T

DETECTOR TUBES, DIRECT-READING PASSIVE BADGES AND DOSIMETER TUBES

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Contents

Development of Detector Tubes

Three types of direct-reading, colorimetric indicators have been in use for the determination of contaminant concentrations in air: liquid reagents, chemically treated papers, and glass indicating tubes containing solid chemicals. A comprehensive bibliography in this area was prepared by Campbell and Miller.[1]

Convenient laboratory procedures using liquid reagents have been simplified and packaged for field use. Reagents are supplied in sealed ampoules or tubes, frequently in concentrated or even solid forms which are diluted or dissolved for use. Unstable mixtures may be freshly prepared when needed by breaking an ampoule containing one ingredient inside a plastic tube or bottle containing the other. Commercial apparatus of this type is available for tetraethyl lead and tetramethyl lead. Certain liquid reagents, such as the nitrogen dioxide sampling reagents, produce a direct color upon exposure without requiring additional chemicals or manipulations. These permit simplified sampling equipment. Thus, relatively high concentrations of nitrogen dioxide may be determined directly by drawing an air sample into a 50- or 100-ml glass syringe containing a measured quantity of absorbing liquid reagent, capping, and shaking. Liquids containing indicators have been used for determining acid or alkaline gases by measuring the volume of air required to produce a color change. These liquid methods are somewhat inconvenient and bulky to transport and require a degree of skill to use. However, they are capable of good accuracy, as measurement of color in liquids is inherently more reproducible and accurate than measurement of color on solids.

Chemically treated papers have been used to detect and determine gases because of their convenience and compactness. An early example of this is the Gutzeit method in which arsine blackens a paper strip impregnated previously with mercuric bromide. Such papers may be freshly prepared and used wet or stored and used in the dry state. Special chemical chalks or crayons have been used[2] to sensitize ordinary paper for phosgene, hydrogen cyanide, and other war gases. Semiquantitative determinations may be made by hanging the paper in contaminated air. Inexpensive detector tabs are available commercially which darken upon exposure to carbon monoxide.[3] The accuracy of such procedures is limited by the fact that the volume of the air sample is rather indefinite and the degree of color change in the paper is influenced by air currents and temperature. More quantitative results may be obtained by using a sampling device capable of passing a measured volume of air over or through a definite area of paper at a controlled rate, as is done in a commercial device for hydrogen fluoride. Particulate matter contaminants such as chromic acid and lead may be determined similarly, usually by addition of liquid reagents to the sample on a filter paper. Visual evaluation of the stains on the paper may be made by comparison with color charts or by photoelectric instruments. Recording photoelectric instruments utilizing sensitized paper tapes operate in this manner and are described in another section. Accuracy of these methods requires uniform sensitivity of the paper, stability of all chemicals used, and careful calibration. In the case of particulate matter analysis, it may be necessary to calibrate with the specific dust being sampled if the degree of chemical solubility is an important factor.

Glass indicating tubes containing solid chemicals are another type of convenient and compact direct-reading device. The early detector tubes were made for carbon monoxide,[4-6] hydrogen sulfide,[7,8] and benzene.[9,10] During the past decades, there has been a great expansion in the development and use of these tubes,[11-32] and more than 400 different types are now available commercially. Several manuals provide comprehensive descriptions and listings.[33-35] Because of the great popularity and wide use of glass detector tubes, the bulk of this introduction will deal with them, although much of the information will be applicable to the liquid and paper indicators as well.

Applications of Detector Tubes

There are many uses for detector tubes. They are convenient for qualitative[36] and quantitative evaluation of toxic hazards in industrial atmospheres. They

are also useful for air pollution studies, although in most situations currently available tubes do not have the required sensitivity. Detector tubes may be used for detection of explosive hazards, as well as for process control of gas composition. Confirmation of carbon monoxide poisoning may be made by determining carbon monoxide in exhaled breath or in gas released from a sample of blood (*after an appropriate procedure*). Detector tubes may be used for law enforcement purposes, such as determining alcohol in the breath, or gasoline in soil in cases of suspected incendiarism or of leakage from underground tanks. Minute quantities of ions in aqueous solutions also may be determined such as sulfide in waste water from pulp manufacturing, chromic acid in electrolytic plating waste water, and nickel ion in waste water of refineries.

Detector tubes have been widely advertised as being capable of use by unskilled personnel. While it is true that the operating procedures are simple, rapid, and convenient, many limitations and potential errors are inherent in this method. The results may be dangerously misleading unless the sampling procedure is supervised and the findings interpreted by an adequately trained occupational hygienist.

Operating Procedures

The use of detector tubes is extremely simple. After its two sealed ends are broken open, the glass tube is placed in the manufacturer's holder which is fitted with a calibrated squeeze bulb or piston pump. The recommended air volume is then drawn through the tube by the operator. Adequate time must be allowed for each stroke. Even if a squeeze bulb is fully expanded, it may still be under a partial vacuum and may not have drawn its full volume of air. The manufacturer's sampling instructions must be followed closely.

The observer then reads the concentration in the air by examining the exposed tube. Some of the earlier types of tubes are provided with charts of color tints to be matched by the solid chemical in the indicating portion of the tube. This visual judgment depends, of course, upon the color vision of the observer and the lighting conditions. In an attempt to reduce the errors due to variations among observers, most recent types of tubes are based upon producing a variable length of stain on the indicator gel. Although in a few tubes a variable volume of sample is collected until a standard length of stain is obtained, in most cases a fixed volume of sample is passed through the tube and the stain length is measured against a calibration scale. The scale may be printed either directly upon the tube or on a provided chart. In a few tubes, such as those for arsine and stibine, a variable volume of sample is drawn through the tube until the first visible discoloration is noted. This is a very difficult judgment which must be made retrospectively. The range in the interpretation of results by different observers is large, since in many cases the end of a stain front is not sharp. Experience in sampling known concentrations is of great value in training an operator to know whether to measure the length up to the beginning or end of the stain front, or some other portion of an irregularly shaped stain. In some cases, the stains change with time; thus, the reading should not be unduly delayed.

