

## DIRECT READING INSTRUMENTS FOR DETERMINING CONCENTRATIONS OF AEROSOLS, GASES AND VAPORS

*Robert G. Keenan*

### INTRODUCTION

This chapter deals with direct reading instruments which may be portable devices or fixed-site monitors; it does not include those instruments which have been designed primarily for use in the laboratory.

Direct reading instruments are used for on-site evaluations for a number of reasons, including:

1. To find the sources of emission of hazardous substances on the spot;
2. To ascertain if select OSHA air standards are being exceeded;
3. To check the performance of control equipment;
4. As continuous monitors at fixed locations,
  - a. To trigger an alarm system in the event of a breakdown in a process control which could result in the accidental release of copious amounts of harmful substances to the workroom atmosphere;
  - b. To obtain permanent recorded documentation of the concentrations of a contaminant in the atmospheric environment for future use in epidemiological and other types of occupational studies, in legal actions, to inform employees as to their exposure, and for information required for improved design of control measures.

Such on-site evaluations of the atmospheric concentrations of hazardous substances make possible the immediate assessment of undesirable exposures and enable the industrial hygienist to make an immediate correction (including a shutdown) of an operation, in accordance with his judgment of the seriousness of a situation, without permitting further risk of injury to the workers. It cannot be over-emphasized that great caution must be employed in the use of direct reading instruments and in the interpretation of their results. Many of these instruments are nonspecific and the industrial hygienist may find it necessary before recommending any action to make certain of his on-site findings by supplemental sampling and laboratory analyses to characterize fully the chemical nature of the contaminants in a workroom area and to develop the supporting quantitative data with more specific methods of greater accuracy. Such precautions become the more mandatory if the industrial hygienist has not had extensive experience with the particular process

area in question or when the possibilities of a change in the process or in the substitution of chemical substances may have occurred. The last possibility must always be foremost in the minds of industrial hygienists.

### Calibration

The calibration of any direct reading instrument is an absolute necessity if the data are to have any meaning. Considering this to be axiomatic, we must also recognize that the frequency of calibration is dependent upon the type of instrument as well as individual instruments within any one class. It is well known that certain classes of instruments, because of their design and complexity, require more frequent calibration than others. It is also recognized that peculiar "quirks" in an individual instrument produce greater variations in its response and general performance, thus requiring a greater amount of attention and more frequent calibration than other instruments of the same design. Direct personal experience with a given instrument serves as the best guide in this matter.

Another unknown factor which can be evaluated only by experience is the variability of sampling locations. For example, when locating a particular fixed-station monitor at a specific site, consideration must be given to such problems as the presence of interfering chemical substances, the corrosive nature of contaminants, vibration, voltage fluctuations and other disturbing influences which may affect the response of the instrument.

Finally, the required accuracy of the measurements must be determined initially. Obviously, if an accuracy of  $\pm 3$  percent is needed, more frequent calibration must be made than if  $\pm 25$  percent accuracy is adequate in the solution of a particular problem.

### Properties of Aerosols

An aerosol is an airborne solid or liquid substance. Aerosol particles normally present in ambient air have been dispersed as a result of nature's or man's activities. The latter source is of greatest concern to environmental control specialists. Aerosols are generated by fire, erosion, sublimation, condensation and the abrading action of friction on minerals, metallurgical materials, organic and other inorganic substances in construction, manufacturing, mining, agriculture, transportation and other gainful pursuits.

Aerosols are classified conveniently as dusts, fumes, smokes, mists and fogs according to their physical nature, their particle size, and their

method of generation. Dusts range from 1 to 150  $\mu\text{m}$  in diameter; they are produced mechanically by grinding and other abrasive actions occurring in natural and commercial operations.

Fumes are particulate substances whose diameters range from 0.2 to 1  $\mu\text{m}$ ; they are produced by such processes as combustion, distillation, calcination, condensation, sublimation, and chemical reactions. They form true colloidal systems in air. Examples are such substances as heated metals or metallic oxides, ammonium chloride, hot asphalt and volatilized polynuclear hydrocarbons from coking operations.

Smokes are colloidal systems whose particle sizes range from 0.3 to 0.5  $\mu\text{m}$  in diameter. They are produced by the incomplete combustion of carbonaceous materials such as coal, oil, tobacco, and wood.

Mists and fogs cover a wide range of particle sizes and are considered to be primarily liquid; they may consist of liquids, such as water vapor, condensed on the surfaces of submicroscopic particles of dust or gaseous ions.

Mineral, vegetable and animal fibers constitute a unique situation insofar as exposures are concerned. Inhalation of asbestos fibers up to 200  $\mu\text{m}$  in length has been reported.<sup>1,2</sup> Microscopic procedures are used to assist in the identification of, and to determine, the atmospheric concentration of fibrous materials.

#### Properties of Gases and Vapors

Gases and vapors are "elastic fluids," so-called because they take the shape and volume of their containers. A fluid is generally termed a gas if its temperature is very far removed from that required for liquefaction; it is called a vapor if its temperature is close to that of liquefaction. In the field of occupational health, a substance is considered a gas if this is its normal physical state at room temperature and atmospheric pressure. It is considered a vapor if, under the existing environmental conditions, conversion of its liquid or solid form to the gaseous state results from its vapor pressure affecting its volatilization or sublimation into the atmosphere of the container, which may be the process equipment or the workroom. Our chief interest in distinguishing between gases and vapors lies in our need to assess the potential occupational hazards associated with the use of specific chemical agents, an assessment which requires a knowledge of the physical and chemical properties of these substances (see Chapter 15).

#### Characteristics of Direct Reading Instruments

Direct reading instruments for atmospheric contaminants are classified as those devices which provide an immediate indication of the concentration of aerosols, gases, or vapors by a dial reading, a strip chart recording, a tape printout or a color change on an impregnated paper or in an indicator tube. These devices, when properly calibrated and when used with full cognizance of their performance characteristics and limitations, can be extremely helpful to industrial hygienists who are engaged in on-site evaluations of potentially hazardous conditions. There are many types of

instruments which depend on certain physical or chemical principles for their operation. They are discussed later in this chapter.

The advantages of direct reading instruments include:

1. Immediate estimations of the concentration of a contaminant, permitting on-site evaluations;
2. Provision of permanent 24-hour records of contaminant concentrations using continuous monitors;
3. Attachment of alarm system to instrument to warn workers of build-up of hazardous situations;
4. Reduction of number of manual tests;
5. Reduction of number of laboratory analyses;
6. Provision of more convincing evidence for presentation at hearings and litigation proceedings;
7. Reduced cost of obtaining individual results.

The disadvantages of different types of direct reading instruments may include some of the following:

1. High initial cost of instrumentation;
2. Need of frequent calibration;
3. Lack of adequate calibration facilities;
4. Lack of portability;
5. Lack of specificity.

### DIRECT READING PHYSICAL INSTRUMENTS

The physical properties of aerosols, gases, and vapors are used in the design of direct reading physical instruments for quantitative estimations of these types of contaminants in the atmosphere. The principles upon which these instruments are based are presented in the following discussion.

