purchased singly for the unit are under $40, and if the primary transistor battery and the disk were changed each week, the unit would incur an additional maintenance charge of $1.75 weekly. In the event of a mine disaster generating a large amount of CO, the use of this unit to warn a miner to don protective breathing equipment and exit the mine would substantially improve the miner's chance of survival.

Successful operation of the CO alarm in mines depends critically upon a reliable source of reproducible disks. Thus, it is necessary to obtain data on the disk quality control, or alternately, to find a separate source of high-quality CO reactive disks. The present CO alarm uses a palladium salt to react with the CO. The chemistry of other potentially CO reactive compounds should be examined to find alternate color-changing reactions which may be more sensitive and more reversible. Gaseous interferents to the operation of the CO reactive disks such as H_2S were verified and techniques can be devised to remove these interferences for in-mine use. Ultimately, in-mine tests need to be conducted for testing of durability and for identifying potential problems caused by operation in the presence of water aerosol and coal dust.

REFERENCES

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APPENDIX.–ELECTRICAL SCHEMATIC AND COMPONENT LIST FOR PEMCOAL 2

Table A-1 is a listing of the electrical components and figure A-1 is the electrical schematic for the PEMCOAL 2.

B	Battery, 9-V, NEDA 1604 A.
C1, C2	Capacitor, 1-μF.
C3	Capacitor, 4-μF.
C4, C5	Capacitor, 0.01-μF.
D1, D2, D3	Diode, 1N645.
D4	Diode, 1N4002.
D5	Diode, 1N4007.
F	Flash tube.[2]
J	Optocoupler, OPB 702A (TRW).
N	Neon bulb, NE.
R1	Resistor, 10-kohm.
R2	Resistor, 2.2-kohm.
R3	Resistor, 270-kohm.
R4	Resistor, 10-kohm.
R5	Resistor, 1-kohm.
R6	Resistor, 390-kohm.
R7	Resistor, 30-kohm.
R8, R9	Resistor, 4.7-kohm.
R10	Resistor, 2.2-kohm.
R11	Resistor, 1-Mohm.
R12	Resistor, 1-kohm.
R13	Resistor, 100-kohm.
R14, R15	Resistor, 1-kohm.
R16	Resistor, 100-kohm.
R17	Resistor, 1.47-kohm.
R18	Resistor, 15-kohm.
R19	Resistor, 10.5-kohm.
R20	Resistor, 22- to 47-ohm, adjustable.
R21	Resistor, 3-kohm.
R22	Resistor, 100-kohm.
R23	Resistor, 3.9-Mohm.
R24	Resistor, 1-Mohm.
S	Switch, 1-SM-1.
T1	Transistor. 2N2222.
T2	Transistor. 2N2707.
T3, T4	Transistor. 2N2222.
T5	Transistor, SCR, 24 NEC.
U1, U2	Transformer.[2]
Z	Transparent silicone elastomer, Sylgard 182 (Dow Corning).

[1]See figure A-1.
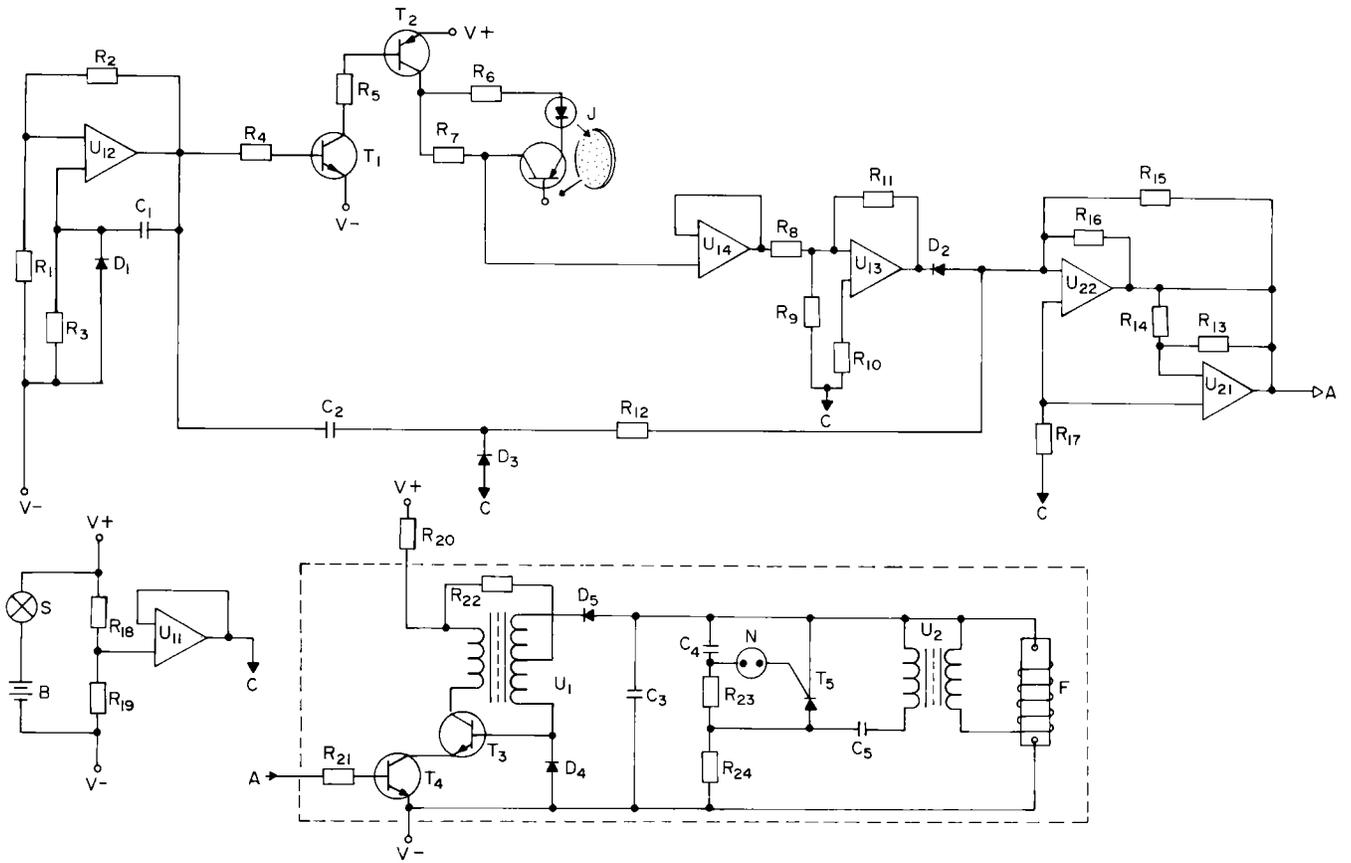[2]Kit C 35655, Edmond Scientific.

Figure A-1.–Electrical schematic for PEMCOAL 2. See table A-1 for a description of components.