CONTINUOUS HYDROGEN SULFIDE MONITORING SYSTEMS

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INTRODUCTION

Commonly known as sour gas, hydrogen sulfide (H_2S) is a highly toxic chemical agent found in petroleum drilling, production and refining operations. As secondary and tertiary recovery efforts are undertaken on older reservoirs, H_2S is being found where previously it was not recorded. The gas is present in many crudes and is produced in common refinery processes such as cracking and desulfurization.

Hydrogen sulfide is formed primarily by decomposition of organic matter containing sulfur. The gas occurs naturally in many geologic formations throughout the United States and is both toxic and corrosive. This colorless gas has the characteristic odor of rotten eggs and can be readily detected by the human nose. One can usually smell concentrations of less than 10 parts per million (ppm), with concentrations of 700 to 1000 ppm being fatal, even if exposure is brief. It is important to realize that continuous exposure to low concentrations of H_2S (approximately 50 ppm) deaden the olfactory nerves, causing the sense of smell to become an ineffective detection tool.

A variety of both federal and state regulations apply to the petroleum industry in areas known or suspected to contain sour gas. Federal regulations basically are designed to protect the employee and are handled through such agencies as the Occupational Safety and Health Administration (OSHA), the National Institute of Occupational Safety and Health (NIOSH), and the U.S. Geological Survey (USGS). Most state regulations are designed to protect the general public and require certain precautions be followed to minimize the chance of accidental public exposure to H_2S. Probably the best known state regulation is Texas Railroad Commission Rule 36, whose degree of operator compliance depends on the radius of exposure based on the calculated concentration of H_2S and the rate at which it is expected to flow from a well.

Due to the occurrence and toxicity of hydrogen sulfide and the array of regulations concerning sour gas areas, a method of monitoring H_2S becomes essential. Factors to consider in selecting a monitoring system include reliability and accuracy, ease of operation and maintenance, response time and expected lifespan of the system components. Another important concern of any H_2S detector is proper placement of the sensor units, with special care taken to ensure all installation and location guidelines are clearly understood.

TYPES OF DETECTORS

One of the early methods used to detect hydrogen sulfide is based on using paper or tape which has been chemically coated with lead acetate. When H_2S contacts the paper in these badge-type detectors, a reaction occurs to form lead sulfide. This causes the paper to change color from white to various shades of brown. The degree of color change is dependent on the H_2S concentration, which is estimated by comparing the badge to a color chart.

Another widely used tool for hydrogen sulfide detection consists of a calibrated glass tube filled with chemically impregnated granules. Known as the Draeger detector, this unit operates by drawing a gas sample into the tube and then observing the level of a color change on the tube's scale. This unit is simple to operate and capable of rather accurate readings, although the precision of the reading depends on the training and practice of personnel using the unit.

Probably the most widespread monitoring method in recent years involves the use of metal oxide semiconductor (MOS) solid state sensors. This type of sensor has been incorporated into portable, belt-type detectors as well as continuous, fixed location monitoring systems (also known as area monitors). Portable monitors operate on a rechargeable or replaceable battery and typically sound an internal audible alarm when H_2S is detected. In both portable and area monitors the sensor operates via gas diffusion and adsorption. When H_2S adsorbs into the sensor's surface, a decrease in the resistance of the semiconductor material occurs which is proportional to the gas concentration.

Lead acetate paper detectors and chemical tubes are commonly used as a program of personal monitoring to determine the ceiling exposures of employees occupationally exposed to H_2S. Portable battery operated monitors are also frequently applied for the purpose of providing low ppm time weighted averages over the work shift period. However, there is often an equal or even greater concern with being able to both monitor H_2S and provide an early warning of potentially fatal sour gas conditions.

For this purpose, continuous area monitors are used as these systems provide an alarm when dangerous gas levels are detected, regardless of whether or not workers are present. If personnel are present, both visual and audible alarms can be activated almost immediately, followed by emergency shut down and evacuation procedures when appropriate. For unmanned areas, phone lines can be dialed and equipment can be shut down, thereby minimizing both the time to respond to the situation and the potential hazard from the leak. A discussion of area monitors follows and includes the topics of sensor technology, installation guidelines and monitoring system maintenance.