#### Operating Principles

*Aerosol Photometry (Light Scattering).* The principle of aerosol photometry is the generation of an electrical pulse by a photocell which detects the light scattered by a particle. A pulse height analyzer estimates the effective particle diameter. The number of electronic pulses is related to the number of particles counted per unit flowrate of the sampled gaseous medium. Calibrations may be made using a reference standard such as polystyrene spheres whose diameters and refractive index are known although the aerosol under study is the reference of choice because of the unique effects of shape factor, angle of scatter, and refractive index, as well as particle size. Whereas certain commercial instruments are designed to give a size analysis based upon the above principles, there are others which use a forward light scattering principle to provide an integrated measurement of total particle concentration in a large illuminated volume. The latter are used in monitoring particulate concentrations in experimental rooms and exposure chambers.

Aerosol photometry can usually provide only an approximate analysis of particulate classified according to particle size in plant surveys because

of the impracticality of calibrating the instrument with each type of particulate suspension which is to be measured. The great variations in shape, size, degrees of agglomeration and refractive indices of the mixture of chemical components in a given dust or fume suspension make such a calibration exceedingly difficult. Whereas aerosol photometry can, therefore, provide an indication of the particulate concentration in the different particle size ranges of interest, it is still necessary to perform size distribution analyses by microsieveing and microscopic procedures for greatest accuracy.

**Chemiluminescence.** Chemiluminescence is a phenomenon which occurs with certain chemical reactions. The process provides a distinctly colored glow which accompanies such reactions as the oxidation of certain decaying wood, of luciferin in fireflies and of yellow phosphorus. Recently, analytical advantage of this phenomenon is taken in the reaction of ozone with such other gases as ethylene and nitric oxide for the measurement of ozone or nitrogen oxides in ambient atmospheres.

The chemiluminescent principle has been incorporated into continuous ambient air monitors which are selective for ozone or for  $\text{NO} - \text{NO}_x$ . Measurements of ozone at concentrations extending from 0.001 to 1 ppm in ambient atmospheres are based upon the photometric (photomultiplier tube) detection of the chemiluminescence produced by the flameless gas phase reaction of the ozone in the air sample stream with ethylene gas whose flow from a bottled supply is regulated through a calibrated capillary tubing to the reactor chamber.

Similarly,  $\text{NO}$  measurements from 0.01 to 5,000 ppm are based upon the chemiluminescent reaction of  $\text{NO}$  and ozone to produce  $\text{NO}_2$  and  $\text{O}_2 + h\nu$ . The ozone is produced from bottled oxygen by an in-line ozone generator. Monitoring of  $\text{NO}_x$  is accomplished by means of an  $\text{NO}_2$  to  $\text{NO}$  catalytic converter which operates in a bypass line on a timed sequence basis. Thus,  $\text{NO}_2$  measurements can be obtained by difference.

The selectivity of these instruments is enhanced by the use of narrow-band optical filters to provide negligible interference effects from other atmospheric contaminants. Although designed for ambient air studies, these instruments may be used advantageously as fixed-station monitors of in-plant atmospheres.

**Colorimetry** (see Photometry)

**Combustion.** A combustible gas or vapor mixture is passed over a filament heated above the ignition temperature of the substance of analytical interest. If the filament is part of a bridge circuit, the resulting heat of combustion changes the resistance of the filament, and the measurement of the imbalance is related to the concentration of the gas or vapor in the sample mixture. The method is basically nonspecific, but it may be made more selective by choosing appropriate filament temperatures for individual gases or vapors or by using an oxidation catalyst for a desired reaction such as Hopcalite for carbon monoxide.

Combustible gas indicators must be calibrated

in the laboratory for their response to the anticipated individual test gases and vapors, such as benzene, toluene, hexane (for hydrocarbons in general), carbon monoxide, acetone, and styrene. These instruments are definitely portable and they are valuable survey meters in the industrial hygienist's collection of field instruments. Readings are in terms of 0-1000 ppm or 0-1.0 Lower Explosive Limit (LEL). However, it is essential to recognize that industrial atmospheres rarely contain one gaseous contaminant and that these indicators will respond to all the combustible gases present. Hence, supplementary sampling and analytical techniques should be used for a complete definition of hazardous environmental conditions.

**Conductivity, Electrical.** A gas-air mixture is drawn through an aqueous solution. Those gases which form electrolytes produce a change in the electroconductivity as a summation of the effects of all ions thus produced. Hence, the method is nonspecific. If the concentrations of all other ionizable gases are either constant or insignificant, then the resulting changes in conductivity may be related to the gaseous substance of interest. Temperature control is extremely critical in conductance measurements; if thermostated units are not used, then electrical compensation must enter into the measurements to allow for the 2% per degree C conductivity temperature coefficient average for many gases.

The electrical conductivity method has found its greatest application in the continuous monitoring of sulfur dioxide in ambient atmospheres. However, a lightweight portable analyzer which uses a peroxide absorber to convert  $\text{SO}_2$  to  $\text{H}_2\text{SO}_4$  is now available; this battery operated instrument can provide within one minute an integrated reading of the  $\text{SO}_2$  concentration over the 0-1 ppm range. A larger portable model which may be operated off a 12-volt automobile battery is also available for the higher concentration ranges of  $\text{SO}_2$  encountered in field sampling.

**Conductivity, Thermal.** The specific heat of conductance of a gas or vapor is a measure of its concentration in a carrier gas such as air, argon, helium, hydrogen, or nitrogen. However, thermal conductivity measurements are nonspecific and the method finds its greatest usefulness in estimating the concentration of the separately eluted components from a gas chromatographic column. The method operates by virtue of the loss of heat from a hot filament to a single component of a flowing gas stream, the loss being registered as a decrease in electrical resistance measured by a Wheatstone bridge circuit. The applications of this method are limited mostly to binary gas mixtures and are based upon the electrical unbalance produced in the bridge circuit by the difference in the filament resistances of the sample and reference gases passed through the separate cavities in the thermal conductivity cell.

**Coulometry.** Coulometry is the precise measurement of the quantity of electricity passing through a solution during an electrochemical reaction. The substance of analytical interest is oxidized or reduced at one electrode in a primary coulometric

analysis or it may react stoichiometrically (in a secondary coulometric analysis) with one of the electrolytic products. The method is capable of a high degree of precision. It is used in the automatic monitoring of part per billion to part per million concentrations of reactive inorganic gases present in ambient atmospheres; air samples are drawn through the electrolytic cell in which the reactant is generated in controlled quantities to meet the concentration requirements.

The method is basically nonspecific; it is made more selective for specific atmospheric oxidants by adjusting the concentration, pH and composition of the electrolyte used in the reaction. In certain instances a chemical filter or a selective membrane is used to remove serious interferents from the sampled gas stream. Both portable and fixed monitor types of instruments, based upon this principle, are used to monitor ozone, nitrogen dioxide and sulfur dioxide concentrations.

