Intern. J. Environ. Anal. Chem., Vol. 44, pp. 21–39
Reprints available directly from the publisher
Photocopying permitted by license only

DEVELOPMENT OF A THIN FILM ENVIRONMENTAL MONITOR*

G. EDWARD BURROUGHS and DAVID J. HUEBENER

National Institute for Occupational Safety and Health, 4676 Columbia Parkway, Cincinnati, OH 45226

(Received 14, June, 1990; in final form 23 October 1990)

A device has been developed by researchers at the National Institute for Occupational Safety and Health (NIOSH) for real-time monitoring of exposure to airborne contaminants, including in-mask respirator sampling. The device consists of a small breathing-zone sensor connected to a belt-mounted unit. The cylindrical sensor, which weighs 15 g and is 2 cm in diameter and 2.5 cm long, contains a thin film of chemical reagent that changes color upon exposure to a particular contaminant, and an optical system that monitors the color change. The belt-mounted unit (450 grams) provides power to the sensor, pulls air through it, and processes its electrical output. The output signal is a function of the total contaminant exposure, can be processed to provide real-time concentration data, can be recorded, or can be used to trigger an audible alarm. Five prototype devices were constructed and their capability to monitor ammonia and mercury was investigated. Evaluation of this device using a commercially-procured reagent film for ammonia, indicated good correlation for response of individual units as a function of dose and for interunit and intraunit response ($R^2 = 0.99$). However, evaluation with a reagent film for mercury vapor manufactured in-house produced varying results depending on the film's conditioning prior to use. Currently, the techniques for monitoring personal exposure to these contaninants are limited to conventional environmental sampling and analytical techniques which require laboratory analysis (producing only time-weighted average measurements) or instrumental techniques which provide a real-time determination of concentration, but seldom allow the determination of analyte in as workers breathing zone. From the present research, it was concluded that, when the proper film is available, this device provides a convenient method for accurate, real-time measurement of a contaminant at levels near the applicable environmental criteria. Therefore, the advancement of this monitoring technique will depend on the reliable production of suitable films based on the many colorimetric reactions already known.

KEY WORDS: Environmental monitor, real time monitor, ammonia, mercury, invention.

The changing nature of work, as well as the need to better understand the etiology of occupationally related disease, requires new analytical devices capable of monitoring workers exposure on a real-time basis. Among the approaches being investigated at the National Institute for Occupational Safety and Health (NIOSH) for this purpose is a series of color-producing reactions which can be

---

*Mention of the name of any company or product does not constitute endorsement by the National Institute for Occupational Safety and Health.

performed in a non-liquid phase and miniaturized to a level which enables personal monitoring. The goal of this research is a real-time, personal monitoring device which, if commercialized, would be priced approximately equal to a personal sampling pump.

The technology developed in this research has been tested for ammonia and mercury vapor, but could be expanded to additional analytes in the form of both breathing zone personal monitors and monitors for use inside air purifying respirators. The personal sampling devices would create the ability to relate exposure to task in the workplace, and monitor the magnitude and duration of peak exposures. The in-mask monitor would help to allow safer use of respirators for vapors, including those with no odor or other warning properties.

Ammonia and mercury were selected because their chemical and toxicological properties have been extensively studied, as well as the usefulness of a successful device for monitoring their concentrations. Sensor materials included commercially available analytical films and self-manufactured chemical coatings. The monitoring device was a miniature colorimeter which continuously measures the color change in the sensor due to exposure to the analyte of interest, and converts this to an electrical signal. This signal can be used to activate an alarm or can be fed into a data storage device.

BACKGROUND

This effort was the combination of two separate research activities, one in the area of development of direct reading monitoring methods, the other in the area of in-respirator mask monitoring. Background work previously had been conducted in both areas with little positive achievement.[1,2] Both efforts reported here proceeded independently for a period of time subsequent to the earlier research until it was seen that the same analytical technique, colorimetry, was being used, at which time a combined effort was initiated.

Ammonia was selected as the initial analyte for use in the research on development of environmental monitor because it has a well defined chemistry with several potential color change reactions. It has a reasonably high workplace evaluation criteria (i.e., NIOSH recommends as 50 ppm exposure limit of 5 minutes duration),[3] which makes it relatively easy to work with in the laboratory and relatively easy to measure. Additionally, there seemed to be interest among the NIOSH field research groups and others in an analytical device for this compound. Current monitoring techniques for ammonia include NIOSH Method P&CAM 205[4] which requires that a sampler containing sulfuric acid be attached to the worker, with a 10 to 15 minute time weighted average exposure determined by subsequent laboratory analysis of the sample. NIOSH Method S347[5] replaces the liquid acid with a solid sorbent tube, but extends the sampling period to approximately two and a half hours, and still requires post-sampling laboratory analysis. Also, NIOSH Method 6701[6] measures environmental ammonia with a passive sampler for a minimum of two and a half hours followed by laboratory ion chromotrographic analysis. Thus, none of these methods allow for real-time determination of workers exposures.

The use of direct reading instrumental techniques, such as infrared analyzers, provide a real-time determination of ammonia concentration in the air, but it is seldom possible to determine the concentration of analyte in a person's breathing zone by this technique. Since this type of analyzer may require 110 VAC power and weigh up to 50 pounds (depending on the model), it is often not possible to follow a worker to various work stations, i.e., the device lacks reasonable portability. Therefore, only in those rare instances where an individual remains in one location is this a practical method for measuring personal exposure to contaminant, and even then there are significant limitations.

Mercury vapor was selected as a target substance because it has no warning properties such as odor or taste at concentrations near the recommend exposure limit, and a dosimeter/alarm would allow NIOSH respirator certification for a substance with inadequate warning properties. NIOSH has certified mercury vapor cartridges with an effective, passive end-of-service-life indicator. However, NIOSH prefers active indicators since they require less interaction with the wearer. Thus, the development of an active indicator (i.e., an alarm) is needed.

The latest sampling and analytical method for mercury published by NIOSH calls for sampling onto a solid sorbent for as little as 2.5 minutes, with samples requiring laboratory analysis by flameless atomic absorption.[7] Personal passive monitors also are availale which collect sample for subsequent end of shift analysis on site,[8] and hand held direct reading instruments capable of 15 second response times[8] also are available.