SENSOR TECHNOLOGY

As previously mentioned, the solid state H_2S sensor typically operates by utilizing a metal oxide semiconductor film whose electrical resistance changes proportionally to varying concentrations of H_2S. Sensor construction is usually in the form of a non-conductive ceramic substrate material fitted with two conductive electrodes. The MOS film is applied between the electrodes and the sensor substrate is heated to an appropriate operating temperature (Fig. 1).

Under ambient H_2S-free conditions oxygen molecules adhere to the MOS film and "tie-up" electrons, inhibiting the electrical flow and thus creating a high film resistance. The value of this resistance is somewhere in the meg-ohm range, which allows the solid state sensor to have excellent zero stability. In the presence of H_2S oxygen competes for space on the film as H_2S molecules also have a great affinity for the metal oxide semiconductor. The nature of the H_2S molecule is such that it is incapable of tying up electrons in the MOS film. Therefore when oxygen becomes displaced by hydrogen sulfide, electrons will begin to flow between the two electrodes. As the H_2S concentration increases, more molecules adsorb onto the film surface, displacing oxygen and allowing a greater number of electrons to flow.

This increase in conductance is associated with a decrease in the film resistance, such that in the presence of ppm levels of H_2S the film resistance drops into the kilo-ohm range (Fig. 2). The change in resistance of the film is proportional to the concentration of H_2S in a logarithmic fashion. This logarithmic signal is then linearized by a conversion circuit to allow for linear meter display of H_2S concentration.

One of the major factors determining solid state sensor performance is slection of the semiconductor material. Generally the materials used for H_2S sensors are transition metal oxides, although tin oxide and indium oxide are also used. The semiconductor is usually doped with trace amounts of materials such as zinc, arsenic, aluminum, gallium or indium. The primary purpose of the dopant is to stabilize the MOS film at its operating temperature, although specificity and response time can also be affected by dopant selection. For example, tungsten oxide has excellent specificity but can lose sensitivity and develop a slower response unless regularly exposed to H_2S. Dopants can help offset these negative characteristics but at the expense of sacrificing specificity.

Inherent to solid state MOS sensors is the requirement for the sensor substrate to be heated to an appropriate elevated temperature. Film temperature can affect sensor performance in several ways. At optimum operating temperature the film's affinity for H_2S is enhanced, and the exchange of H_2S and oxygen reaches equilibrium. Both the speed of response and repeatability are maximized with correct sensor temperature. Sensors operated below optimum temperature tend to be very slow in response, whereas too much heat can cause inaccurate readings and poor repeatability.

To ensure maximum sensor performance, it is necessary to determine optimal operating temperature individually and then be able to maintain this value over a very broad range of ambient conditions. Although most solid state H_2S sensors have similar operating temperatures, individual adjustment is highly desirable as several degrees in either direction will adversely affect performance. Each sensor should be burned-in thoroughly and tested to various ppm levels of hydrogen sulfide so that its unique signal (i.e. response curve) can be optimized. The correct operating temperature should be factory set and require no further adjustment once the sensor has left the manufacturer.

Maintenance of this optimal temperature is another critical design consideration. Simply heating the sensor is insufficient as cold ambient conditions will cause heat loss to the environment. The core of any gas monitoring system is the sensor, and the sensor must be reliable over a broad range of adverse ambient conditions, typically -40° to +140°F. A proven and reliable method of maintaining the operating temperature is to tie a thermistor feedback circuit to the sensor heater. As the temperature of the sensor heater changes, so does the resistance of the thermistor. The thermistor resistance is closely tracked by the feedback circuit, which will increase or decrease the current to the heater accordingly. A properly designed feedback circuit has an on/off duty cycle capable of rapid variation which allows for maintenance of film temperature with $\pm$ 2°C. Thus, a sudden change in ambient temperature is compensated for within seconds.