Care must be taken to see that leak-proof pump valves and connections are maintained. A leakage test may be made by inserting an unopened detector tube into the holder and squeezing the bulb; at the end of two minutes any appreciable bulb expansion is evidence of a leak. If the apparatus is fitted with a calibrated piston pump, the handle is pulled back and locked. Two minutes later, it is released cautiously and the piston allowed to pull back in; it should remain out no more than 5% of its original distance. Leakage indicates the necessity of replacing check valves, tube connections, or the squeeze bulb, or of greasing the piston.

At periodic intervals, the flow rate of the apparatus should be checked and maintained within specifications for the tube calibrations (generally $\pm$ 10%). This may be done simply by timing the period of squeeze bulb expansion. A more accurate method is to place a used detector tube in the holder and to draw an air sample through a calibrated rotameter. Alternatively, the air may be drawn from a burette in an inverted vertical position, which is sealed with a soap film, and the motion of the film past the graduations timed with a stop watch.[37] The latter method also provides a check on the total volume of the sample which is drawn. In some devices, the major resistance to the air flow is in the chemical packing of the tube; thus, each batch might require checking. An incorrect flow rate indicates a partially clogged strainer or orifice which should be cleaned or replaced.

With most types of squeeze bulbs and hand pumps, the sample air flow rate is variable, being high initially and low towards the end when the bulb or pump is almost filled. This has been claimed to be an advantage because the initially high rate gives a long stain and the final low rate sharpens the stain front. Flow patterns for six commonly used pumps were found to be different.[38,39] When five popular brands of carbon monoxide tubes were used with pumps other than their own, grossly erroneous results were obtained, even with identical sample volumes. The stains may depend more on flow rate than on concentrations. It should be noted that accuracy requires a close reproduction of the flow rate pattern for the calibrations to be correct.

A number of special techniques may be used in appropriate cases. When sampling in inaccessible places, the indicator tube may be placed directly at the sampling point and the pump operated at some distance

away. A rubber tube extension of the same inside diameter as the indicator tube may be inserted between the pump and indicator tube. Such tubes are available commercially as accessories. Lengths as great as 60 feet have been successfully used without appreciable error, provided that more time is allowed between strokes of the pump to compensate for the reservoir effect and to obtain the full volume of sample. This method has the disadvantage that the detector tube cannot be observed during the sampling.

A second arrangement may be used when sampling hot gases such as from a furnace stack or engine exhaust. Cooling the sample is essential in these cases, otherwise the calibration would be inaccurate and the volume of the gas sample uncertain. A probe of glass or metal, available commercially as an accessory, may be attached to the inlet end of the detector tube with a short piece of flexible tubing.[40] If this tube is cold initially, as little as 10 cm of tubing outside of the furnace is sufficient to cool the gas sample from 250°C to about 30°C. Such a probe has to be employed with caution. In some cases, serious adsorption errors occur either on the tube or in condensed moisture. The dead volume of the probe should be negligible in comparison to the volume of sample taken. Solvent vapors should not be sampled with this method. When sampling air colder than 0°C, clasping the tube in the hand warms it sufficiently to eliminate any error.[40] Critical studies[41,42] of applications to analysis of diesel exhaust showed serious errors for some tubes.

Other special techniques may also be employed. Some symmetrical tubes can be reversed in the holder and used for a second test. In certain special cases, tubes may be re-used if a negative test was previously obtained or after the color has faded. Two tubes also may be connected in series in special cases; e.g., first passing crude gas through a Kitagawa hydrogen sulfide tube and then a phosgene tube to obtain two simultaneous determinations and remove interferences. These techniques may be used only after testing to demonstrate that they do not impair the validity of the results.

Tubes also have been used in pressures as high as several atmospheres. This situation would exist, for example, in underwater stations. If both the tube and pump are in the chamber, the calibrations and sample volumes are altered. It has been reported[40,43] that only the latter occurs for the following Draeger tubes: ammonia 5/a, arsine 0.05/a; CO_2 0.1%/a; CO 5/c, 10/b; H_2S 1/c, 5/b. For these tubes, the corrected concentration is equal to the scale reading (ppm or vol %) divided by the ambient pressure (in atmospheres) at the pump. When tube tips are broken in a pressure chamber, the tube filling should be checked for possible displacement.

Specificity and Sensitivity

The specificity of the tubes is a major consideration for determining applicability and interpreting results. Most tubes are not specific. Chromate reduction is a common reaction used in tubes for detection of organic compounds. In the presence of mixtures, the uncritical acceptance of such readings can be grossly misleading. Comprehensive listings of reactions, as well as a discussion of other major aspects, are available.[33,34,44] Six common reactions and the associated tube types are listed in Table T-1. It can be seen that the name of the compound listed on the tube often refers to its calibration scale rather than to a unique chemical reaction of its contents.

The lack of specificity of some tubes may be used to advantage for detection of substances other than those indicated by the manufacturer. In this respect, tubes using colorimetric reactions 1, 2, and 6 (Table T-1) are widely applicable. Thus, the Draeger Polytest screening tube (reaction 2) and ethyl acetate tube (reaction 1) may be used for qualitative indications of reducing and organic materials, respectively.[45] The Draeger trichloroethylene tube (reaction 6a) is also applicable to chloroform, o-dichlorobenzene, dichloroethylene, ethylene chloride, methylene chloride, and perchloroethylene. The methyl bromide tube may be used for chlorobromomethane and methyl chloroform. The chlorine tube may be used for bromine and chlorine dioxide. The toluene tube may be used for xylene. Such use requires specific knowledge of the identity of the reagent and of the proper corrections to the calibration scales.