A number of patents have been issued on devices which are designed to detect change in some optical property as a result of exposure of a sensor to a gas phase material. The most similar to the device described here is U.S. Patent No. 3,114,610 to Gafford *et al.*[9] This discloses a continuous sampling gas analyzer which contains a neutral gel which changes color due to changes in pH of a dye when reacted with analytes of interest. U.S. Patent No. 3,853,477 to Block *et al.*,[10] discloses a device for measuring only ethanol in discrete samples of air, for example breath. Block's device has both an active and a reference side in the detector, however both sides use liquid reagent. While smaller in size than many laboratory instruments, its portability is nonetheless limited by its utilization of 110 VAC power. U.S. Patent No. 4,848,818 to Houston[11] only covers oxygen detection using a barium metal film. It does not measure analyte in the sense that it provides information on the amount present, rather it is an end-point indicator providing evidence that a predetermined level has been obtained. U.S. Patent No. 4,513,087 to Giuliani, *et al.*,[12] covers only oxazine perchlorate reactions in an optical waveguide. Thus it is only sensitive to ammonia, hydrazine or pyridine, and the reaction is reversible (the color of the indicator will return to normal when the concentration of ammonia is zero) and leaves no permanent record of reaction. U.S. Patent No. 4,661,320 to Ito *et al.*,[13] is for hydrogen only and specifically only for a detetector which uses a 'catalytic metal.' The principle on which this device is based precludes the possibility of using such a device to measure other analytes in air. None of these patents provide a device which can

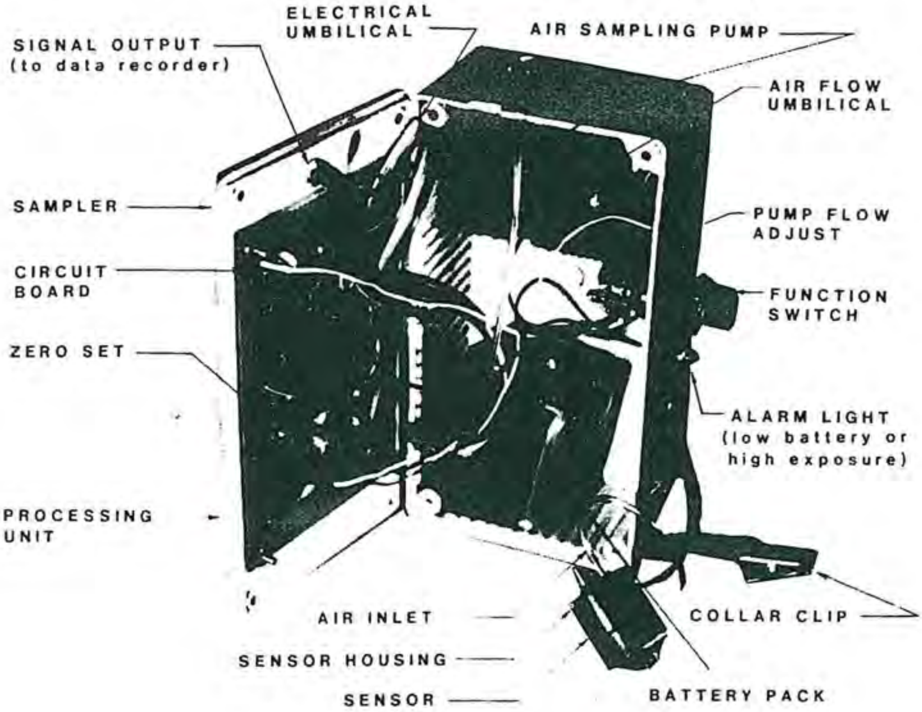


Figure 1 Thin film environmental monitor.

monitor, in real time, the amount of contaminants in the environment to which a person has been exposed.

DESCRIPTION OF DEVICE

The device developed in this work (shown in Figure 1) consists of a breathing zone sensor connected by an umbilical to a belt-mounted processing unit which provides power, signal processing, alarm and air moving capabilities. The cylindrical sensor weighs 15 g and is 2 cm in diameter and 2.5 cm long. The belt unit weighs 450 g (including batteries), and is 15 cm high, 8 cm wide and 6 cm deep. A collar clip is attached to hold the sensor in its desired location.

The principle of operation is a colorimetric reaction of contaminant with a translucent layer of reactant on a plastic substrate. The change in transmitted light intensity due to a color change reaction between the contaminant and the reactant is monitored by dual beam optics, to compensate for power fluctuations. The color change is used to quantitate the amount of analyte according to the Beer–Lambert principle. The color change occurs in the sensor, detailed in Figure 2. The sensor is made air-tight by means of an o-ring seal to ensure that the only air entering the system is through the designated air inlet. This seal, the bends of the air inlet and

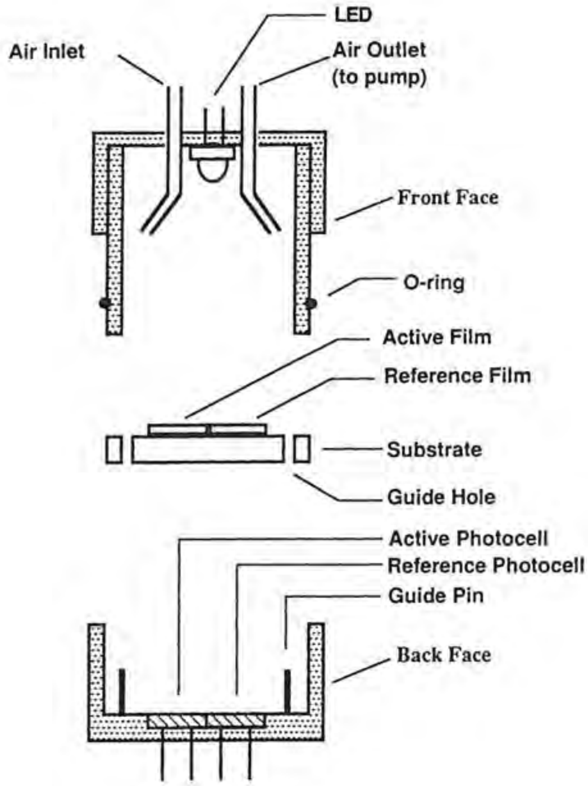


Figure 2 Sensor diagram.

the air outlet, and the matt black finish of the exterior render the sensor light-tight. An air sample is pulled into the sensor by the air sampling pump in the belt unit via tubing in the umbilical.

The sensor contains dual beam optics for reference and active photocells. Guide pins extend perpendicularly from the back face. Clear substrate on which the reference and active films are disposed is provided with two guide holes. When the substrate is inserted into the sensor, guide holes mate with guide pins to ensure accurate film alignment.

As the air sample containing the analyte of interest is drawn into the sensor, it flows past the reference and active films which are supported on a clear substrate. The sample is allowed to react with the chemical coating on the active portion of the film which undergoes a color change, the intensity of which is proportional to the amount of analyte in the air.. As the color changes and/or the color intensity of the active film increases, less light is transmitted from the light emitting diode (LED) to the active photocell, the LED being disposed on the front face and connected to the power source in the processing unit by LED electrical leads in the umbilical. This results in a voltage change across the active photocell which is transmitted to the circuit board in the processing unit by the electrical umbilical.