Today's gas monitoring technology allows solid state H_2S sensors to have excellent zero stability and a high degree of specificity. These sensors are applicable over a very wide range of ambient conditions and can typically detect dangerous sour gas concentrations in a matter of seconds. By following proper installation and maintenance guidelines, a solid state sensor can provide years of reliable, trouble-free operation.

INSTALLATION AND LOCATION GUIDELINES

Many factors influence the effectiveness of area monitoring systems, although the most important are sensor location and system reliability. If a gas monitoring system is to provide the protection for which it was purchased, it is imperative that a sufficient number of properly placed sensors be installed. There are no hard and fast rules governing sensor quantity and placement, and invariably it is a matter of judgment based on each particular application. For example, in refinery operations monitor selection and location factors include process areas where equipment failures would result in H_2S emission, and areas requiring operator action during process upsets. Also to be considered are off battery limit areas where plant personnel would normally be present such as control rooms, offices, cafeterias and main roads.

In offshore drilling operations federal regulations state that monitoring equipment shall be capable of sensing a minimum of 5 ppm H_2S in air with sensing points located at the bellnipple, shale shaker, mud pits, driller's stand, living quarters and any other areas where H_2S might accumulate in hazardous quantities. In pipeline and well site operations sensors should be placed at a distance from the installation such that a severe gas release is readily detected, especially when the installation is adjacent to populated areas.

When designing an H_2S monitoring system there are two basic approaches to sensor placement. The first, known as point monitoring, is to locate sensors in the immediate vicinity where a leak is most likely to occur, such as valves, flanges, seals, etc. The second approach, known as perimeter monitoring, is to space sensors out around the edge of the sour gas area and detect the H_2S cloud as it diffuses through the atmosphere (Figs. 3 through 5).

Perimeter monitoring is an effective method to allow leak detection in relation to changes in wind direction, and is generally planned using 50 to 75 centers for sensor placement. However, these distances can be increased to several hundred feet in the case of remote pipeline, well site and tank battery locations. A radius of exposure should be calculated for a predetermined ppm level, and factors such as weather conditions, wind speed, discharge rate and amount of H_2S available for escape should be considered in the calculation.

Deciding on whether to use point monitoring, perimeter monitoring, or a combination of both approaches requires evaluation. No one knows the facility better than the owners and operators of each individual location. They, after weighing the pertinent factors discussed below, plus any unique factors of the facility, are the best judge of the number of sensors required and where the sensors should be located.

As the specific gravity of H_2S is approximately twenty percent greater than that of air, the gas will tend to settle in low areas. As such, sensors are generally located 12 to 24 inches above ground level. In regard to air currents, the general guideline is to locate sensors where prevailing air currents contain the maximum sour gas concentration. It should also be realized that all sensors have ambient temperature limitations, and that the installation of the sensor must be within the vendor's specified temperature range.

Vibration may be damaging to the sensor and must be considered in selecting sensor locations. This generally means anchoring the sensor to a wall or firm base rather than to a structure subject to vibration such as a motor housing. Good instrument wiring practices should be incorporated in the sensor installation. The sensor cable should be shielded, especially when run near high power electrical circuits or R-F equipment. The cable should be continuous, and if splices are required they should be soldered to ensure trouble-free operation of the low level sensor signal.

Sensors may be adversely affected by prolonged exposure to certain poisons or contaminants such as halides, silicones, and acidic or caustic vapors. Sensitivity loss and/or corrosion may be gradual if these are present in low concentrations, or it may be rapid at high concentrations. The presence of such materials does not necessarily preclude the use of a solid state sensor, although the feasibility of monitoring such an area must be determined by an analysis of the specific factors in each application. The sensor life may be shortened with calibration checks required on a more frequent basis than normal, and the vendor's standard warranty may not apply.

Since it is desirable to calibrate on a periodic basis, sensors should be installed in a location permitting reasonable access. Sensors should always be mounted pointing downward to prevent the collection of dust, moisture or contaminants. They should also be protected from immersion or direct contact with water, with splash guards installed where wash downs or water spray can occur. Finally, dust protection should be provided in dirty or dusty environments and the sensor guards periodically cleaned or replaced if necessary. Fig. 6 shows a typical outdoor sensor installation.