**Flame Ionization.** The hydrogen flame ionization detector (FID) is a stainless steel burner in which hydrogen is mixed with the sample gas stream in the base of the unit; combustion air or oxygen is fed axially and diffused around the jet through which the hydrogen — gas mixture flows to the cathode tip where ignition occurs. A loop of platinum serves as the collector electrode which is set about 6 mm above the tip of the burner. The current carried across the electrode gap is proportional to the number of ions generated during the burning of the sample; the detector responds to all organic compounds, except formic acid, but its response is greatest with hydrocarbons and diminishes with increasing substitution of other elements: notably oxygen, sulfur and chlorine. Its low noise level of  $10^{-12}$  amperes provides a high sensitivity of detection and it is capable of the wide linear dynamic range of  $10^7$ . Its usefulness is enhanced by its insensitivity to water, the permanent gases and most inorganic compounds thus simplifying the analysis of aqueous solutions and atmospheric samples. It is used to great advantage in both laboratory and field models of gas chromatographs as well as in hydrocarbon analyzers which are set up as fixed station monitors of ambient atmospheres in the laboratory or field.

Hydrocarbon analyzers, operating with an FID detector, are carbon counters; their response to a given quantity of a typical  $C_n$  hydrocarbon is six times to that of methane, at a fixed flowrate of the sample stream. Thus, the instrumental characteristics such as sensitivity, are usually given as methane equivalent. In addition to hydrocarbons, these analyzers respond to alcohols, aldehydes, amines and other compounds which will produce an ionized carbon atom in the hydrogen flame. The electronic stability of at least one model is within 1 percent over 24 hours of operation; this instrument is equipped with electronic span calibration to improve the accuracy of the data.

**Gas Chromatography.** Gas chromatography is a physical process for separating the components of complex mixtures and is now being used profitably as a portable technique for in-plant studies. A gas chromatograph consists of (1) a carrier gas sup-

ply complete with a pressure regulator and flow meter, (2) an injection system for the introduction of a gas or vaporizable sample into a port at the front end of the separation column, (3) a stainless steel, copper or glass separation column containing a stationary phase consisting of an inert material, such as diatomaceous earth, used alone as in gas-solid chromatography (GSC) or as a support for a thin layer of a liquid substrate, such as silicone oils, in gas-liquid chromatography (GLC), (4) a heater and oven assembly to control the temperature of the column(s), injection port and detector unit, (5) a detector and (6) a recorder for the chromatograms produced during the separations. The separations are based upon the varied affinities of the sample components for the packing materials of a particular column, the rate of carrier gas flow and the operating temperature of the column. Improved separations are made possible by the use of temperature programming. The sample components, as a consequence of their varied affinities for a given column, are eluted sequentially and thus evoke separate responses by the detection system whose signal is amplified to produce a peak on the strip chart recorder. The height and area of the peak are proportional to the concentration of the eluted sample component. Calibrations are made using known mixtures of the pure substance in a gas-air mixture prepared in a 5- to 100-liter Saran bag or other suitable container. The time of retention on the column and supporting analytical techniques (infrared spectrophotometry, for example) are used in the identification of the individual peaks of a chromatogram. The method is capable of providing extremely clean-cut separations and is one of the most useful techniques in the field of organic analysis. It is sensitive to fractional part per million concentrations of organic substances. The most commonly used detectors include flame ionization, thermal conductivity and electron capture (see Chapter 21 on Gas Chromatography).

Rugged, battery operated, portable gas chromatographs have been refined to the point where they may now be considered practical for many field study applications. These instruments may now be obtained with a choice of thermistor-type thermal conductivity, flame ionization and electron capture detectors and, in some instances, the latter two types are interchangeable. Complete with gas sampling valve, rechargeable batteries, appropriate columns and self-contained supplies of gases, these chromatographs have much to offer to the industrial hygienist engaged in on-site analyses of trace quantities of organic compounds and the permanent gases. The gas lecture bottles provide 8 to 20 hours of operation dependent on the flowrates and must be recharged using high pressure gas regulators. The retention times of the compounds of analytical interest must be determined in the laboratory for a given type of column, as is true for the laboratory type chromatographs.

**Photometry (Colorimetry).** Photometry is the measurement of the relative radiant power of a beam of radiant energy, in the visible, ultraviolet or infrared region of the electromagnetic spectrum,

which has been attenuated as a result of passing through a solution, a gas-air mixture containing a substance such as mercury vapor, ozone or benzene vapor, a suspension of solid or liquid particulates in air or other gaseous medium, or a photographic image of a spectral line or an x-ray diffraction pattern on a photographic film or plate. Photometers used for the indicated types of applications contain (1) a lamp or other generating source of energy, (2) an optical filter arrangement to limit the bandwidth of the incident beam of radiation, (3) an optical system to collimate the filtered beam, which is then passed through (4) the sample system contained in a cuvette or gas cell to (5) a photocell, bolometer, thermocouple or pressure sensor type of detector where the signal is amplified and fed to a (6) readout meter or to a strip chart recorder.

The more sophisticated technique is termed spectrophotometry which makes use of prisms made of glass (visible region), quartz (ultraviolet), and sodium chloride or potassium bromide (infrared) or of diffraction gratings, instead of optical filters, to provide essentially monochromatic radiation as a "purer" source of energy. Spectrophotometers are used mostly in laboratories for highly specific and precise analytical determinations.

Most field type colorimetric analyzers have been designed to function as fixed-station monitors for the active gases such as oxides of nitrogen, sulfur dioxide, "total oxidant," ammonia, aldehydes, chlorine, hydrogen fluoride, and hydrogen sulfide. These instruments require frequent calibration with zero and span gases at the sampling site to assure the provisions of reliable data. However, built-in automated calibration systems, which standardize regularly zero and span controls against pure air and a calibrated optical filter, are now available from one source of colorimetric analyzers for the nitrogen oxides, sulfur dioxide and aldehydes. A further advantage is the 0-10 ppm working range of these instruments with the optional capability of extending the upper limit to 10,000 ppm.

Another recent advance is the provision of a portable, colorimetric analyzer for  $\text{NO}_2\text{-NO}_x$  by another manufacturer. This instrument, which uses dual photometric cells, is designed for rugged field use, may be operated from a 12-volt automobile battery and operates over the 0-2.0 ppm range, with higher ranges available. It may also be used as a field monitor, if desired.

**Polarography.** Polarographic analysis is based on the electrolysis of a sample solution using an easily polarized microelectrode (the indicator electrode) and a large nonpolarizable reference electrode. In laboratory instruments the indicator electrode is a noble metal, usually a dropping mercury electrode for reduction reactions and a platinum electrode for oxidation reactions. The reference electrode may be a pool of mercury on the bottom of the electrolysis vessel or a saturated calomel electrode.

The method provides both qualitative and quantitative information. As the increasing voltage to the polarographic cell is applied at a steady

rate, the decomposition potentials of electroreducible (or electrooxidizable) ions are reached in turn. At the decomposition potential of a given ion, the current increases rapidly and then levels off to a limiting current thus producing an S-shaped curve or "wave." The value of the half-wave potential is characteristic of the discharged ion in a given electrolyte. The height of the wave, i.e., the rise in the current, is proportional to the concentration of the discharged ion species in the sample.

The method has been used largely for the analysis of metallic ions and organic species. Manufacturers of modern field instruments, however, are taking advantage of advanced, compact, long-lived polarographic sensors to provide continuous monitors for oxygen in such diversified environments as furnace atmospheres, flue gases, auto exhausts, space vehicles, manholes and physiology test chambers.