For some brands of indicator tubes, the units of the calibration scales are in milligrams per cubic meter. Although it has been said that this method of expression eliminates the necessity of making temperature and pressure corrections, such a claim is debatable since the scale calibrations themselves may be highly dependent upon these variables. Units of parts per million or percent by volume are most common for industrial hygiene purposes and are used on most of the newer tubes. Conversions may be made from milligrams per cubic meter to parts per million by the formula given in *Chapter F.*

Although detector tubes are generally designed for detection of relatively high gas concentrations found in industrial workplaces, some have been applied to the much lower outdoor air pollutant concentration. Kitagawa[46] determined 0.01 to 2 ppm of NO_2 using two glass tubes in series, with the temperature controlled at 40°C. The first tube contained diatomaceous earth impregnated with a specific concentration of sulfuric acid to regulate the humidity of the air sample. The second tube, 120 mm long × 2.4 mm inside diameter, contained white silica gel impregnated with ortho-

TABLE T-1. Common Colorimetric Reactions in Gas Detector Tubes

1. Reduction of chromate or dichromate to chromous ion:

   Draeger: Acetaldehyde 100/a; alcohol 100/a; aniline 0.5/a; cyclohexane 100/a; diethyl ether 100/a; ethyl acetate 200/a; ethyl glycol acetate 50/a; n-hexane 100/a; methanol 50/a; n-pentane 100/a.

   Gastec: Acetone 151; aniline 181; butane 104; butyl acetate 142; ethanol 112; ethyl acetate 141; ethyl ether 161; ethylene oxide 163; gasoline 101, 101L; hexane 102H, 102L; isopropanol 113; LP gas 100A; methanol 111; methyl ethyl ketone 152; methyl isobutyl ketone 153; propane 100B; sulfur dioxide 5H; vinyl chloride 131.

   Kitagawa: Acetone 102A; acrylonitrile 128A, 128B; butadiene 168A; butyl acetate 138; cyclohexane 115; dimethyl ether 123; dioxane 154; ether 107; ethyl acetate 111; ethyl alcohol 104A; ethylene oxide 122; furan 161; n-hexane 113; isobutyl acetate 153; isopropanol 150; isopropyl acetate 149; methyl acetate 148; methyl alcohol 119; methyl ethyl ketone 139B; methyl isobutyl ketone 155; propyl acetate 151; propylene oxide 163; sulfur dioxide 103A; tetrahydrofuran 162; vinyl chloride 132.

   MSA: *Part 95097* for n-amyl alcohol, iso-amyl alcohol, sec-amyl alcohol, tert-amyl alcohol, 2-butoxyethanol (butyl Cellosolve), n-butyl alcohol, isobutyl alcohol, sec-butyl alcohol, tert-butyl alcohol, cyclohexanol, 2-ethoxyethanol (Cellosolve), ethyl alcohol (ethanol), ethylene glycol monomethyl ether, furfuryl alcohol, 2-methoxyethanol, methyl alcohol (methanol), 2-methylcyclohexanol, methyl isobutyl carbinol (methyl amyl alcohol), n-propyl alcohol, isopropyl alcohol.

   Part 460423 for acetone, methyl methacrylate.

2. Reduction of iodine pentoxide plus fuming sulfuric acid to iodine:

   Draeger: Benzene 5/b; carbon disulfide 5/a; carbon monoxide 2/a, 5/c, 8/a, 10/a, 10/b, 0.001%/a, 0.1%/a, 0.3%/a, 0.3%/b; ethyl benzene 30/a; hydrocarbon 0.1%/b; natural gas*; perchloroethylene 0.1%/a; petroleum hydrocarbons 100/a; polytest; toluene 5/a, 25/a.

   Gastec: Acetylene 171; benzene 121, 121L; carbon monoxide 1H, 1M; Stoddard solvent 128; toluene 122; vinyl chloride 131; xylene 123.

   MSA: *Part 93074* for benzene (benzol), chlorobenzene, monobromobenzene, toluene (toluol), xylene (xylol).

3. Reduction of ammonium molybdate plus palladium sulfate to molybdenum blue:

   Draeger: Ethylene 0.5/a; 50/a; methyl acrylate 5/a; methyl methacrylate 50/a.

   Gastec: Butadiene 174; ethylene 172, 172L.

   Kitagawa: Acetylene 101; butadiene 168B; carbon monoxide 106A, 106B, 106C*; ethylene 108B; hydrogen sulfide and sulfur dioxide 120C.

   MSA: *Part 47134* for carbon monoxide (NBS color change).

   Part 85802 for acetylene, ethylene, propylene.

4. Reaction with potassium palladosulfite:

   Gastec: Carbon monoxide 1L, 1La, 1LL; hydrogen cyanide 12H.

   MSA: *Part 91229* for carbon monoxide (length of stain).

5. Color change of pH indicators (e.g., bromphenol blue, phenol red, thymol blue, methyl orange):

   Draeger: Acetic acid 5/a; acrylonitrile 5/a*, 5/b*; ammonia 2/a, 5/a, 0.5%/a; chlorobenzene 5/a*; cyanide 2/a*; cyclohexylamine 2/a; dimethyl acetamide 10/a*; dimethylformamide 10/b*; formic acid 1/a; hydrazine 0.25/a; hydrochloric acid 1/a, 50/a; hydrogen cyanide 2/a ($HgCl_2$ μ methyl red); methacrylonitrile 1/a*;nitric acid 1/a; sulfur dioxide 0.1/a*, 50/a; triethylamine 5/a; vinyl chloride 0.5/a*.

   Gastec: Acetaldehyde 92*; acetic acid 81; acrolein 93*; acrylonitrile 191*, 191L*; amines 180: ammonia 3H, 3M, 3L; tert-butyl mercaptan 75; carbon dioxide 2H, 2L; carbon disulfide 13*, 13M; carbonyl sulfide 21; dimethylacetamide 184*; dimethylformamide 183*; formaldehyde 91L*; hydrogen chloride 14L, 14M; hydrogen cyanide 12L*; methacrylonitrile 192; nitric acid 15L; perchloroethylene 133*; pyridine 182; sulfur dioxide 5M, 5L, 5La; trichloroethylene 132H*, 132L*; vinyl chloride 131La*, 131L*.

   Kitagawa: Acetaldehyde 133; ammonia 105B; carbon dioxide 126A, 126B; hydrogen cyanide 112B.

   MSA: *Part 85976* for carbon dioxide. *Part 91636* for hydrogen chloride.