SYSTEM MAINTENANCE

The sensor technology of solid state area monitors allows these systems to offer reliable performance with minimum maintenance. Because solid state H_2S sensors are very specific, the possibility of a false alarm from an interfering gas is quite remote. With routine maintenance and periodic calibration, a high degree of operator confidence can be achieved in the monitoring system.

The frequency of calibration varies from one manufacturer to the next, with recommended cycles ranging from every 15 to 30 days to four times a year. Factors unique to each installation should be considered when establishing a calibration cycle. Mud collecting on the sensor head, sensors being accidently painted over, and direct contact with water due to rain or washdowns are distinct possibilities in many applications. A clogged flame arrestor or sensor guard will block the diffusion path of H_2S, causing the sensor to appear inoperative. In these applications frequent checks will help ensure the sensor's diffusion path is kept clear.

By recommending frequent calibration checks, it is not being implied that users of area monitors should expect problems with sensor life or stability. Industry experience has shown that solid state sensors have a typical lifespan of several years and offer excellent stability. Frequent calibration (i.e. once every one to two weeks) merely helps to ensure the integrity of this life-protecting equipment when installed in harsh environments. In applications where dirt, dust, moisture and sensor contamination problems are not severe, calibration checks can be made on a monthly or even quarterly basis.

The calibration procedure typically involves application of an H_2S sample of known concentration to the sensor, and then adjusting the gain of the system accordingly. The hydrogen sulfide sample can come from a variety of sources, although the most common calibration techniques involve the use of either ampoules, permeation tubes or compressed gas cylinders. Ampoule calibration has the advantage of being very simple and requires little operator expertise. A sealed glass vial is inserted into a plastic breaker cup, and then broken with a thumbscrew to give known H_2S-in-air mixture (Fig. 7). Besides offering simplicity, ampoules can easily be accurate to within ten percent of their stated ppm value and have a shelf life of several years. Their one disadvantage is the dependence on the diffusion rate of H_2S, in that colder temperatures can cause calibration time to increase due to a slower mixing of the ampoule contents with the air inside the breaker cup.

Another method used to generate calibration gas involves the use of sealed, liquid filled sources known as permeation tubes. These were first developed as low level toxic gas sources for calibration of air pollution analyzers. To provide an accurate gas blend it is necessary to have precise control of the permeation tube temperature and the diluent flow rate, plus materials must be carefully selected which will be in contact with the gas sample. In operation a tube is placed in an oven at a constant temperature (to obtain a fixed permeation rate), and then diluent air is piped into the oven and mixed with the H_2S emitted from the tube. The diluent rate is controlled via a needle valve and flow meter, and the blended output is calculated on the permeation rate and rate of diluent. Permeation tube calibrators typically have a one hour warm-up period, and use a rechargeable battery for a power supply. Since the tubes are continuously outgassing, when not in use they are often stored refrigerated as this reduces the permeation rate, allowing the tubes to last up to twelve months.

An alternative to ampoules and permeation tubes involves the use of compressed gas cylinders. Generally two cylinders are used with the first being a mixture of H_2S in nitrogen and the second being dry air. Compressed H_2S mixtures balanced with air have poor long-term stability, hence the use of nitrogen, plus cylinder walls are often passivated to prevent adsorbtion. The H_2S in nitrogen and dry air are fed through flow blocks and then mixed to provide various ppm samples of H_2S in air (Fig. 8). Alternatively, cylinder kits may be supplied which provide a fixed flow and fixed ppm valve, and are disposed of when empty. Although bulky and requiring a certain degree of operator skill, compressed gas cylinders do have the advantage of flowing the H_2S sample to the sensor, potentially allowing for less calibration time than required for ampoules.