These portable instruments may be easily calibrated for gaseous oxygen by exposing the sensor to ambient air and adjusting the calibration pot to provide a meter reading of 20.9 on the 0-25 percent scale. These instruments provide a rapid response to changes in the concentration of oxygen and should prove valuable to the industrial hygienist who may encounter oxygen deficient atmospheres during his surveys.

**Radioactivity.** Radioactive substances emit three principal types of radiation, viz. alpha ( $\alpha$ ), beta ( $\beta$ ), and gamma ( $\gamma$ ). Radioactive particles and gases may be monitored manually or automatically in gas streams, in ambient atmospheres, in process water or in solid process materials or products by means of ionization chambers, scintillation detectors or Geiger-Mueller counters. Choice of detectors for alpha, beta-gamma or alpha-beta-gamma monitors is determined by the isotopes of interest. Electronic recorders are available for graphic presentation of monitoring data.

Portable lightweight air monitors for gamma, beta-gamma, and alpha-beta-gamma radiation are available with interchangeable probes to survey work areas for the different types of radiation encountered. One such instrument thus provides the capability of measuring alpha and weak beta radiation using one probe and gamma radiation up to 10 or 60 mr per hour with the others. Other portable survey meters include the "Cutie Pie" with ranges of 50, 500, and 5000 mr per hour and a fast neutron survey meter designed with tissue equivalent response in making health hazard surveys in the range of 0.2 to 14 MEV around reactors and neutron generators.

A summary of the operating characteristics of the current (1972) commercially available direct reading physical instruments is presented in Table 16-1. The information provided in this table is based upon that given in the manufacturers' literature; in certain instances, e.g., repeatability, a range of values may represent either the specifications given by more than one source of supply or different applications of an operating principle to the estimation of multiple chemical entities. In other cases, the information has not been provided

**TABLE 16-1**  
**Direct Reading Physical Instruments**

Principle of Operation	Applications & Remarks	Code*	Range	Repeatability (Precision)	Sensitivity	Response Time
Aerosol Photometry	Measures, records and controls particulates continuously in areas requiring sensitive detection of aerosol levels; detection of 0.05 to 40 $\mu\text{m}$ diameter particles. Computer interface equipment is available.	A & B	$10^{-3}$ to $10^2$ $\mu\text{g}$ per liter	Not given	$10^{-3}$ $\mu\text{g}$ per liter (for 0.3 $\mu\text{m}$ DOP)	Not given
Chemiluminescence	Measurement of NO in ambient air selectivity and NO <sub>2</sub> after conversion to NO by hot catalyst. Specific measurement of O <sub>3</sub> . No atmospheric interferences.	B	0 to 10,000 ppm	$\pm 0.5$ to $\pm 3\%$	Varies: 0.1 ppb to 0.1 ppm	ca 0.7 sec NO Mode and 1 sec NO <sub>x</sub> mode; Longer period when switching ranges
Colorimetry	Measurement and separate recording of NO <sub>2</sub> -NO <sub>x</sub> , SO <sub>2</sub> , total oxidants, H <sub>2</sub> S, HF, NH <sub>3</sub> , Cl <sub>2</sub> and aldehydes in ambient air.	A & B	ppb & ppm	$\pm 1$ to $\pm 5\%$	0.01 ppm (NO <sub>2</sub> , SO <sub>2</sub> )	30 sec. to 90% of full scale
Combustion	Detects and analyzes combustible gases in terms of percent LEL on graduated scale. Available with alarm set at 1/3 LEL.	A	ppm to 100%	—	ppm	<30 sec.
Conductivity, Electrical	Records SO <sub>2</sub> concentrations in ambient air. Some operate off a 12-volt car battery. Operate unattended for periods up to 30 days.	A & B	0 to 2 ppm	$<\pm 1\%$ to $\pm 10\%$	0.01 ppm	1 to 15 sec. (lag)
Coulometry	Continuous monitoring of NO, NO <sub>2</sub> , O <sub>3</sub> and SO <sub>2</sub> in ambient air. Provided with strip chart recorders. Some require attention only once a month.	A & B	Selective: 0 to 1.0 ppm overall, or to 100 ppm (optional)	$\pm 4\%$ of full scale	varies: 4 to 100 ppb dependent on instrument range setting.	<10 min. to 90% of full scale.
Flame Ionization (with gas chromatograph)	Continuous determination & recording of methane, total hydrocarbons and carbon monoxide in air. Catalytic conversion of CO to CH <sub>4</sub> . Operates up to 3 days unattended.	B	Selective: 0 to 1 ppm; 0 to 100 ppm	$\pm 1\%$ of full scale	Not given	5 min. (cycle time)
Same as above	Separate model for continuous monitoring of SO <sub>2</sub> , H <sub>2</sub> S and total sulfur in air. Unattended operation up to 3 days.	B	0-20 ppm	$\pm 4\%$ of full scale	0.005 ppm (H <sub>2</sub> S); 0.01 ppm (SO <sub>2</sub> )	5 min. (cycle time)
Flame Ionization (Hydrocarbon Analyzer)	Continuous monitoring of total hydrocarbons in ambient air; potentiometric or optional current outputs compatible with any recorder. Electronic stability from 32° to 110°F.	B	0 to 1 ppm as CH <sub>4</sub> ; X1, X10, X100, X1000 with continuous span adjustment	$\pm 1\%$ of full scale	1 ppm to 2% full scale as CH <sub>4</sub> ; 4 ppm to 10% as mixed fuel.	<0.5 sec. to 90% of full scale

TABLE 16-1 (Continued)

Principle of Operation	Applications & Remarks	Code*	Range	Repeatability (Precision)	Sensitivity	Response Time
Gas Chromatograph, Portable	On site determination of fixed gases, solvent vapors, nitro and halogenated compounds and light hydrocarbons. Instruments available with choice of flame ionization, electron capture or thermal conductivity detectors and appropriate columns for desired analyses. Rechargeable batteries.	A	Depends on detector	Not given	<1 ppb (SF <sub>6</sub> ) with electron capture detector; <1 ppm (HC's)	—
Infrared Analyzer (Photometry)	Continuous determination of a given component in a gaseous or liquid stream by measuring amount of infrared energy absorbed by component of interest using pressure sensor technique. Wide variety of applications include CO, CO <sub>2</sub> , Freons, hydrocarbons, nitrous oxide, NH <sub>3</sub> , SO <sub>2</sub> and water vapor.	B	From ppm to 100% depending on application	±1% of full scale	0.5% of full scale	0.5 sec. to 90% of full scale
Photometry, Ultraviolet (tuned to 253.7 mμ)	Direct readout of mercury vapor; calibration filter is built into the meter. Other gases or vapors which interfere include acetone, aniline, benzene, ozone and others which absorb radiation at 253.7 mμ.	A	0.005 to 0.1 and 0.03 to 1 mg/m <sup>3</sup>	±10% of meter reading or ± minimum scale division, whichever is larger	0.005 mg/m <sup>3</sup>	Not given
Photometry, Visible (Narrow-centered 394 mμ band pass)	Continuous monitoring of SO <sub>2</sub> , SO <sub>3</sub> , H <sub>2</sub> S, mercaptans and total sulfur compounds in ambient air. Operates more than 3 days unattended.	B	1 to 3,000 ppm (with air flow dilution)	±2%	0.01 to 10 ppm	<30 sec. to 90% of full scale.
Particle Counting (Near Forward Scattering)	Reads and prints directly particle concentrations at 1 of 3 preset time intervals of 100, 1000 or 10,000 seconds, corresponding to 0.01, 0.1 and 1 cubic foot of sampled air.	B	Preset (by selector switch) Particle Size Ranges: 0.3, 0.5, 1.0, 2.0, 3.0, 5.0, and 10.0 μm. Counts up to 10 <sup>7</sup> particles per cu. ft. (35 × 10 <sup>3</sup> /liter)	±0.05% (probability of coincidence)	—	Not given
Polarography	Monitor gaseous oxygen in flue gases, auto exhausts, hazardous environments and in food storage atmospheres and dissolved oxygen in wastewater samples. Battery operated, portable, sample temperature 32° to 110°F, up to 95% relative humidity. Potentiometric recorder output. Maximum distance between sensor and amplifier is 1000 feet.	A	0-5 and 0-25%	±1% of reading at constant sample temperature	Not given	20 sec. to 90% of full scale