   *Part 92030*** for 1-chloro-1,1-difluoroethane (Genetron 142B), chlorotrifluoromethane (Freon 13), 1,2-dichloroethane (ethylene dichloride), dichloroethylene (trans-1,2), ethyl chloride, fluorotrichloromethane (Freon 11), methyl chloride, methylene chloride (dichloromethane), propylene dichloride (1,2-dichloropropane), 1,1,2-trichloro-1,2,2-trifluoroethane (Freon 113), vinyl chloride (chloroethylene).

   Part 92115 for ammonia, n-butylamine, cyclohexylamine, diisopropylamine, di-n-propylamine, ethylamine, ethylene imine, N-ethylmorpholine, isopropylamine, methylamine, propylene imine, triethylamine, trimethylamine.

   Part 92623 for sulfur dioxide. *Part 93865* for ozone. *Part 95739*** for dimethyl sulfoxide. *Part 460021* for acetic acid. *Parts 460103* and *460158* for ammonia.

   Part 460425 for hydrazine, monomethyl hydrazine, unsymmetrical dimethyl hydrazine.

TABLE T-1 (con't). Common Colorimetric Reactions in Gas Detector Tubes

6a. Reaction with o-tolidine:

Draeger: Chlorine 0.2/a, 0.3/b, 50/a; chloroform 2/a*; epichlorohydrin 5/b*; perchloroethylene 10/b; trichloroethylene 2/a*, 10/a*, 50/d*; vinyl chloride 1/a*.

Gastec: Chlorine 8H, 8La; chloroform 137*; methyl bromide 136*; methyl chloroform 135*; methylene chloride 138*; nitrogen dioxide 9L; nitrogen oxides 10*, 11*.

Kitagawa: Bromine 114; chlorine 109; chlorine dioxide 116; nitrogen dioxide 117.

6b. Reaction with tetraphenylbenzidine:

MSA: *Part 82399* for bromine, chlorine, chlorine dioxide.

Part 83099 for nitrogen dioxide.

*Part 85833** for chlorobromomethane; 1,1-dichloroethane; dichloroethylene (cis-1,2 and trans-1,2); ethyl bromide; ethyl chloride; perchloroethylene (tetrachloroethylene); trichloroethylene; 1,2,3-trichloropropane; vinyl chloride (chloroethylene).

*Part 85834** for chlorobenzene (mono); 1,2-dibromoethane (ethylene dibromide); dichlorobenzene (ortho); 1,2-dichloroethane (ethylene dichloride); dichloroethyl ether; 1,1-dichloroethylene (vinylidine chloride); methyl bromide; methylene chloride (dichloromethane); propylene dichloride (1,2-dichloropropane); 1,1,2,2-tetrabromoethane; 1,1,2,2-tetrachloroethane; 1,1,3,3-tetrachloropropane; trichloroethane (beta 1,1,2); vinyl chloride (chloroethylene).

Part 87042 for bromine; chlorine.

*Part 88536*** for carbon tetrachloride; chlorobromomethane; 1-chloro-1,1-difluoroethane (Genetron 142B); chlorodifluoromethane (Freon 22); chloroform (trichloromethane); chloropentafluoroethane (Freon 115); chlorotrifluoromethane (Freon 13); 1,2-dibromoethane (ethylene dibromide); dichlorodifluoromethane (Freon 12); 1,1-dichloroethylene (vinylidine chloride); dichloroethylene (cis-1,2); dichlorotetrafluoroethane (Freon 114); fluorotrichloromethane (Freon 11); Freon 113; Freon 502; methyl bromide; methyl chloroform (1,1,1-trichloroethane); methylene chloride (dichloromethane); perchloroethylene (tetrachloroethylene); trichloroethane (beta 1,1,2); trichloroethylene; 1,1,2-trichloro-1,2,2-trifluoroethane (Freon 113); trifluoromonobronomethane (Freon 13B1).

*Part 91624*** for acetonitrile; acrylonitrile; 1-chloro-1-nitropropane; cyanogen; 1,1-dichloro-1-nitroethane; dimethylacetamide; dimethylformamide; fumigants (Acritet, Insect-O-Fume, Fumi-I-Gate, termi-Gas, Termi-Nate); methacrylonitrile; nitroethane; nitromethane, 1-nitropropane; 2-nitropropane; n-propyl nitrate; pyridine; vinyl chloride.

Part 460225 for chlorine. *Part 460424** for nitric oxide.

* Multiple reaction or multiple layer tube for improved specificity or preliminary reaction.
** Pyrolyzer required.

tolidine. (It is not clear whether or not this is identical with the commercial No. 117.) Air was drawn through the tubes for 30 minutes at 180 ml/min by an electric pump with a stainless steel orifice plate at its inlet. Accuracy was ± 10%; no comments on the specificity were given. Grosskopf[47,48] determined 0.007 to 0.5 ppm NO_2 by drawing air through a Draeger 0.5/a nitrous gas tube with a diaphragm pump for 10 to 40 minutes at the rate of 0.5 L/min. Readings were not affected by flow rates if the flow rates exceeded 0.5 L/min. No comments were given on the specificity, except that humidity from 30 L of air at 70% relative humidity did not impair the sensitivity. This tube responds to nitric oxide and to oxidants, both of which commonly may be present. Leichnitz[49] reported a new tube (Draeger SO_2 0.1/a) capable of measuring 0.1 to 3 ppm of sulfur dioxide. This tube requires 100 strokes of a hand bellows pump (each taking 7 to 14 seconds) or use of the Draeger Quantimeter electric pump in which a motor-driven crank controlled by a timer or counter operates a bellows. This pump is described in the manufacturers' listing.