The reference film transmits incident light independently of concentration of analyte in the air sample. Any changes in voltage in the reference photocell will, therefore, be a result of changes in conditions common to both the active and the reference photocells (e.g., voltage changes due to battery drain or temperature effects on battery or circuits). By measuring these changes with the reference photocell, compensation is made automatically at the circuit board, thereby making the output from the device independent of temperature and voltage fluctuations. This significantly improves the accuracy and sensitivity of the monitor.

The particular coating used on the active film depends on the analyte which is to be measured by the monitor. A commercial film was found,[14] designed for monitoring aqueous ammonia in clinical laboratories, which was adapted for use in monitoring ammonia vapor in air. The major ingredient of this film was bromphenol blue, and other ingredients included pigment, binders, surfactants, buffer and humectant. For mercury monitoring, a clear plastic was coated with small particles of copper iodide. This latter film was manufactured in our laboratory. The advantages and disadvantages of both will be discussed.

The belt mounted processing unit is composed of a battery pack, an air sampling pump, and a circuit board. Mounted on the back of the processing unit is a belt clip (not shown in Figure 1) used to attach the device to the belt of the worker.

The circuit board in the processing unit is shown schematically in Figure 3. This board consists of three sections, each described below.

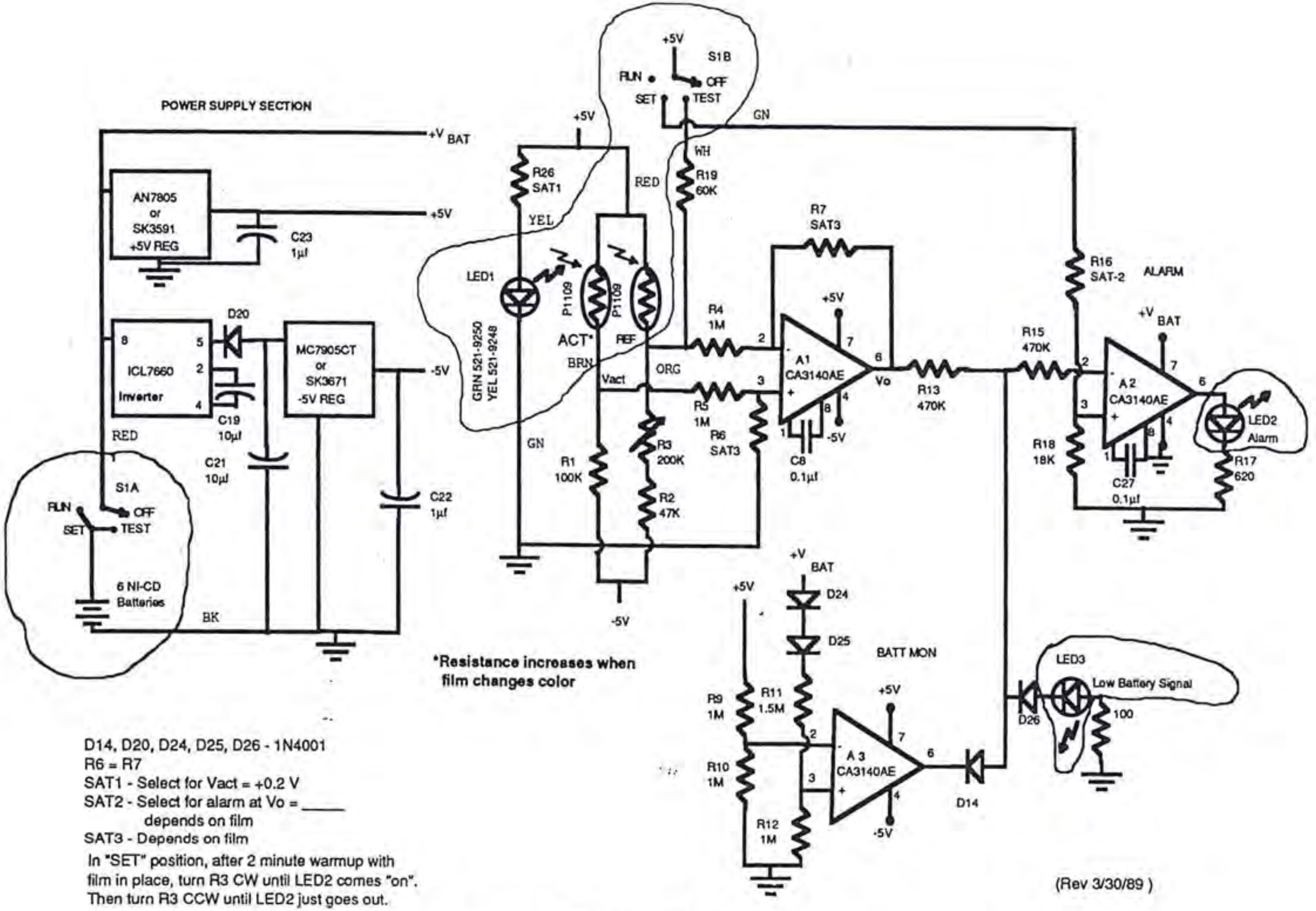
The power supply section takes the voltage from the six nickel-cadmium batteries and provides unregulated battery voltage and regulated voltages of $+5$ and -5 volts to power the rest of the electronics.

The battery test section constantly monitors the battery voltage. If the battery voltage drops below $+7$ volts, LED 2 and LED 3 will light.

The main section electronics includes LED 1, the active (ACT) and reference (REF) photocells, amplifiers A1 and A2, the switch and the associated resistors, diodes and capacitors. The operation of the system for each of the three active positions of the function switch are as follows:

Position 1. FUNCTION CHECK—This operation determines that A1, A2, and LED 2 are working. When the switch is in the 'Function check' mode, a voltage which is higher than normal is placed on inverting input of op-amp "A1" via R19. This forces the output of A1 to go negative, which puts a negative voltage on the inverting input of A2. Since the non-inverting input of A2 has zero volts on it, the output of A2 will go to $+V_{\mathrm{BAT}}$ and LED 2 will turn on. This is a crude test for proper operation of the electronics which may be performed anytime.