After the test gas has been applied to the sensor, adjustments are made at the controller to match the sensitivity of the system to the known calibration standard. In most area monitors, the calibration procedure requires two people - one at the sensor location to apply the test gas and one at the controller location to make the necessary span adjustments (Fig. 9). Because the sensor and controller can be separated by a distance of several thousand feet, some form of two-way communication is required between operators. Furthermore, alarm inhibit switches are usually activated to prevent false alarms due to calibration gas.

Most manufacturers now provide systems which can be calibrated by one man at the sensor location, reducing the time and cost of system maintenance. These systems typically consist of a 4-20mA transmitter assembly where a sensor and circuit boards are housed together in a junction box. The junction box cover is removed and a meter is plugged in, with the span adjustments being made after the sensor signal has stablilized. Recent advances in microprocessor technology have allowed for significant improvement in remote, one man calibration. Monitors are now available which offer pushbutton calibration and require no tools or adjustments. After the test gas is applied, the microprocessor adjusts the circuitry according to the sensor output, doing away with the need to open the junction box. Often referred to as "smart" sensors, these monitors can substantially reduce maintenance costs and require minimum operator training for proper calibration (Fig. 10).

Routine calibration is a procedure which is required on all area monitoring systems. It insures compensation for any sensitivity changes in the sensor and checks for proper operation of all system components. Calibration also serves to familiarize operating personnel with the equipment, promoting confidence in the system and enhancing its overall reliability.

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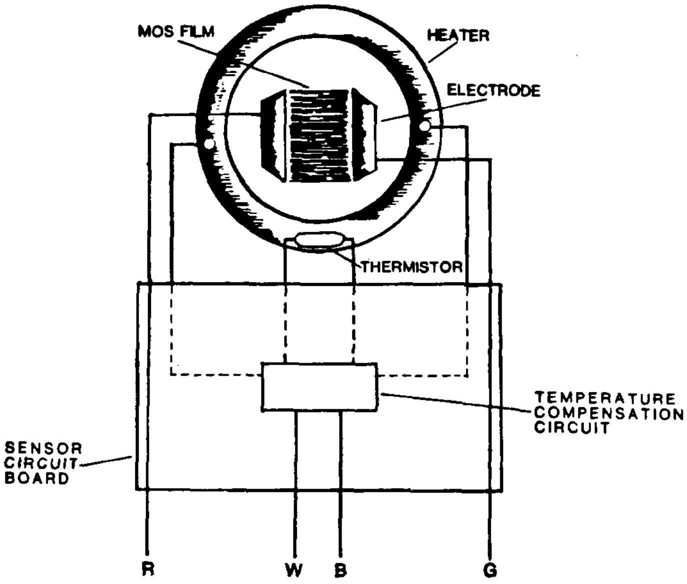

Figure 1—Typical solid state H_2S sensing element

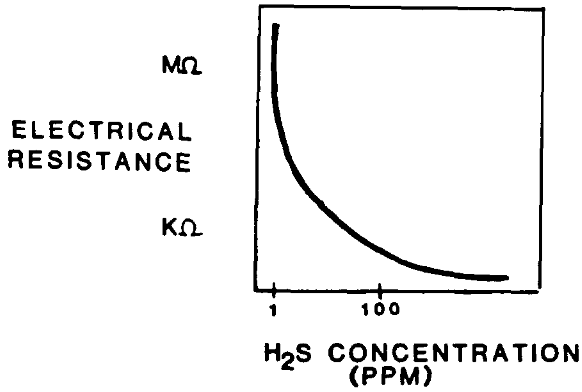

Figure 2—Non-linear relationship of the film resistance versus H_2S concentration