TABLE 16-1 (Continued)

Principle of Operation	Applications & Remarks	Code*	Range	Repeat-ability (Precision)	Sensitivity	Response Time
Radio-activity	Continuous monitoring of ambient gamma and x-radiation by measurement of ion chamber currents, averaging or integrating over a constant recycling time interval, sample temperature limits 32°F to 120°F; 0 to 95% relative humidity (weatherproof detector); up to 1,000 feet remote sensing capability. Recorder and computer outputs. Complete with alert, scram and failure alarm systems. All solid-state circuitry.	B	0.1 to 10 <sup>7</sup> mR/hr.	±10% (Decade Accuracy)	—	<1 sec.
Radio-activity	Continuous monitoring of beta or gamma emitting radioactive materials within gaseous or liquid effluents; either a thin wall Geiger-Mueller tube or a gamma scintillation crystal detector is selected depending on the isotope of interest; gaseous effluent flow — 4 cfm; effluent sample temperature limits 32°F to 120°F using scintillation detector and —65°F to 165°F using G-M detector. Complete with high radiation, alert and failure alarms.	B	10 to 10 <sup>6</sup> cpm	±2% full scale (rate meter accuracy)	<10 <sup>-7</sup> μCi of I-131 per cc of air and 10 <sup>-7</sup> μCi of Cs-137 per cc of water using a scintillation detector	0.2 sec. at 10 <sup>6</sup> cpm (rate-meter)
Radio-activity	Continuous monitoring of radioactive airborne particulates collected on a filter tape transport system; rate of air flow — 10 SCFM; scintillation and G-M detectors, optional but a beta sensitive plastic scintillator is provided to reduce shielding requirements and offer greater sensitivity. Air sample temperature limits 32°F to 120°F; weight 550 pounds. Complete with high and low flow alarm and a filter failure alarm.	B	10 to 10 <sup>6</sup> cpm	±2% of full-scale (rate-meter accuracy)	10 <sup>-12</sup> μ Ci of Cs-137 per cc of air using a scintillation detector	0.2 sec. at 10 <sup>6</sup> cpm (rate-meter)

\* Code: A-Portable Instruments; B-Fixed Monitor or "Transportable" Instruments.

Taken from Draeger Detector Tube Handbook, Draegerwerk, Lübeck, West Germany, 1970, pp. 33-71.

in a manufacturer's list of specifications for an instrument and this has been so noted in Table 16-1. The material presented under "Applications and Remarks" provides information on the individual substances which may be analyzed directly by the stipulated technique along with specified interferences and other important considerations. This tabulation is not an official certified list; it is intended as a useful guide in selecting direct read-

ing physical instruments on the basis of desired operating parameters.

#### DIRECT READING COLORIMETRIC DEVICES

##### Operating Principles

Direct-reading colorimetric devices utilize the chemical properties of an atmospheric contaminant for the reaction of that substance with a

color-producing reagent. Reagents used in detector kits may be in either a liquid or a solid phase or provided in the form of chemically treated papers. The liquid and solid reagents are generally supported in sampling devices through which a measured amount of contaminated air is drawn. On the other hand, chemically treated papers are usually exposed to the atmosphere and the reaction time noted for a color change to occur.

**Liquid Reagents.** Liquid reagents may be supplied in sealed ampoules or in tubes for field use. Such preparations are provided in a concentrated or a solid form for easy dilution or dissolution at the sampling site. Representative of this type of reagent are the ortho-tolidine and the Griess-Iso-vay kits for chlorine and nitrogen dioxide, respectively. Although the glassware needed for these applications may be somewhat inconvenient to transport to the field, methods based on the use of liquid reagents are more accurate than those which use solid reactants. This is due to the inherently greater reproducibility and accuracy of color measurements made in a liquid system.

**Chemically Treated Papers.** Papers impregnated with chemical reagents have found wide applications for many years for the detection of toxic substances in air. Examples include the use of mercuric bromide papers for the detection of arsine, lead acetate for hydrogen sulfide, and a freshly impregnated mixture of o-tolidine and cupric acetate for hydrogen cyanide. When a specific paper is exposed to an atmosphere containing the contaminant in question, the observed time of reaction provides an indication of the concentration of that substance. Thus, in the case of hydrogen cyanide a 5-second response time by the o-tolidine-cupric acetate paper is indicative of a concentration of 10 ppm of HCN in the tested atmosphere.

Similarly, sensitive detector crayons have been devised for the preparation of a reagent smear on a test paper whose response to a specific toxic substance in a suspect atmosphere may then be timed to obtain an estimation of the atmospheric concentration of a contaminant. Crayons for phosgene, hydrogen cyanide, cyanogen chloride, and Lewisite (ethyl dichloroarsine) have been formulated for this purpose.<sup>3</sup>

**Colorimetric Indicator Tubes.** Colorimetric indicating tubes containing solid reagent chemicals provide compact direct-reading devices, which are convenient to use for the detection and semiquantitative estimation of gases and vapors in atmospheric environments. There are tubes for nearly two hundred atmospheric contaminants on the market, and seven U.S. companies manufacture and/or distribute these devices currently in this country.<sup>4</sup> Whereas it is true that the operating procedures for these tubes are simple, rapid and convenient, there are distinct limitations and potential errors inherent in this method of assessing atmospheric concentrations of toxic gases and vapors. Therefore, dangerously misleading results may be obtained with these devices unless they are used under the supervision of an adequately trained industrial hygienist who (1) enforces rig-

idly (a) the periodic (as required) calibration of individual batches of each specific type of tube for its response to known concentrations of the contaminant and (b) the refrigerated storage of all tubes to minimize their rate of deterioration; (2) informs his staff of the physical and chemical nature and extent of interferences to which a given type of tube is subject and limits the tube's usage accordingly; and (3) stipulates how and when other independent sampling and analytical procedures will be employed to derive needed quantitative data.