Position 2. SET—This sets the electronics to correct for slight variations in films. For the purpose of explaining circuit operation: the switch is in the SET position; R16 (SAT-2) is 27 Kohms; R6 and R7 (SAT-3) are 1 Mohm. Thus, the voltage on the non-inverting input of A2 is $+2.0$ volts and the gain of A1 is one. With the switch in the SET mode, the film is inserted and R3 is adjusted until LED 2 (the alarm) just goes out. This happens when the voltage on the inverting input of A2 is $+2.0$ volts (i.e., the inverting input equals the non-inverting input).,



*Resistance increases when film changes color

D14, D20, D24, D25, D26 - 1N4001
R6 = R7
SAT1 - Select for Vact = +0.2 V
SAT2 - Select for alarm at Vo = _____ depends on film
SAT3 - Depends on film
In "SET" position, after 2 minute warmup with film in place, turn R3 CW until LED2 comes "on". Then turn R3 CCW until LED2 just goes out.

(Rev 3/30/89)

Figure 3 Electronic schematic.

The switch S1 is then turned to the RUN mode, removing the +2.0 volts source from the non-inverting input of A2 and replacing it with 0.0 volts. The +2.0 volts input is still on the inverting input. The instrument is now ready for operation. LED 2 will not come on again until the voltage on the inverting input drops below 0.0 volts. This can occur via a signal from A1 or from the Battery Monitor circuit (A3). As mentioned above, the output voltage of A1 is now approximately +2.0 volts. The output voltage of A3 is positive but is blocked (by diode D14) from affecting A2.

Position 3. RUN—During the SET operation, the output of A1 was set to approximately +2.0 volts. Since the gain of A1 is one, this happened when the voltage differential between junction R3/R4 and R1/R5 was about −2.0 volts.

$$V_{R3/R4} - V_{R1/R5} = -2.0 \text{ volts}$$

Another way of looking at this is to say the voltage differential between the ACTIVE and REFERENCE photocells is 2.0 volts.

$$V_{REF} - V_{ACT} = +2.0 \text{ volts}$$

This is the condition at the start of the RUN operation.

As the vapor of interest reacts with the coating on the active side of the sample film, the quantity of light which reaches to the ACTIVE photocell decreases. This causes the resistance of the ACTIVE photocell to increase. The reference side of the film is inert to the vapor and there is no change in light intensity, and the resistance of the REFERENCE photocell remains constant. Thus, the voltage at junction R5/R1 drops and the voltage at junction R4/R3 remains constant. This causes the output of A1 to decrease from +2.0 volts. When the resistance of the active photocell increases further, the output voltage decreases further. When the output voltage of A1 drops below 0.0 volts, the output of A2 goes to $+V_{BAT}$, and the alarm LED 2 is activated.

An operational cycle would consist of inserting a set of reference and active films into the sensor by inserting the guide pins into guide holes to properly align the film in the sensor, going through the steps outlined in the previous paragraphs, and allowing the unit to sample in the "RUN" position for up to one work shift, or until the alarm light comes on. At the end of a run, the voltage output would be read from the signal output jack, and compared with a calibration plot prepared previously using an identical film exposed to a known quantity of analyte via the sampler. Thus, the degree of exposure of the worker during each work period could easily be determined. Alternatively, a continuous data logging device could also be worn on the worker's belt to continuously record voltage change (i.e., concentration change) during the run providing a time history of the exposure.

During instrument operation, the alarm light (LED 2, Figure 3) would be activated if the battery dropped below a predetermined voltage, or if a high exposure was indicated by the signal from the sensor. Either of these conditions would be an indication to the wearer to leave the work area. Although the alarm light is shown in Figure 1 as consisting of one LED display which lights when either the battery is low or the exposure level to the contaminant is too high, it would be possible to have two separate LED displays. In this way, the worker would know immediately whether he has been exposed to high levels of contaminant or whether he simply needs new batteries. Figure 3 includes two LEDs used for display (LEDs 2 and 3). Further, one or both of the alarms could have an audio alarm in addition to or in place of the LED display.

EXPERIMENTAL

Five prototype devices were constructed for testing by exposure to analytes generated by dynamic and static systems. Most testing to date has been with ammonia and mercury in clean air. However, some study of potential interferences has also been made.

Protocol

The purposes of these tests were: (1) to establish the stability of the monitor with time when exposed to clean air, and (2) to determine the response of the sensor on exposure to contaminant vapor in both steady and changing concentrations. Since this device was intended as a workplace environmental monitor, 35 ppm ammonia was selected as an appropriate target concentration for testing that compound. This is between the NIOSH Recommended Exposure Limit (REL) of 50 ppm (ceiling) and the 25 ppm Threshold Limit Value (TLV) established by the American Conference of Governmental Industrial Hygienists for an eight hour time weighted average.[15] For mercury, the minimum test concentration (other than zero) was set at $0.05 \, mg/m^3$ since this is both the NIOSH REL and one-half the Occupational Safety and Health Administration (OSHA) Permissible Exposure Limit (PEL) for mercury.[16, 17] The maximum test concentration was $1.0 \, mg/m^3$ because this is ten times the OSHA Acceptable Ceiling Concentration, and the maximum level allowable for a half-mask respirator when following the NIOSH Respirator Decision Logic.[18]

Ammonia was generated using a permeation tube system as described by Woodfin[19] with concentration determined from tube weight loss and air flow. Mercury test atmospheres were generated with a static system where a known quantity of clean air was metered into an inert sampling bag and a known quantity of saturated mercury vapor or a measured quantity of interfering compound was added. Sensors were exposed to identical test environments by connecting them to a common sampling manifold.

The instrument outputs were digitized for direct input into an Apple MacIntosh personal computer, or readings taken and entered manually. To facilitate comparison among tests of varying analyte concentrations, sampler flow rate and duration, the total dose was calculated (as the product of concentration times flow rate times duration) for comparison with instrument response.

Response parameters which were investigated include:

1) Zero Drift—This was the instrument's response to long term (four hours) exposure to clean air, and is a measure of their stability under these conditions.
2) Range—This provides a measure of both the lowest and also highest dose quantifiable by these units.
3) Interunit reproducibility and linearity—This was measured by exposing the prototypes to the same test environment and plotting response of the photocell (in volts) *vs* dose of contaminant to which the active film was exposed.
4) Intraunit reproducibility and linearity—This was measured by multiple exposures of each prototype to contaminant vapor and plotting response *vs* dose for each unit.
5) Effects of variation in analyte concentration—Instrument response was measured with time as the concentration of contaminant to which the sensors were exposed was varied.
6) Sensor efficiency—For ammonia, two sensors (Units A and C) were placed in series, making it possible to monitor the ammonia concentration passing unreacted through the first (Unit C) by means of the second (Unit A). For mercury, a calibrated Bacharach MV-2 ultraviolet mercury analyzer was used to monitor the concentration of mercury passing un-reacted through the sensor.