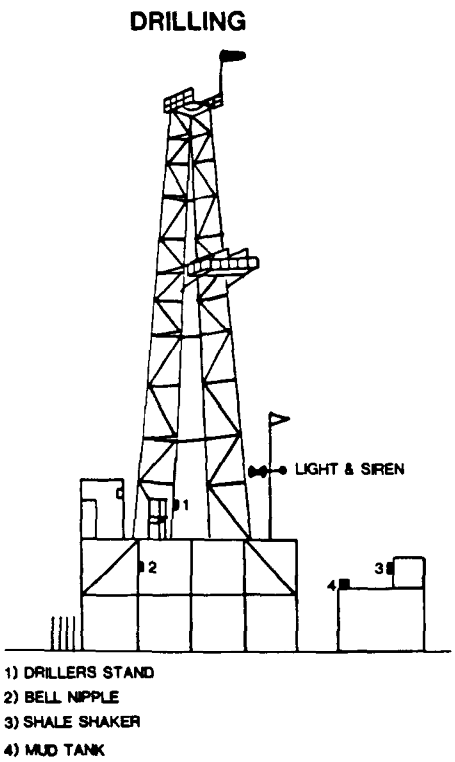

Figure 3—Typical sensor locations for drilling operations include the above four areas

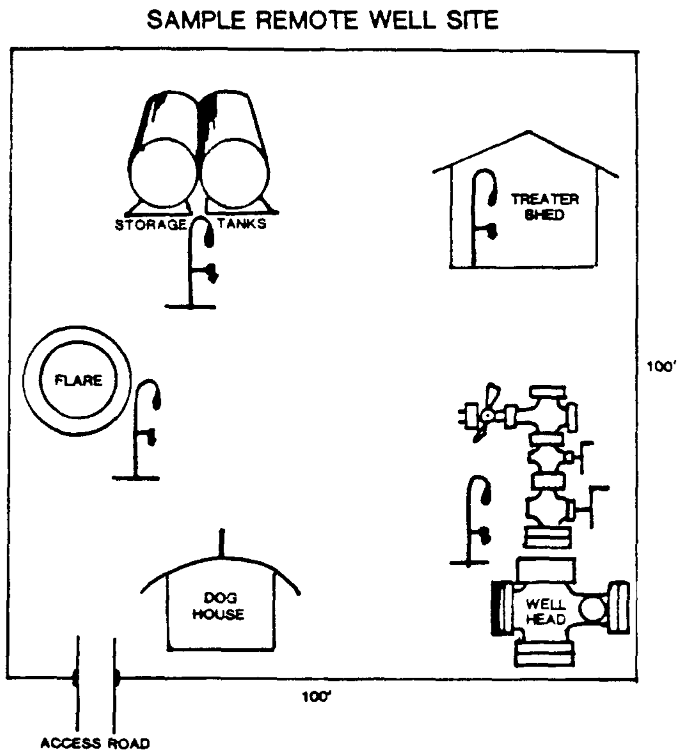

Figure 4—Point monitoring at a well site could include sensors at storage tanks, flares, treater shed and well head