Colorimetric indicating tubes are filled with a solid granular material, such as silica gel or aluminum oxide, which has been impregnated with an appropriate chemical reagent. The ends of the glass tubes are sealed during manufacture. When a tube is to be used, its end tips are broken off, the tube is placed in the manufacturer's holder, and the recommended volume of air is drawn through the tube by means of the air moving device provided by the manufacturer. This device may be one of several types such as a positive displacement pump, a simple squeeze bulb, or a small electrically operated pump with an attached flow meter. Each air moving device must be calibrated after each usage or after sampling 100 tubes as an arbitrary rule or more often if there are reasons to suspect changes due to effects of a corrosive action from contaminants in tested atmospheres. An acceptable pump should be correct to within  $\pm 5\%$  by volume; with use, its flow characteristics may change. It should also be checked for leakage and plugging of the inlet after every 10 samples.

In most cases, a fixed volume of air is drawn through the detector tube although, with some systems, varied amounts of air may be sampled. The operator compares either an absolute length-of-stain produced in the column of the indicator gel or a ratio of the length-of-stain to the total gel length against a calibration chart to obtain an indication of the atmospheric concentration of the contaminant that reacted with the reagent. In another type of tube, a progressive change in color intensity is compared with a chart of color tints in making the estimation. In a third type of detector, the volume of sampled air which is required to produce an immediate color change is noted; it is intended that this air volume should be inversely proportional to the concentration of the atmospheric contaminant. The remainder of this chapter is devoted to the direct-reading, colorimetric indicating detector tube systems because of the widespread use of these devices.

#### **Detector Tube Characteristics**

**Reagents and Interferences.** Complete information on the formulations of the chemical reagents used in the manufacture of the commercial devices is not available owing to the understandably competitive nature of this enterprise. However, there is sufficient knowledge of the chemical nature of certain solid reactants commonly used for this purpose to provide the limited information on chemical reactants, products, color changes, and stated interferences given in Table

TABLE 16-2  
Select List of Detecting Reactions in  
Colorimetric Indicating Tubes\*

Test Gas or Vapor	Reagents in			Product(s)	Color Change	Stated Interferences
	Pre-cleanse Layer	Ampoule or Conversion Layer	Indicating Layer			
Acetone	None	None	2, 4-Dinitrophenylhydrazine	A hydrazone	Pale Yellow to Yellow	Other ketones and aldehydes, alcohols, esters
Acrylonitrile	None	(1) Chromate (VI) Compound	(2) Mercuric chloride (3) Methyl red	(1) Hydrogen cyanide (2) Hydrogen chloride (3) Red form of indicator	Yellow to red	HCl, HCN, organic CN compounds, aromatic solvents
Alcohol	Drying agent	None	Chromate (VI) compound	Chromic (III) compound	Yellow to green	Other oxygenated compounds
Ammonia	None	None	(1) Acid (2) Bromophenol blue	(1) Ammonium salt (2) Blue form of indicator	Orange to dark blue	Amines, Hydrazines
Aniline	None	(1) Furfural	(2) Acid	(1) Schiff base (2) Dianiline derivative	White to red	Ammonia
Arsine	Copper compound (to retain reduced S compounds, H <sub>2</sub> Se, NH <sub>3</sub> and HCl)	None	Gold compound	Colloidal gold	White to weak violet grey	Phosphine, stibine
Benzene	Acid and aldehyde (to retain other aromatics)	None	(1) Formaldehyde (2) Sulfuric acid	(1) Diphenylmethane (2) p-Quinoid compound	White to brown	None affect the indication
Carbon Dioxide	None	None	(1) Hydrazine (2) Crystal violet	(1) Carbonic Acid Monohydrazide (2) Blue form of indicator	White to blue	None affect the indication
Carbon Disulfide	Copper compound (to retain H <sub>2</sub> S)	None	(1) Copper compound (2) Amine	Copper Dialkyldithiocarbamate	Pale blue to yellowish green	None affect the indication (except H <sub>2</sub> S)
Carbon Monoxide	Chromate (VI) compound (to retain H <sub>2</sub> S, C <sub>6</sub> H <sub>6</sub> , petroleum compounds)	None	(1) Iodine pentoxide (2) Selenium dioxide (3) Fuming sulfuric acid	Iodine (and carbon dioxide)	White to brownish green	Acetylene and easily cleaved halogenated hydrocarbons

TABLE 16-2 (Continued)  
Select List of Detecting Reactions in  
Colorimetric Indicating Tubes\*

Test Gas or Vapor	Reagents in			Product(s)	Color Change	Stated Interferences
	Pre-cleanse Layer	Ampoule or Conversion Layer	Indicating Layer			
Carbon Tetrachloride	None	(1) Fuming Sulfuric acid	(2) Dimethyl-amino-benzaldehyde (3) Dimethyl-aniline	(1) Phosgene (2) "Blue reaction product"	Yellow to blue	Fluorochloromethane compounds
Chlorine	Drying agent	None	o-Tolidine	"Yellow reaction product"	White to yellow	Bromine, chlorine dioxide; discoloration by nitrogen dioxide
Chloroprene	None	None	Permanganate	"Yellowish Brown Reaction Product"	Violet to yellowish brown	Other organic compounds with carbon-carbon double bonds
Cyanogen Chloride	None	(1) Pyridine (2) Water	(3) Barbituric acid	(1) & (2) Glutaconaldehyde cyanamide (3) "Pink Reaction Product"	White to pink	Cyanogen bromide
Ethyl acetate	Drying agent	None	Chromosulfuric acid	Chromic (III) compound	Orange to brown green	Easily oxidized organic compounds including other acetates
Formaldehyde	None	(1) Xylene vapor	(2) Sulfuric acid	(1) Dixylyl methane (2) "Pink quinoid compound"	White to pink	Other aldehydes and styrene
Hydrazine	None	None	(1) Acid (2) Bromophenol blue	(1) Hydrazinium salt (2) Blue form of indicator	Yellow to blue	1,1-Dimethyl hydrazine, ammonia, amines
Hydrochloric Acid	Drying agent	None	Bromophenol blue	Yellow form of indicator	Blue to yellow	Chlorine; R.H. > 80%
Hydrocyanic Acid	Lead compound (to retain H <sub>2</sub> S, HCl, SO <sub>2</sub> , NO <sub>2</sub> and NH <sub>3</sub> )	None	(1) Mercuric Chloride (2) Methyl red	(1) Hydrogen chloride (2) Red form of indicator	Yellow to red	None affect the indication (except those not retained in pre-cleanse layer)
Hydrogen fluoride	None	None	Zirconium-alizarin lake	Alizarin	Pale violet to pale yellow	High humidity
Hydrogen sulfide	None	None	Lead compound	Lead Sulfide	White to light brown	None affect the indication
Mercaptan	None	(2) Sulfur solution	(1) Copper compound	(1) Copper mercaptide (2) Yellowish brown copper compound	White to yellowish brown	Other mercaptans, hydrogen sulfide, ammonia, amines

TABLE 16-2 (Continued)  
Select List of Detecting Reactions in  
Colorimetric Indicating Tubes\*