In addition to the tests above, a preliminary study of potential interferences was done. Samples of active ammonia film were placed in contact with saturated vapor or liquid of several suspected interferences for less than two minutes and visual observation of color change was noted. Major trace constituents of human breath as identified by Krotoszynski[20] were added to the test atmosphere for the mercury film.

Ammonia Test Results

Initial tests indicated that the monitors were capable of detecting sub-REL levels of ammonia in an eight hour sample at flow rates of 1–2 cc per minute (the lowest steady flow rate attainable using the pump installed in the prototype devices). At a flow rate of 1 cc/minute and a concentration of 35 ppm, no further color change would occur after a few minutes, presumably because all reagent on the film had reacted. To enable the completion of long term tests, it was necessary to either reduce the air flow rate, lower the analyte concentration, increase the reagent loading on the film, or perform some combination of these changes. It was impractical to change film loading given the available resources and, therefore, testing of the ammonia configuration was conducted at flow rates ranging from 0.16 to 0.70 cc/minute, and at analayte concentrations of 35 ppm or below. Air flow through each sensor was regulated by placing a limiting orifice in line between the sensor and a vacuum source. Air flow rates were measured by a moving film flow meter.

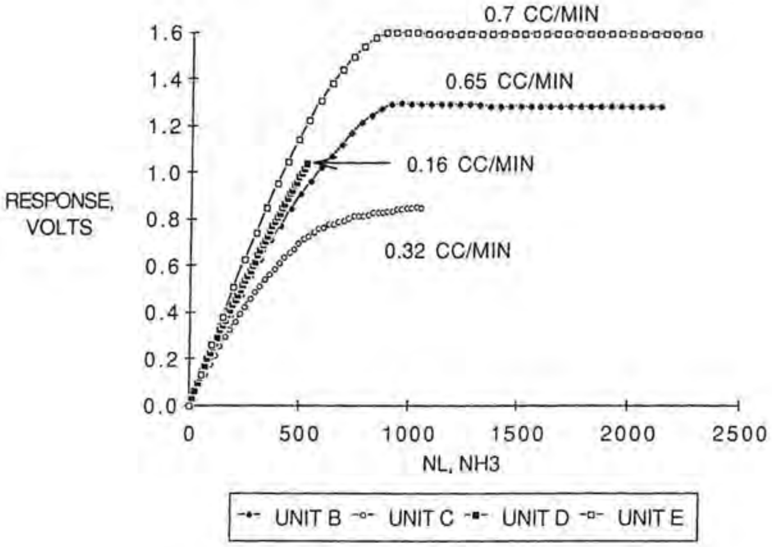


Figure 4 Dose *vs* response at 35 ppm.

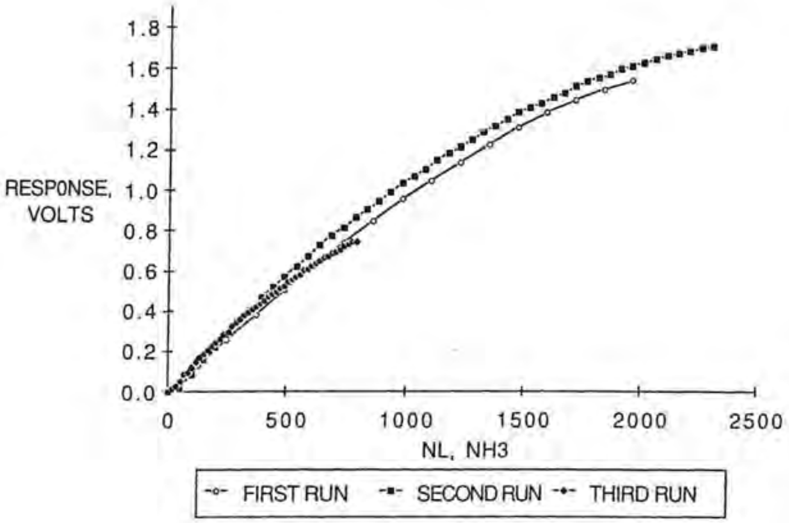


Figure 5 Dose *vs* response for multiple runs.

Zero drift was determined by exposing the five prototype devices to clean air for four hours. All five had a slight positive response over the run, ranging from 0.01 to 0.07 volts. This zero drift is considered acceptable relative to the 1 to 2 volt responses shown in Figures 4, 5, and 6.

Figure 4 shows the results of four devices subjected to a constant ammonia concentration of 35 ppm for one and a half hours. (Sensor "A" was configured to measure the efficiency of sensor "C", as described in item six of the protocol, and

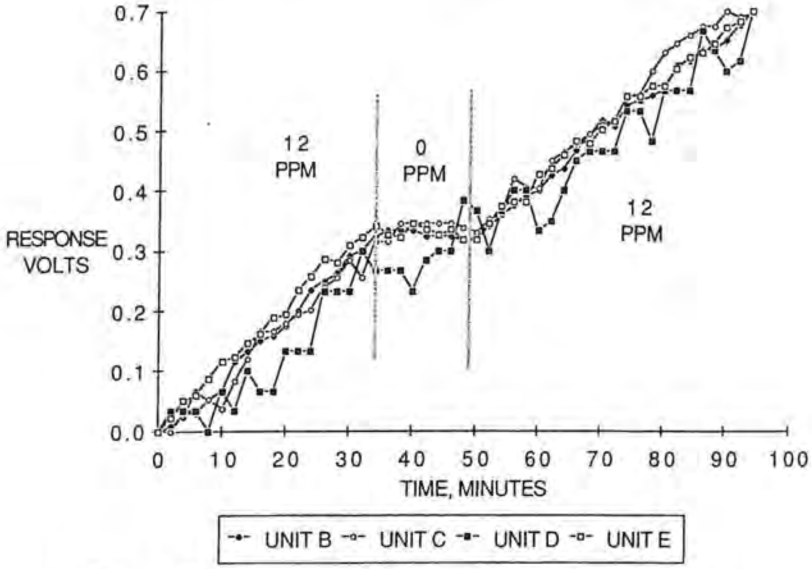


Figure 6 Dose *vs* response (normalized) at varying concentrations.

therefore is not included in this data.) The flow rate through each sensor is indicated. The horizontal axis of this figure has been transformed from units of time to units of ammonia volume or dose (nl) by multiplying time (minutes) by concentration (ppm) and flow rate (ml/min). The sensor with the lowest flow rate did not reach saturation during the test. The magnitude of the response at saturation is related to both chemical and electrical parameters of the sensor. The electronic saturation voltage is determined by the bias setting of the individual sensor and can be extended somewhat. Chemical saturation (when no further color changes is possible) results when all reagent on the active film has been utilized, and is therefore, a function of dose and reagent loading. Extending the chemical saturation point by increasing reagent loading has not been pursued.