Less success was attained when carbon monoxide detector tubes were used for sampling periods of four hours or longer with continuous pumps. It was found that at low concentrations, after an initial period, the stain lengths ceased to increase.[23] However, at higher concentrations a new calibration could be made[50] (for 3- to 5-hour samples at 8 ml/min through a Kitagawa 100 tube in the range 30–100 ppm of carbon monoxide). The latter investigator hypothesized that the oxygen in air bleached the black palladium stain and caused the front produced by low concentrations to remain stationary after the first 20–30 minutes. Effects of water vapor and of other contaminants also must be considered in this application. A new calibration is essential under the flow conditions to be used. Studies confirmed that secondary reactions, which bleached the indication and prevented long-term sampling, could be avoided with appropriate reagent systems.[51]

Recently, a considerable number of indicator tubes have been developed[52,53] for long duration sampling (4–8 hrs). These appear to be very similar to the tubes

designed for short duration sampling and are effective within the same concentration ranges. They are calibrated for use with a continuous sampling pump, but they operate at lower flow rates. The application of these tubes is to provide time-weighted average concentrations, rather than short-term (few minutes) values. In order to provide valid averages, the calibrations must be linear both with concentration and time and should display uniformly spaced markings for uniform increments of contaminants. The scales on these tubes usually are in terms of microliters of test gas (ppm × liters), rather than ppm, and the latter is calculated by dividing the scale reading by the liters of air sampled. Over 30 types of long duration tubes are now available commercially. It should be noted that they must be used within the ranges of flow rate and total sampling time established during their calibration by the manufacturer, using the specified continuous sampling pump. Low flow MDA Accuhaler pumps have been utilized, with some loss of accuracy.[54] They generally are not suitable for analysis of concentrations in lower ranges than those of ordinary tubes designed for short duration sampling[55] because of the previously mentioned problems of water vapor, oxygen, and other contaminants.

Greater accuracy can be obtained when several detector tubes are used for replicate sampling. A simplified statistical approach based on an assumed normal distribution of values was recommended for three to ten samples.[56] However, subsequent work indicated that most of the variations were due to the environmental fluctuations rather than to the relatively small analytical errors, and that a lognormal distribution was more appropriate. A step-by-step procedure was presented,[57] which categorized the results into noncompliance (less than 5% chance of erroneously citing when actually compliance exists), no decision, and compliance (less than 5% chance of failing to cite when actually noncompliance exists).

Problems in the Manufacture of Indicator Tubes

The accuracy, limitations, and applications of detector tubes are highly dependent upon the skill with which they were manufactured. Generally, the supporting material is silica gel, alumina, ground glass, pumice, or resin. This is impregnated with an indicator chemical which should be stable, specific, sensitive, and produce a color which strongly contrasts with the unexposed color and is nonfading for at least an hour. If the reaction with the test gas is relatively slow, a color is produced throughout the length of the tube, since the gas is incompletely absorbed and the concentration at the exiting end is an appreciable fraction of that at the entrance. Such a color must be matched against a chart of standard tints. A rapidly reacting indicating chemical is much more desirable and yields a length-of-stain type of tube in which the test gas is completely absorbed in the stained portion.

There is a very wide and unpredictable variation in the properties of different batches of indicating gel. The major portion of the chemical reaction probably occurs upon the surface. Therefore, the number of active centers, which are highly sensitive to trace impurities, affects the reaction rate. These problems are well known in the preparation of various catalysts. Close controls must be kept on the purity and quality of the materials, the method of preparation, the cleanliness of the air in the factory or glove box in which the tubes are assembled, the inside diameter of the glass tubes, and even upon the size analysis of the impregnated gel which, in some cases, is important in controlling the flow rate. The manufacturer also must accurately calibrate each batch of indicating gel.

Some tube types are constructed with multiple layers of different impregnated gels with inert separators. Generally, the first layer is a precleansing chemical to remove interfering gases and improve the specificity of the indication. Thus, in the case of some carbon monoxide tubes, chemicals are provided to remove interfering hydrocarbons and nitrogen oxides. In carbon disulfide tubes, hydrogen sulfide is first removed. In hydrogen cyanide tubes, hydrogen chloride or sulfur dioxide are removed first. In other cases, the entrance layer provides a preliminary reaction essential to the indicating reaction. Thus, in some trichloroethylene tubes, the first oxidation layer liberates a halogen which is indicated in the subsequent layer. In some tubes for NO_x gases, a mixture of chromium trioxide and concentrated sulfuric acid is used to oxidize nitric oxide to nitrogen dioxide, which is the form to which the sensitive indicating layer responds. While such multiple layer tubes are advantageous when properly constructed, they frequently have a shorter shelf life because of diffusion of chemicals between layers and consequent deterioration.

A shelf life of at least two years is highly desirable for practical purposes. A great deal of disappointment with various tube performances is no doubt due to inadequate shelf life. Since some tubes have only been on the market for a short time, the manufacturer himself may have inadequate experiences as to the shelf life of his product. Small variations in impurities, such as the moisture content, may have a large effect upon the shelf lives of different batches. The storage temperature, of course, greatly affects the shelf life, and it is highly desirable to store these tubes in a refrigerator. In some cases, shelf life has been estimated by accelerated tests at higher temperatures. Such a variation of shelf life (length of time within which the calibration accuracy is maintained at ± 25%) is illustrated by the data listed in Table T-2 received in a personal communica-

TABLE T-2. Shelf Life of Draeger Carbon Monoxide Tubes

Temperature °C	Shelf Life
25	> 2 yr
50	> 1/2 yr
80	weeks
100	1 week
125	3 days
150	1 day

tion from Dr. Karl Grosskopf of the Draeger Company. These data plot as an approximately straight line when the logarithm of the shelf life time is plotted against a linear scale of the reciprocal of absolute temperature. Such a plot is usual for the reaction rate of a simple chemical reaction. In other cases, relationships may be more complex.

The shipping properties of tubes must also be controlled carefully. Loosely packed indicating gels may shift, causing an error in the zero point of scales printed directly upon the tube, as well as an error in total stain length. When the size analysis includes an appreciable range, the fines may segregate to one side of the bore causing different flow resistances and rates on each side of the tube. This may cause oval stain fronts which are not perpendicular to the tube bore. If the indicating gel is friable, the size analysis may change during shipping.

Obviously, satisfactory results can be obtained only if the manufacturers take great pains in the design, production, and calibration of tubes.