Test Gas or Vapor	Reagents in			Product(s)	Color Change	Stated Interferences
	Pre-cleanse Layer	Ampoule or Conversion Layer	Indicating Layer			
Methyl bromide	None	(1) Sulfur trioxide (2) Permanganate	(3) o-dianisidine	(1) & (2) Bromine (3) "Brown Reaction Product"	White to brown	Halogens, halides, halogenated hydrocarbons
Mono-styrene	Drying agent	None	Sulfuric acid	"Yellow Reaction Product"	White to yellow	Butadiene and other polymertending organic compounds
Nickel tetracarbonyl	None	(2) Dioxime	(1) Iodine	(1) Nickel iodide (2) Nickel dioxime complex	Pale brown to pink	Iron pentacarbonyl, hydrogen sulfide, sulfur dioxide
Nitrogen dioxide (NO <sub>2</sub> )	Drying agent	None	N,N'-diphenylbenzidine	"Bluish grey Reaction Product"	White to bluish grey	Ozone, chlorine
Nitrous fumes (NO + NO <sub>2</sub> )	None	(1) Chromium (VI) compound	(2) N,N'-diphenylbenzidine	(1) Nitrogen dioxide (2) "Bluish grey reaction product"	White to bluish grey	Ozone, chlorine
Ozone	None	None	Indigo	Isatine	Pale blue to white	Chlorine, nitrogen dioxide
Perchloroethylene	None	(1) Permanganate	(2) N,N'-diphenylbenzidine	(1) Chlorine (2) "Greyish blue Reaction Product"	White to greyish blue	Halogens, hydrogen halides, easily cleaved halogenated hydrocarbons, petroleum vapor
Phenol	None	(1) 2,6-dibromoquinone chlorimide	(2) Activated silica gel	(1) & (2) Indophenol dye	White to blue	Other aromatic hydroxy compounds, quinones; ammonia and amines discolor indicating layer
Phosgene	Drying agent	None	(1) Dimethylaminobenzaldehyde (2) Diethylaniline	Bluish green complex	Yellow to bluish green	Carbonyl bromide
Phosphine	Copper compound (to retain reduced sulfur compounds, NH <sub>3</sub> , H <sub>2</sub> S & H <sub>2</sub> Se)	None	Gold compound	Colloidal gold	White to weak greyish violet	Arsine, stibine
Sulfur dioxide	Copper compound (to retain H <sub>2</sub> S)	None	Iodine/ Starch	Sulfuric acid	Blue to white	Nitrogen dioxide

**TABLE 16-2 (Continued)**  
**Select List of Detecting Reactions in**  
**Colorimetric Indicating Tubes\***

Test Gas or Vapor	Reagents in			Product(s)	Color Change	Stated Interferences
	Pre-cleanse Layer	Ampoule or Conversion Layer	Indicating Layer			
Toluene	Drying agent	None	(1) Iodine pentoxide (2) Dilute sulfuric acid	(1) & (2) Iodine	White to brown	Xylenes, benzene
Trichloroethane	None	(1) Sulfuric acid (2) Oxidizing agent	(3) o-dianisidine	(1) & (2) Chlorine (3) "Brownish red Reaction Product"	Pale grey to brownish red	Some other halogenated hydrocarbons; petroleum hydrocarbons & aromatic compounds >1000 ppm
Trichloroethylene	None	(1) Permanganate	(2) o-tolidine	(1) Chlorine (2) "Orange Reaction Product"	White to orange	Halogens, halides, easily cleaved halogenated hydrocarbons, petroleum distillate vapors
Vinyl chloride	None	None	Permanganate	Light brown manganese compound	Violet to light brown	Organic compounds with carbon-carbon double bond

\* Taken from Draeger Detector Tube Handbook, Draegerwerk. Lübeck, West Germany, 1970, pp. 33-71.

16-2. From this table it is apparent that the lack of specificity encountered with certain detector tubes is due to the use of common reagents for numerous compounds. Thus, the use of a hexavalent chromium compound for the oxidation of a wide variety of organic substances with the production of a green chromic reaction product is a completely nonspecific procedure for these substances. This type of detector tube must be used with the realization that all readily oxidizable substances may affect the indication and efforts should therefore be taken to ascertain the chemical nature of the various associated contaminants in each exposure situation. Further, aromatic hydrocarbons, hydrides, halides, and chlorinated hydrocarbons provide other examples of class compounds for which single formulations in detector tube reactants may have been used. Such formulations limit the usefulness of these tubes in mixed exposure areas as the estimations are then based on the results of the reaction of a mixture of contaminants. Furthermore, errors of estimation may be positive or negative depending upon whether a stain is intensified (or lengthened) by the presence of a similarly reacting contaminant or bleached by a differing chemical contaminant present in the sampled air stream. This general situation has evoked a great deal of criticism of detector tube systems by the industrial hygiene profession which recognizes the need for improved devices of this type.

Efforts to overcome this cross sensitivity have been attempted by: a. Use of a pre-layer to remove certain known interferences from the air stream before they reach the indicating layer; and b. Use of a conversion layer to transform the desired gaseous substance to a different chemical compound which can then react with the indicating layer.

Examples of the incorporation of a pre-layer in the formulation of a tube include the Dräger Arsiné 0.05/a and the Benzene 0.05 tubes. The former uses a copper compound to retain in the pre-layer such interferences as hydrogen sulfide, hydrogen selenide, mercaptans, ammonia, and hydrogen chloride, but allows arsine to pass through to the indicating layer containing a gold compound with which the arsine reacts to yield a weak violet-gray color. The benzene 0.05 tube has an acid-aldehyde reagent to remove toluene, xylene and naphthalene; benzene passes on into the indicating layer where it produces a brown color from its reaction with formaldehyde and sulfuric acid.

Another difficulty arising from detector tube reagents is the catalyzed reaction of gaseous contaminants with one another due to the active contact surface provided by the column of chemicals in the detector tube. This phenomenon has been observed with sulfur dioxide and nitrogen dioxide when these gases are brought into closer molecular contact in detector tubes than that prevailing

in ambient atmospheres where their reaction rate with each other is generally low.

**Quality Control.** The rigid control of the purity of reagents, grain size of the gel, method of packing the tubes, moisture content of the gel, uniformity of tube diameter, and proper storage precautions is required for the optimal performance of any detector tube. The lack of such controls will lead to an inferior product whose use may produce disastrous results in the evaluation of health related problems. Thus, an incompletely responsive tube could cause a hazardous situation to remain uncorrected. Conversely, an overly reactive response may cause undue concern, wasted effort and needless expense for unwarranted corrections.

Failure of certain manufacturers to maintain a rigid control over manufacturing practices has been observed in the past. Although it has been established<sup>5</sup> that an elevated moisture content above 20% will cause a rapid deterioration of the silica gel used in the potassium pallado-sulfite formulation for a carbon monoxide tube, one observer found during a visit to a detector tube manufacturing facility that there was a lapse of many hours following the packing but preceding the hermetical sealing of the tubes.<sup>6</sup> Indeed, such a practice permits the entry of not only moisture but also other contaminating vaporous substances which might produce a deleterious effect on the reagent's future response to the analysis substance.

Another critical parameter is the tube diameter. Manufacturing variations in the internal diameter of the narrower tubes can produce appreciably different cross sectional areas. Saltzman has pointed out that this situation leads to calibration errors as high as 50 percent due to a varying volume of air sample per unit cross sectional area as compared with those provided under standard test conditions.<sup>7</sup> At least one manufacturer minimizes the effect of this source of error by loading equal amounts of the indicating gel into each tube; the variations in cross sectional areas are then compensated by corresponding variations in the filled lengths of the tubes.<sup>8</sup> The manufacturer provides calibration scales which permit the positioning of each tube in accordance with its filled length when measuring the length of stain and thus reduce the overall error of measurement of the gas concentration.