The interunit reproducability and linearity is observable in the pre-saturation portions of the curves in Figure 4. Linear regression of these data gives values for slope from 1.63×10^{-3} to 1.94×10^{-3} volts per nl, and values for intercept from 0.02 to 0.07 volts for all units, with all correlation coefficients greater than 0.98.

The reproducibility within a unit is exemplified in Figure 5. In three separate runs, Unit E was subjected to ammonia concentrations of 35, 35, and 12 ppm for plots identified as first, second and third runs, respectively. Since the sensor's flow rate was the same for all three tests, the total dose to which it was exposed was less at the lower concentration. Linear regression lines for these runs produced slopes from 0.75×10^{-3} to 0.90×10^{-3} volts per nl, and for intercept from 0.04 to 0.19 volts, with all correlation coefficients greater than 0.98.

The ability of the sensors to respond differently to changing concentrations of analyte is shown in Figure 6. In this test, the four prototype devices were subjected first to 12 ppm of ammonia for approximately 34 minutes, followed by 16 minutes in clean air, then the balance of the 90 minute run at 12 ppm. Results of this run

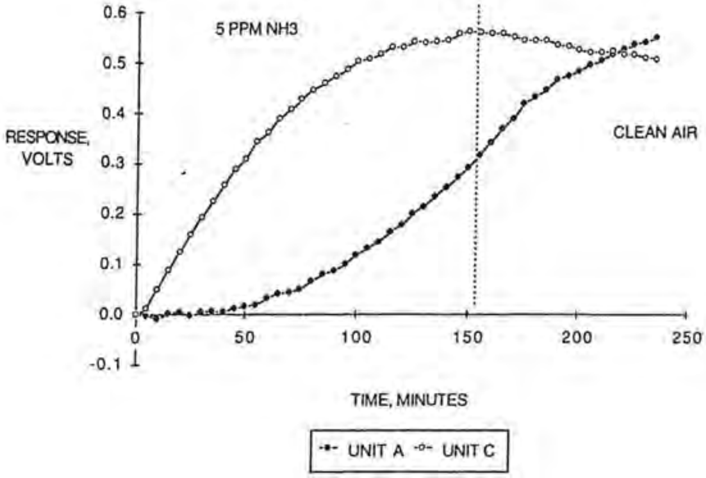


Figure 7 Time *vs* response for sensors in series.

have been normalized to a common value in order to compare the four units. This figure again shows the unformity of response of the four devices.

Figure 7 illustrates the efficiency of the reaction by plotting the two units which were connected in series. The contaminant air stream containing 5 ppm of ammonia was pulled first through Unit C, then through Unit A, for 155 minutes. This was followed by 85 minutes of clean air through the units. Since the units were in series, the flow rate through both was the 1.2 cc/minute. Figure 7 indicates that at the beginning of the experimental period, most of the ammonia being drawn into the first sensor (Unit C) was being consumed since little was being measured by the second (Unit A). As the exposure continues, and available reaction sites in Unit C decrease, the efficiency of this unit decreases, and the film in Unit A begins to react with the ammonia now in the air. By the time the system is switched to clean air (indicated by vertical dashed line), Unit C has reached saturation. A continued increase in the response of Unit A, accompanied by a slight decrease in voltage output of Unit C, indicates the possibility that the clean air actually removes some contaminant from the first sensor and this was carried to the second sensor where it reacted. The reversibility or stability of the color change were not quantitated, and even though the reversibility appeared from this data to be minimal, this would be necessary if estimates of time weighted average exposure were to be made.

Qualitative testing for interfering compounds was done by exposing reagent film to saturated vapor of various substances and visually estimating the degree of response compared with the exposure of the film to 10% aqueous ammonia. Ethylamine, a primary aliphatic amine, produced a very strong positive response. 1,3-dimethylbutylamine, diethanolamine, and dimethylethylamine (primary, secondary, and tertiary aliphatic amines respectively) produced mild positive responses. Diisopropylethylamine, a tertiary aliphatic amine, showed no response. Immersion of reagent film in aqueous sodium hydroxide solution produced no response.

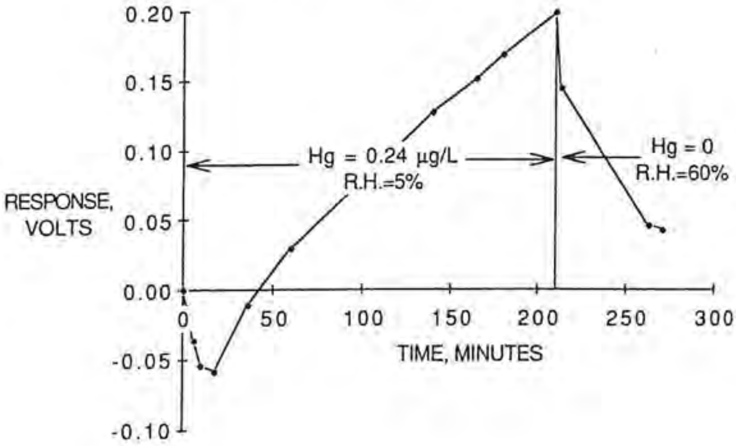


Figure 8 Film response to mercury and humidity.

Color produced on the reagent film by exposure to aqueous ammonia was not reduced on subsequent exposure to aqueous hydrogen chloride.

Mercury Test Results

As mentioned above, the film used to quantitate mercury vapor was prepared in our laboratory by deposition of copper iodide on a transparent substrate. This film produced a color change from white or gray to orange on reaction with mercury, allowing its use with the same yellow LED/detectors used for the ammonia film. All films tested were cut from the same sheet. The coating on this sheet visually appeared uniform in the area used for these tests. The actual particle size distribution of CuI on these films was not investigated.

Initial tests of this copper iodide film showed several factors which affected the set-up and protocol: (1) Humidity must be kept constant during the test; (2) Magnesium perchlorate, used to control humidity, can act as a small mercury reservoir; (3) Films may need to be conditioned before use; (4) Sensors can be inefficient at removing mercury; and (5) The color change is somewhat reversible.

Figure 8 shows the effect of humidity on the film. During this test, the sensor was initially exposed to mercury vapor in dry air. At time = 210 minutes, the sensor was exposed to room air at approximately 60% relative humidity. Because of the negative interference due to humidity, subsequent tests were run with the magnesium perchlorate bottle in line to keep humidity constant at near 0% R.H. However, magnesium perchlorate traps at least temporarily some of the mercury passing throug the chamber. Therefore, a high flow through the system was used to minimize this effect.