Theory of Calibration Scales

Up to now, calibration scales have been entirely empirical. The variables which can affect the length of stain are concentration of test gas, volume of air sample, sampling flow rate, temperature, and pressure, as well as a number of factors related to tube construction. There is a striking similarity in the fact that most of the calibration scales are logarithmic with respect to concentration in spite of the widely differing chemicals employed in different tube types. Although very few data are available for these relationships, a basic mathematical analysis was made by Saltzman.[58] The theoretical formulae discussed below will, of course, have to be modified as more data become available. The relationships were also studied by Grosskopf[48] and Leichnitz.[59]

In the usual case, although the test gas is sorbed completely, equilibrium is not reached between the gas and the absorbing indicator gel because the sampling period is relatively short and the flow rate is relatively high. The length of stain is determined by the kinetic rate at which the gas either reacts with the indicating chemical or is adsorbed on the silica gel. The theoretical analysis shows that the stain length is proportional to the logarithm of the product of gas concentration and sample volume:

$$\frac{L}{H} = \ln (CV) + \ln\left(\frac{K}{H}\right) \qquad (1)$$

where: L = the stain length, cm
C = the gas concentration, ppm
V = the air sample volume, cm^3
K = a constant for a given type of indicator tube and test gas
H = a mass transfer proportionality factor having the dimension of centimeters, and known as the height of a mass transfer unit.

The factor H varies with the sampling flow rate raised to an exponent of between 0.5 and 1.0, depending upon the nature of the process which limits the kinetic rate of sorption. This process may be diffusion of the test gas through a stagnant gas film surrounding the gel particles, the rate of surface chemical reaction, or diffusion in the solid gel particles. If the indicator tube follows this mathematical model, a plot of stain length, L, on a linear scale, versus the logarithm of product CV (for a fixed constant flow rate) will be a straight line of slope H. It is important to control the flow rate as it may affect stain lengths more than gas concentrations because of its influence on the factor H.

If larger samples are taken at low concentrations and the value of L/H exceeds 4, the gel approaches equilibrium saturation at the inlet end, and calibration relationships are modified. The solution to the equations for this case has been presented graphically by Saltzman[58] in a generalized chart. However, there is little advantage to be gained in greatly increasing the sample size, since the stain front is greatly broadened and various errors are increased.

For some types of tubes such as hydrogen sulfide and ammonia, the reaction rate is fast enough so that equilibrium can be attained between the indicating gel and the test gas. Under these conditions, there is a stoichiometric relationship between the volume of discolored indicating gel and the quantity of test gas absorbed. In the simplest case, the stain length is proportional to the product of concentration and volume sampled:

$$L = K'CV \qquad (2)$$

If adsorption is important, the exponent of concentration may differ from unity:

$$L = K'' C^{(1-n)} V \qquad (3)$$

The value of n is the same as that in the Freundlich isotherm equation for equilibrium adsorption, which

states that the mass of gas adsorbed per unit mass of gel is proportional to the gas concentration raised to the power n. If the value of n is unity, which is not unusual, Equation 3 indicates that stain length is proportional to sample volume but is independent of concentration. The physical meaning of this is that all concentrations of gas are adsorbed completely by a fixed depth of gel. Such a tube is obviously of no practical value.

Equilibrium conditions may be assumed for a given type of indicator tube if stain lengths are directly proportional to the volume of air sampled (at a fixed concentration) and are not affected by air sampling flow rate. A log-log plot then may be made of stain length versus concentration for a fixed volume. A straight line with a slope of unity indicates that Equation 2 applies; if another value of slope is obtained, Equation 3 applies.

In some of the narrower indicator tubes, manufacturing variation in tube diameters produces an appreciable percentage variation in tube cross-sectional areas. This results in an error in the calibration as high as 50% because the volume of sample per unit cross-sectional area is different from that under standard test conditions. An additional complicating factor is the variation produced in flow rate per unit cross-sectional area. If an exactly equal quantity of indicating gel is put into each tube, variations in cross-sectional areas will be indicated by corresponding variations in the filled tube lengths. Correction charts are provided by one manufacturer on which the tube is positioned according to the filled length and a scale is given for reading stain lengths. Although the corrections are rather complex, practically linear corrections are very close approximations which can reduce the errors to 10%. In most tubes, the tube diameters are controlled closely enough so that no correction is necessary.

Temperature is another important variable for tube calibrations. The effect is different for different tubes. Since the color tint type of tube depends upon the degree of reaction, it is most sensitive to temperature. For example, some types of carbon monoxide tubes require correction by a factor of two for each deviation of 10°C from the standard calibration conditions.

Errors in judging stain lengths produce equal percentage errors in concentration derived from the calibration scale. Errors in measuring sample volume and in flow rate may also result in errors in the final value, although the exact relationships might vary according to the tubes.

Many other complications can be expected in calibration relationships. Thus, for nitrogen dioxide, the proportion of side reactions is changed at different flow rates. Changing sample volumes freely from calibration conditions is not recommended unless the tube is known to be thoroughly free from the effects of interfering gases and humidity in the air.

A crucial factor in the accuracy of the calibration is the apparatus used for preparing known low concentrations of the test gas. This subject is discussed more fully in *Chapter F* of this manual. Some manufacturers have used static methods. However, in our experience, losses of 50% or more by adsorption are not uncommon. Low concentrations of reactive gases and vapors are best prepared in a dynamic system. This has further advantages of compactness and ability to rapidly change concentrations as required. With either type of apparatus, it is highly desirable to check the concentrations using chemical methods of known adequacy. Some successful systems have been described.[60-66]

A simple and compact dynamic apparatus for accurately diluting tank gas (which may be either pure or a mixture) was developed by Saltzman[61,62] and Avera.[63] The asbestos* plug flowmeter measures and controls gas flows in the range of a few hundreths to a few milliliters per minute. Air vapor mixtures of volatile organic liquids may be prepared in a flow dilution apparatus using a motor-driven hypodermic syringe. High quality gears, bearings, and screws are needed in the motor drive to provide the uniform slow motion. Some commercial devices have been found unsatisfactory in this regard. Many types of permeation tubes now available also have proven useful.