Variations in the grain size of the gel, in the purity of the reagents and the cleanliness of the air in the tube manufacturing facility can affect the properties of different batches of the indicating gel markedly. If not controlled carefully, these parameters can cause marked and unpredictable changes in the number of active centers on the solid surface of the gel and thus affect the reaction velocity of the indicating system.

The method of storage has a profound effect on the shelf life of an indicator tube. Deterioration of the tubes increases greatly at elevated temperatures and storage under refrigeration by both the manufacturer and the user is mandatory to realize a useful shelf life which may approximate

two years for some of the tubes. Multiple layer tubes may have a shorter shelf life due to diffusion of chemicals between layers. For these reasons a realistic expiration date for tubes stored under refrigeration should be stamped on each box of tubes by the manufacturer.

**Calibration.** Saltzman has presented an excellent treatment of the theory of indicator tube calibration where he has developed a basic mathematical analysis of the relationships between the variables which affect the length of stain, i.e., the concentration of test gas, volume of air sample, sampling flowrate, grain size of gel, tube diameter and other variables. This source should be consulted for a full appreciation of the complex interrelationships between the factors affecting the kinetics of indicator tube reactions. It is sufficient to point out in this chapter that the length of stain is proportional to the logarithm of the product of gas concentration and air sample volume as shown in the following equation:<sup>7</sup>

$$L/H = \ln(CV) + \ln(K/H)$$

where: L = the length of stain in centimeters,

C = the gas concentration in parts per million,

V = the air sample volume in cubic centimeters,

K = a constant for a given type of indicator tube and test gas,

H = a mass transfer proportionality factor having the dimensions of centimeters, and known as the height of a mass transfer unit.

If this mathematical model is correct for a given indicator tube, a linear plot of L versus the logarithm of the CV product, for a fixed constant flowrate, will yield a straight line with slope = H. The significance of this equation is the implication that it is important to control the flowrate, which may produce a greater effect on the length of stain than does the concentration of the test gas. Therefore, in the optimal design of an indicator tube it is desirable that the reaction rate be sufficiently rapid to permit the establishment of equilibrium between the indicating gel and the test gas and thus produce a stoichiometric relationship between the volume of stained indicating gel and the quantity of the absorbed test gas. Such equilibrium conditions may be assumed to exist when stain lengths are directly proportional to the volume of sampled air and are not affected by the sampling flowrate.<sup>7</sup> With this situation a log-log plot of stain length versus concentration for a fixed sample volume may be prepared in the calibration of a given batch of tubes.

From the preceding discussion of the complexity of the heterogeneous phase kinetics of indicator tube reactions, the quality control problems associated with their manufacture and storage, and the difficulties posed by interfering substances, it is obvious that frequent, periodic calibration of these devices should be made by the user. Dynamic dilution systems for the reliable preparation of low concentrations of a test gas or vapor are recommended for this purpose (see

Chapter 12). Such calibrations should be performed before each use if there has been an appreciable period since the last calibration was performed.

### Evaluation of Performance

As of January 1, 1972, the results of the evaluation of gas detector tubes for five substances had been published by the National Institute for Occupational Safety and Health.<sup>9,10,11,12,13</sup>

The results are as follows:

Substance	No. of Manufactured Tubes Meeting Approval Criterion Within	
	± 25% at 95% C.L.*	± 50% at 95% C.L.
Benzene	None	3
Carbon Monoxide	None	8
Carbon Tetrachloride	None	None
Perchloroethylene	3	—
Sulfur Dioxide	4	—

\*95% Confidence Level

### References

- HARRINGTON, D. U. S. Bureau of Mines Information Circular No. 7072 (1939), Washington, D.C.
- TIMBRELL, V. "The Inhalation of Fibrous Dusts," Biological Effects of Asbestos, *Annals of the New York Academy of Sciences*, 132, 255-273 (December 31, 1965), New York, New York.
- WITTEN, BENJAMIN and ARNOLD PROSTAK. "Sensitive Detector Crayons for Phosgene, Hydrogen Cyanide, Cyanogen Chloride, and Lewisite." *Analytical Chemistry*, 29, 885-887, 1155 Sixteenth NW, Washington, D. C. (1957).
- SALTZMAN, BERNARD E., Ph.D. "Direct Reading Colorimetric Indicators" *Air Sampling Instruments*, Section S. American Conference of Governmental Industrial Hygienists, P. O. Box 1937, Cincinnati, Ohio, Fourth Edition, pp. S-1 and S-11 (1972).
- SILVERMAN, L. and G. R. GARDNER. "Potassium Pallado-Sulfite Method for Carbon Monoxide Detection," *American Industrial Hygiene Association Journal*, 26, pg. 2, 210 Haddon Ave., Westmont, New Jersey (March-April, 1965).
- KUSNETZ, HOWARD L. "Evaluation of Chemical Detector Tubes," Paper presented at Chemical Section, National Safety Congress, Chicago, Illinois (October 27, 1965).
- SALTZMAN, BERNARD E. "Direct Reading Colorimetric Indicators," Section S, *Air Sampling Instruments*, American Conference of Governmental Industrial Hygienists, Cincinnati, Ohio, Fourth Edition (1972).
- SALTZMAN, BERNARD E. "Basic Theory of Gas Indicator Tube Calibration," *American Industrial Hygiene Association Journal*, 23, pg. 112-126, 210 Haddon Ave., Westmont, New Jersey 08108 (March-April, 1962).
- MORGANSTERN, ARTHUR S., ROBERT M. ASH, and JEREMIAH R. LYNCH. "The Evaluation of Gas Detector Tube Systems: I. Carbon Monoxide," *American Industrial Hygiene Association Journal*, 31, pg. 630-632, 210 Haddon Ave., Westmont, New Jersey 08108 (September-October, 1970).
- ASH, ROBERT M. and JEREMIAH R. LYNCH. "The Evaluation of Gas Detector Tube Systems: Benzene," *American Industrial Hygiene Association Journal*, 32, pg. 410-411, 210 Haddon Ave., Westmont, New Jersey 08108 (June, 1971).
- ASH, ROBERT M. and JEREMIAH R. LYNCH. "The Evaluation of Gas Detector Tube Systems: Carbon Tetrachloride," *American Industrial Hygiene Association Journal*, 32, pg. 552-553, 210 Haddon Ave., Westmont, New Jersey 08108 (August, 1971).
- ASH, ROBERT M. and JEREMIAH R. LYNCH. "The Evaluation of Gas Detector Tube Systems: Sulfur Dioxide," *American Industrial Hygiene Association Journal*, 32, pg. 490-491, 210 Haddon Ave., Westmont, New Jersey 08108 (July, 1971).
- ROPER, C. PAUL. "An Evaluation of Perchloroethylene Detector Tubes," *American Industrial Hygiene Association Journal*, 32, pg. 847-849, 210 Haddon Ave., Westmont, New Jersey 08108 (December, 1971).