Figure 9 (and also 8) shows that the films should get some exposure to mercury before use. These films had no previous exposure to mercury, but they had been dried overnight. For the first 20 minutes or 1–2 microgram of mercury (Figures 8 or 9 respectively) of the test, the film became more transparent. Later it became

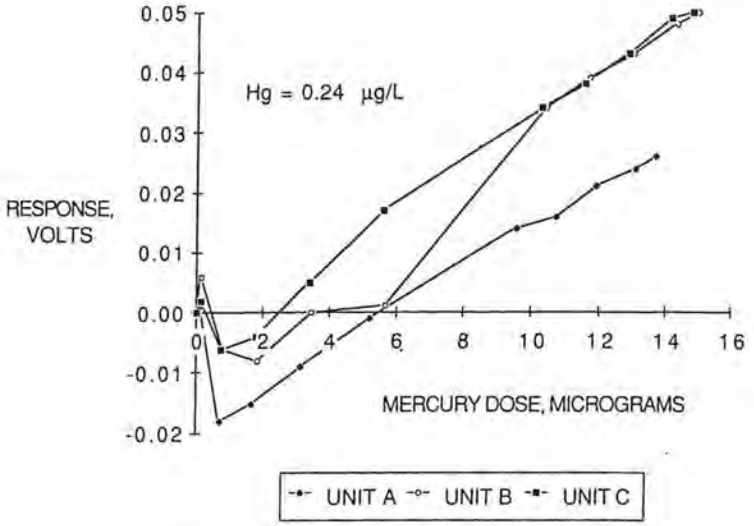


Figure 9 Film response during conditioning.

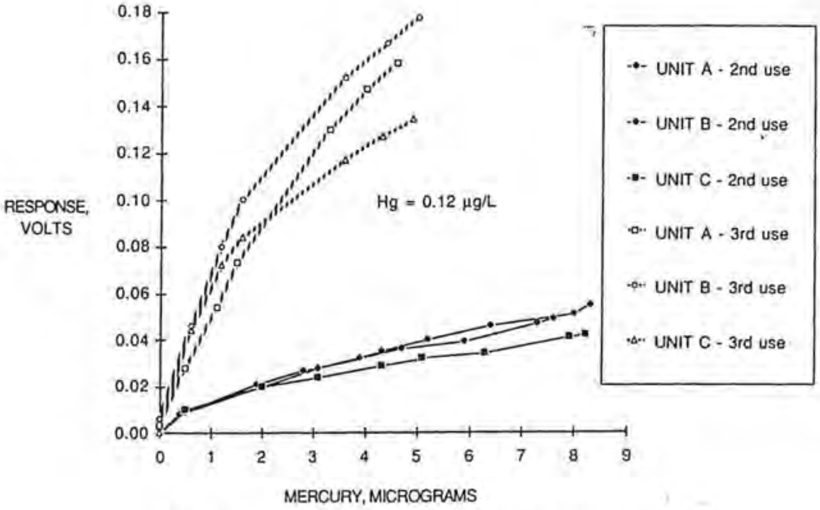


Figure 10 Film response on second and third use.

more opaque, so during th first 40 minutes or 2–4 micrograms of mercury exposure the net voltage change is zero. Exposing the films to mercury for a period of time before actual use (conditioning) eliminated this lost sampling time.

Zero drift was determined for both conditioned and un-conditioned films over a four hour period. Both produced similar results, with drifts from 0.007 to almost 0.02 volts. Most of the zero drift occurs during the first 30 minutes of operation. This may be due to electronic drift, not change in the film transparency. Although the sensitivity of a used film appears to be much better than that of a new film,

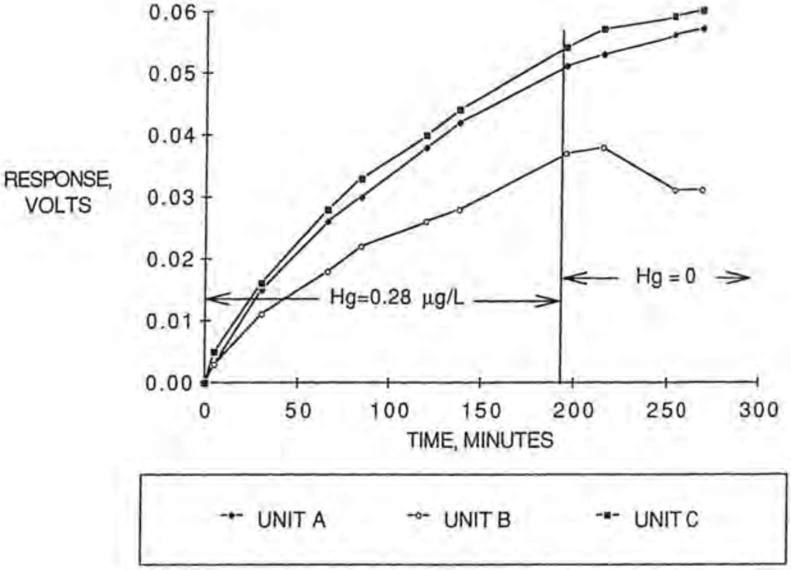


Figure 11 Film reponse, used once.

the zero drift of a used film which has been in the drier in room light for several days was about the same as a new film.

It appeared that film handling also could increase the sensitivity to mercury. After a test, when the film was removed from the sensor and stored in a drying chamber in room light, the film color faded. When the film was reused, it was more sensitive to mercury. Figure 10 shows the results from film "b" when exposed at about the same mercury concentration on two different days. The solid curves show the response when the film was used for the second time. After this exposure, it was stored for several days in the drier in room light. The dashed curves show the result when it was used again. The sensitivity of the film increased by a factor of 6 during this exposure. This increase in sensitivity was apparently due to lighting conditions during film storage.

Color change continues after exposure is discontinued. Figure 11 shows that the chemical reaction causing color change can continue after the mercury bag was removed from the system. For this test the mercury concentration was changed to zero at 190 minutes. At 215 minutes, the concentration at the outlet of the sensors was checked and verified as being zero. However, color change continued (at a reduced rate) for two of the films. It is not known if this increase is due to mercury escaping from the drying chamber, electronic noise, or from another source.

At a flow rate of 250 cc/min (used for all mercury tests), the sensors were about 7% efficient in their absorption of mercury as it passed by the CuI film. This was determined by comparing the concentrations at the outlet of the bag to that at the outlet of the sensor using the ultraviolet mercury analyzer mentioned earlier. Ideally, a different sensor configuration should be found that would react 100% of the mercury. This should increase the signal output by about 15 times. The effects of flow rate on sensor efficiency in the mercury system were not determined.