It is highly desirable for the user as well as the manufacturer to have facilities available for checking calibrations. Only in this manner may the user be confident that the tubes and corresponding technique are adequate for the intended purposes. Tubes also may be applied to gases other than those for which they have been calibrated by the manufacturer, in certain special cases, if the user can prepare a new calibration scale.

Stain Length Passive Dosimeters

An important new advance has been the development of direct-reading, passive dosimeters. Passive dosimetry utilizes diffusion of the test gas and eliminates the need for a sampling pump and its calibration. These attractive devices are compact, convenient, and relatively inexpensive. In early work, detector tubes for toluene, ethanol, and isopropanol were cut open at the entrance of the chemical packing.[67] Later, glass adapters with a membrane (e.g., Millipore, or silicone rubber) were used[68-70] to provide a draft shield, in some cases a pretreatment chemical layer, and a diffusion resistance. Simpler commercial devices merely provided a score mark which permitted breaking the tube at a controlled point.[71] Some allowed a controlled air space (e.g., 15 mm) upstream from the indicating gel to serve as the initial resistance to diffusion.[72] In some devices, rather

*Since asbestos is no longer generally available, a similar inert packing material may be substituted.

than an indicating gel, a strip of chemically impregnated paper is inserted in the glass tube.

The theoretical calibration relationships for these devices rest upon Fick's First Law of Diffusion, which can be expressed as:

$$W = 10^{-6} C t D \left(\frac{A}{X}\right) \quad (4)$$

where: W = cm^3 of test gas collected
t = time, seconds
D = diffusion coefficient, cm^2/s
A = effective orifice cross section area, cm^2
X = orifice length, cm.

This equation assumes that the concentration is completely absorbed in the indicating gel and that there is no significant back pressure. A second common assumption is that the stain length is proportional to the amount absorbed (analogous to Equation 2):

$$L = k W \quad (5)$$

where: k = a constant for a given test gas and tube.

The test gas diffuses through a membrane or air space, then through the stained length of indicating gel, and is finally absorbed at the stain front, which is assumed to be relatively narrow. It is convenient to express X in terms of L:

$$X = r + L \quad (6)$$

where: r = effective length corresponding to the diffusive resistance of the membrane or air space.

Combining Equations 4–6 and rearranging yields:

$$r L + L^2 = (10^{-6} k D A) C t = k' C t \quad (7)$$

where: k′ = a constant equal to the bracketed expression.

This equation has been shown to fit MSA tubes with a 15-mm air space.[72,73] When L was expressed in mm and t in hours, r was taken as 15, and k′ was 0.59 for CO, 11.0 for NH_3, 14.2 for NO_2, 22.6 for H_2S, 67.3 for SO_2, and 74.0 for CO_2. For Draeger tubes, which do not utilize an air space, the equation applied with a zero value for r.[71] For membrane type devices, the equation was modified by adding another constant:[68-70]

$$C t = a + b L + c L^2 \quad (8)$$

where: a, b, c = empirical constants.

These constants may differ for each individual membrane. The inapplicability of a general calibration is a disadvantage of this type.

A more complete mathematical analysis[74] showed that for rapidly changing concentrations the errors would be small. This was experimentally confirmed[75] for both passive dosimeters and for long-term tubes. Most of the published work on passive dosimeters has been by the staffs of manufacturers. Much larger errors were reported[76,77] by users. Some of the stain boundaries were very diffuse and difficult to read, and some calibrations were inaccurate. Since these tubes are in an early state of development, the values should be checked as much as possible.

Another type of passive dosimeter is the direct-reading colorimetric badge. These produce a color tint which is related to the product of time and concentration. Passive badges are more fully treated in *Chapter S*. All passive devices require a minimum air velocity at their entrance (0.008 m/s or 15 ft/min) to avoid "starvation" effects (depletion of the air concentration near the entrance).

Performance Evaluation and Certification

Evaluations by users of some types of tubes have been reported.[30,78-95] Temperature and humidity were found to be significant factors in some cases.[96,97] Accuracy was found highly variable. In some cases, the tubes were completely satisfactory; in others, completely unsatisfactory. Manufacturers, in their efforts to improve the range and sensitivity of their products, are rapidly changing the contents of their tubes, and these reports are frequently obsolete before they appear in print. Improved quality control, and perhaps greater self-policing of the industry, would greatly increase the value of the tubes, especially for the small consumer who is not in a position to check calibrations.

After reviewing this need, a joint committee of the American Conference of Governmental Industrial Hygienists (ACGIH)–American Industrial Hygiene Association (AIHA) made the following recommendations:[98]

1. Manufacturers should supply a calibration chart (ppm) for each batch of tubes.
2. Length-of-stain tubes are preferable to those exhibiting change in hue or intensity of color.
3. Tests of calibrations should be made at 0.5, 1.0, 2.0, and 5.0 times the ACGIH Threshold Limit Value (TLV).
4. The manufacturer should specify the methods of tests. Values should be checked by two independent methods.
5. Calibration at each test point should be accurate within ± 25% (95% confidence limit).
6. Allowable ranges and corrections should be listed for temperature, pressure, and relative humidity.
7. Each batch of tubes should be labeled with a number and an expiration date. Instructions for proper storage should be given.
8. Tolerable concentrations of interferents should be listed.

9. Pumping volumes should be accurate within ± 5%, and flow rates should be indicated.
10. Special calibrations should be provided for extended sampling for low concentrations, and flow rates should be specified.