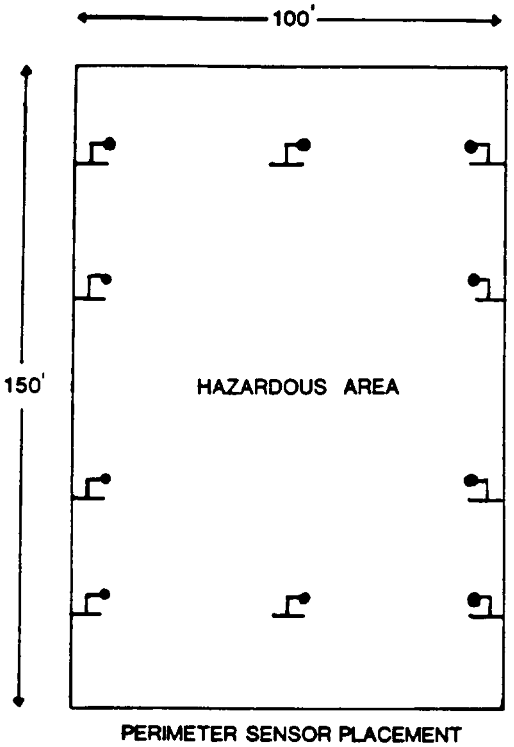

Figure 5—Perimeter monitoring using 25'-50' centers for sensor placement

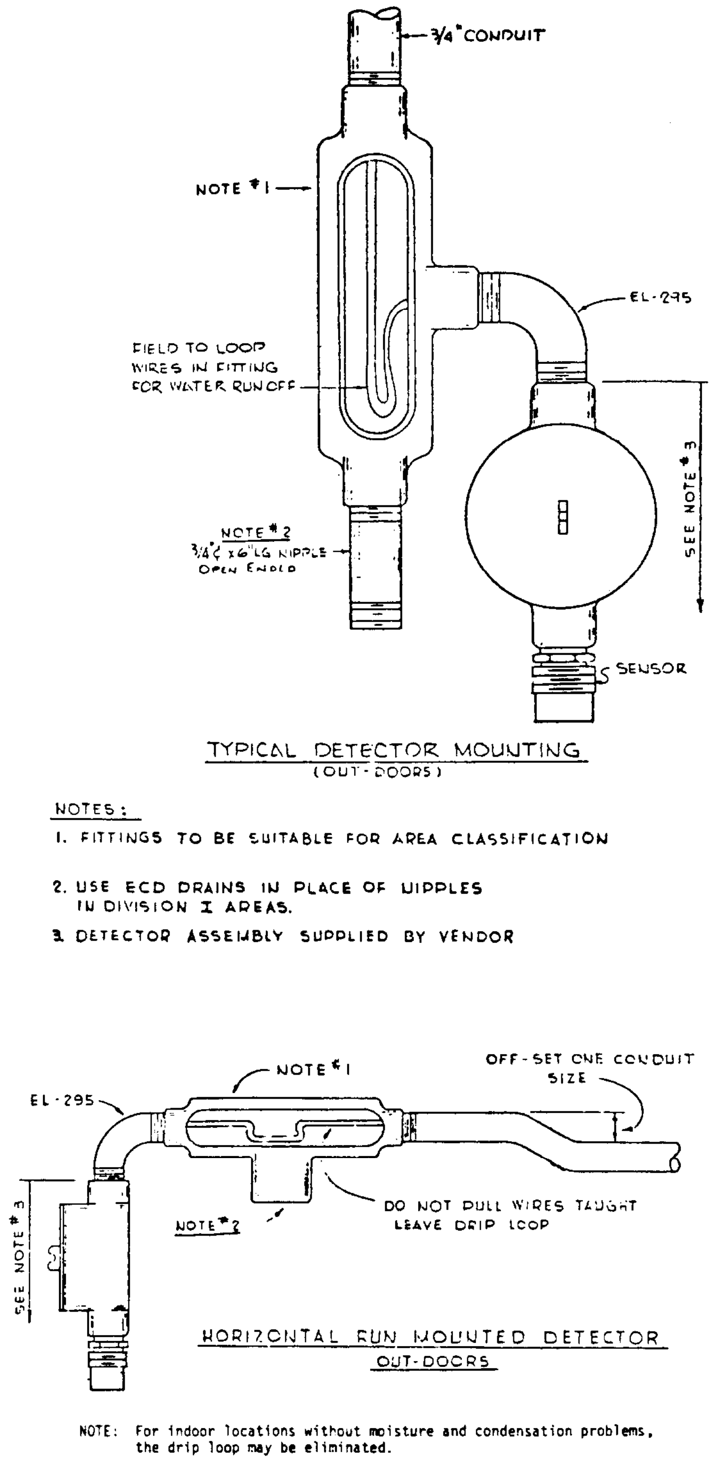

Figure 6—Sensor installation using horizontal or vertical conduit runs

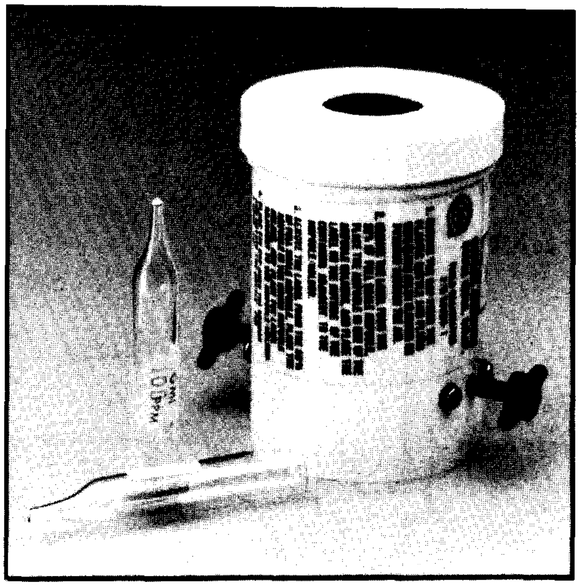

Figure 7—Ampoule calibration offers both simplicity and accuracy

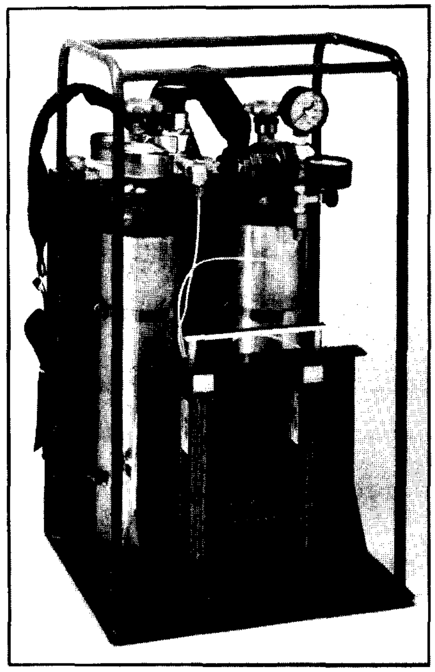

Figure 8—Compressed gas cylinders are used in areas having large numbers of sensors, usually as a cost-reducing alternative to ampoules