Tests using mercury plus a potential interference showed responses similar to those obtained when only mercury was used in the test. Potential interferences and their concentrations used with mercury for the tests were: carbon monoxide (91 ppm); ethanol (1000 ppm) plus acetone (5 ppm); sulfur dioxide (10.5 ppm); and a typical human breath with water vapor and carbon dioxide removed. There appeared to be no dramatic positive or negative interferences at the concentrations tested.

SUMMARY AND CONCLUSIONS

A new device was designed for monitoring environmental contaminants using the color change produced when the contaminant reacts with a thin film of chemical reagent coated on a translucent substrate. This technology has potential for application to area monitoring, personal breathing zone monitoring, and monitoring inside respirator masks.

Five prototype thin film environmental monitors were constructed and evaluated to establish stability with time when exposed to clean air, and to determine response of their sensors on exposure to contaminant. Using a commercially procured film designed to monitor aqueous ammonia concentration, testing indicated:

—Minimal zero drift. Response in the range of 0.01 to 0.07 V was recorded during exposure to clean air over a four hour period, compared to a response of 1 V or greater for exposure to ammonia concentration equal to the recommended occupational exposure level.

—The response of these devices in the lab is predictable and reproducible, both from unit to unit as well as from run to run. Second order polynomial regression fits repeatedly produced correlation coefficients of 0.98 or greater for comparisons of instrument response as a function of dose for both interunit and intraunit measurements.

Additionally, fluctuations in contaminant concentration produced a corresponding fluctuation in instrument response, and at air flow rates on the order of 1 cc/minute essentially all of the ammonia was consumed by reaction with the reagent on the film. Qualitative tests indicate the potential of interference from low molecular weight aliphatic amines, but not from other suspected substances.

Using a self-manufactured film designed to monitor mercury vapor concentration, testing indicated:

—Zero drift ranged from 0.007 to 0.019 V for a four hour test. This drift may or may not be significant, depending on the output of the sensor when exposed to mercury.

—The output of the sensors when exposed to mercury is affected by several variables, including humidity and pre-conditioning with mercury and light. The response of these devices is somewhat predictable, although less so than using the ammonia film.

There appears to be some reproducibility among units for individual runs, but little reproducability between runs, probably due to conditioning of the reagent films. Additionally, response does not closely track fluctuations in concentration, probably due to the small fraction (approximately 7%) of the contaminant being consumed by the reaction at an air flow rate of 250 cc/minute, as well as the somewhat reversible nature of the color change reaction itself. While water vapor was found to interfere with this reaction, no dramatic effects were seen on exposure to carbon monoxide, sulfur dioxide, ethanol and acetone, or typical human breath (with water removed).

Taken together, the data from both the ammonia and mercury testing indicate that the concept of a thin film environmental monitor is viable, that is, with films of proper characteristics the analyte of interest can be measured accurately and precisely at levels near appropriate environmental criteria, and this monitoring data can be output in a convenient and usable format. Further, the electronic and mechanical portions of the device seem to be acceptable in some of the configurations discussed. The most important component of the monitor, the coated film, is the most difficult to produce given the resources available within the working group whose goal was to demonstrate the feasibility of the idea and not to develop a marketable device.

Recommendations for future research would center around the development of coating ability because there are a substantial number of colorimetric reactions available which have been well documented for quantitating various toxic environmental contaminants, and the work presented in this paper indicates that if the chemical reagents required for such reactions are properly coated onto a suitable substrate the thin film environmental monitor is capable of reliably monitoring the analyte of interest. Quantitative evaluation of interferences including water vapor should be made, as well as evaluation of reversibility and stability of color changes.

References

1. Arthur D. Little, Inc., Development of a Prototype Service Life Indicator for Organic Vapor Respirators, Final Report Contract No. 210-76-0613 (April 1976).
2. L. D. Nichols, A. S. Obermayer and M. B. Allen, Method for Monitoring Worker Exposure to Toxic Gases and Vapors in Respirator Masks; Final Report Contract No. 210-80-0075 (September 1982).
3. U.S. Department of Health, Education and Welfare, "Criterion for Recommended Standard—Occupational Exposure to Ammonia," Publication No. (NIOSH) 74–136 (1974).
4. U.S. Department of Health and Human Services, *Method P&CAM 205, NIOSH Manual of Analytical Methods, 2nd Ed., Vol. 1,* Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. (1977).
5. U.S. Department of Health and Human Services, *Method S347, NIOSH Manual of Analytical Methods, 2nd Ed., Vol. 5,* Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. (1977).

6. U.S. Department of Health and Human Services, *Method 6701, NIOSH Manual of Analytical Methods, 3rd Ed.*, Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. (May, 1983).
7. U.S. Department of Health and Human Services, *Method 6000, NIOSH Manual of Analytical Methods, 3rd Ed.*, Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. (Feb., 1984).
8. "The Jerome 431 Gold Film Mercury Vapor Analyzer," Operating Manual, Arizona Instruments Corp., Jerome Division (undated).
9. R.D. Gafford and P. Rosenbaum, Continuous Sampling Gas Analyzer. U.S. Patent No. 3,114,610 (1963).
10. L. A. Block, R. N. DeWilde and G. A. Spampanato, Breath Analyzer. U.S. Patent No. 3,853,477 (1974).
11. J. M. Houston, Apparatus and Method for Detecting the Loss of Vacuum. U.S. Patent No. 4,484,818 (1984).
12. J. F. Giuliani and H. Wohltjen, Reversible Optical Waveguide Vapor Sensor. U.S. Patent No. 4,513,087 (1985).
13. K. Ito, T. Kubo and A. Yamauchi, Gas Sensor. U.S. Patent No. 4,661,320 (1987).
14. "Kodak Ektachem Clinical Chenmistry Products for *in vitro* Diagnostic Use—Test Methodologies," Eastman Kodak Co., Rochester, NY (March 1985).
15. Threshold Limit Values for Chemical Substances and Physical Agents, American Conference of Governmental Industrial Hygienists, Cincinatti, OH. (1989).
16. U.S. Department of Health, Education and Welfare, "Criteria for a Recommended Standard—Occupational Exposure to Mercury," Publication No. HSM 73-11024 (1973).
17. U.S. Department of Labor—OSHA, General Industry Standards; 29CFR1910.1000, July 1, 1980.
18. Joint NIOSH/OSHA Standards Completion Project Program—Respirator Decision Logic: Appendix I, Section B (August 18, 1975).
19. W. J. Woodfin, Gas and Vapor Generation Systems for Laboratories, U.S. Department of Health and Human Services, NIOSH Publication No. 84–113, (August 1984).
20. B. Krotoszynski, G. Gabriel and H. O'Neill, *J. Chromatographic Sci.* **15**, 239 (July, 1977).