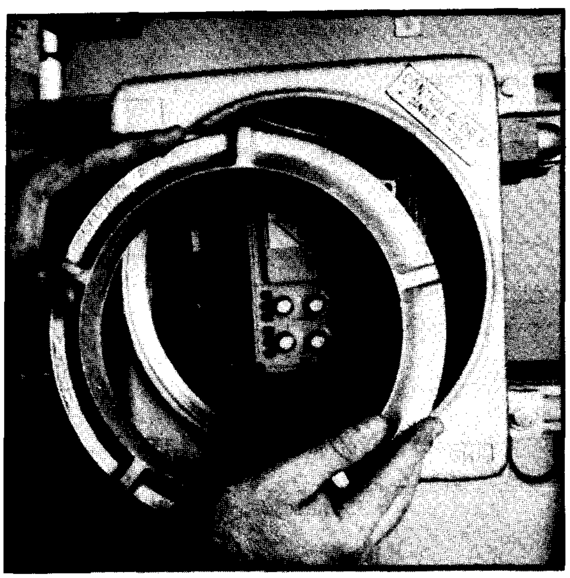

Figure 9—Most area monitors require two people for calibration. While one operator applies test gas to the sensor, a second operator makes the necessary controller adjustments

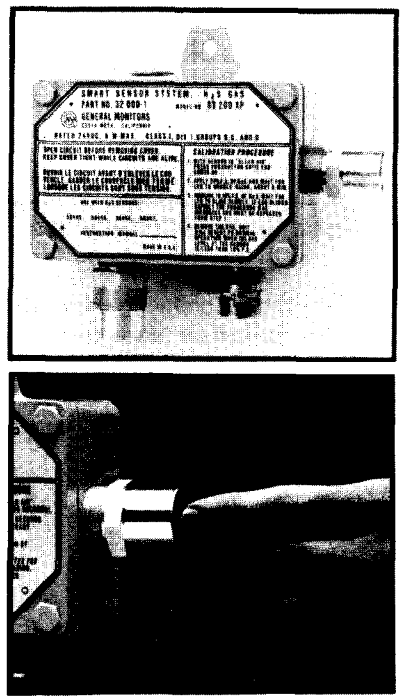

Figure 10—Recent advances in microprocessor technology have been incorporated in gas detectors such that the entire calibration process can be completed by one person at the sensor site without tools or adjustments