A performance evaluation program was initiated by the National Institute for Occupational Safety and Health (NIOSH). Known concentrations of test substances were generated in flow systems from sources such as cylinder mixtures, vapor pressure equilibration at known temperatures, or permeation tubes. Although few tubes achieved an accuracy of ± 25%, many types showed accuracies in the range ± 25% to 35%.[85-91]

A formal certification program[99,100] was the next step. In addition to passing performance evaluation tests at the Morgantown, West Virginia, laboratory of NIOSH, manufacturers were required to provide information on the contents of the tubes and to conduct a specified quality control program. Because of the dependence of the calibrations on the pumps used with the tubes, certifications were periodically updated and issued[101] for specified combinations of tubes and pumps. By 1981, tubes of four manufacturers for 23 contaminants had been certified. Unfortunately, the program was terminated in 1983 for lack of funding.[102]

The requirements for certification generally followed the recommendations of the joint committee. However, the accuracy requirement was modified to ± 35% at 0.5 TLV and ± 25% at 1.0, 2.0, and 5.0 times TLV, to be maintained until the expiration date if the tubes were stored according to the manufacturer's instructions. At the TLV concentration, either the stain length had to be 15 mm or greater, or the relative standard deviation of the readings of the same tube by three or more independent tube readers had to be less than 10%. If the stain front was not exactly perpendicular to the tube axis (because of channeling of the air flow), the difference between the longest and shortest stain length measurements to the front had to be less than 20% of the mean length. Color intensity tubes had to have sufficient charts and sampling volume combinations to provide scale values including at least the following multiples of the TLV: 0.5, 0.75, 1.0, 1.5, 2.0, 2.5, 3.0, 4.0, and 5.0; the relative standard deviation for readings of a tube by independent readers had to be < 10%. Tests were to be conducted generally at 18.3°–29.5°C (65°–85°F) and at relative humidities of 50%, unless the humidity had to be reduced to avoid disturbing the test system. The manufacturer had to file a quality control plan and keep records of his inspections of raw materials, finished tubes, and calibration and test equipment. Acceptable statistical quality levels for defects in finished tubes were as follows: critical 0% where tests were nondestructive, otherwise 1.0%, major 2.5%, minor 4.0%, and accuracy 6.5%. Typical statistical calculations have been described.[103] Certification seals were affixed to approved devices. NIOSH reserved the right to withdraw certification for cause.

Since important legal and economic consequences depend upon the accuracy of measurements of contaminant concentrations, enforcement agencies will most likely prefer certified equipment. Standards for detector tubes have been issued by 25 organizations,[104] including the Occupational Safety and Health Adminis-

TABLE T-3. Certifications of Detector Tubes by Safety Equipment Institute as of May 1988*

Substance	Matheson/ Kitagawa	Mine Safety Appliance Co.	National Draeger, Inc.	Sensidyne/ Gastec
Ammonia	8014-105Sc	460103	5/a CH20501	3La
Benzene	8014-118Sc	460754	2/a 8101231	121
			5/b 6728071	
Carbon dioxide	8014-126Sa	85976	0.1%/a CH23501	2L
Carbon monoxide		465519	5/c CH25601	1La
		91229	10/b CH20601	
Chlorine	8014-109SB	460225	0.3/b 6728411	8La
Hydrogen cyanide	8014-112Sb	93262	2/a (CH25701)	12L
Hydrogen sulfide		460058	2/a 6728821	4LL
			1/c 6719001	
Nitrogen dioxide	8014-117Sb	83099	0.5/a CH30001	9L
			0.5/c CH30001	
Sulfur dioxide		92623	0.5/a 6728491	5Lb
Trichloroethylene	8014-134S	460328	2/a 6728541	132M
Pump model*	8014-400A	Samplair Pump	Bellows Pump	Model 800
		464080	Model 31	Pump
			6726065	7010657-1

*Tubes are certified only when used with specified pump model of same manufacturer.

tration (OSHA),[105] International Union of Pure and Applied Chemistry (IUPAC),[106] The Council of Europe, Great Britain, France, Soviet Union, and a variety of private organizations in the U.S. and Europe. Requirements are mostly similar to those cited above. In 1986, the Safety Equipment Institute (SEI) announced a voluntary program for third-party certification of detector tubes. Manufacturers submit tubes for testing as the schedule for each type is announced. Two AIHA-accredited laboratories were selected to evaluate the tubes according to the NIOSH protocol.[99] Another contractor makes on-site, quality assurance audits of manufacturing facilities every six months for three audits, and then annually. If the tubes meet all requirements, the manufacturer may apply the SEI certification mark. This program should provide a stimulus for greater acceptance and use and for further improvements in detector tube technology. Tubes will be retested every three years. Table T-3 gives the current listing of certified tubes.[107] Types for more substances are in process of testing.

Conclusions

Use of indicating tubes for analysis of toxic gas and vapor concentrations in air is a very rapid, convenient, and inexpensive technique which can be performed by semiskilled operators. These tubes are in various stages of development, and highly variable results have been obtained. Accuracy is dependent upon a high degree of skill in the manufacture of the tubes. At present, results may be regarded as only range-finding and approximate in nature. The best accuracy which can be expected from indicator tube systems of the best types is of the order of ± 25%. Since many of the tubes are far from specific, an accurate knowledge of the possible interfering gases present is very important. The quantitative effect of these interferences depends upon the volume sampled in an irregular way. In order to avoid dangerously misleading results, the operation and interpretation should be under the supervision of a skilled occupational hygienist.

The manufacturers' descriptions for individual instruments are given in the pages which follow this discussion. It was not possible to check the accuracy of every detail of the description and claims made, and the responsibility for this material rests entirely with the individual manufacturers.

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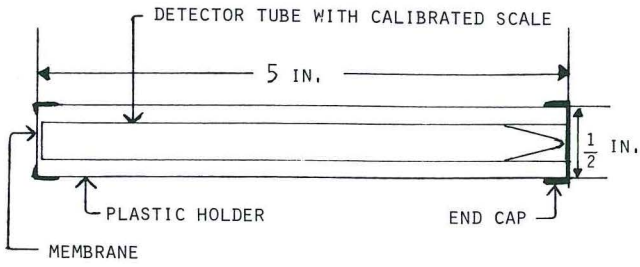
Instrument Descriptions

Introduction

The instruments described below can be classified by certain general characteristics. A short-term air sample is aspirated through most types of detector tubes using a few strokes of a hand piston pump or rubber bulb. The long-term types use a continuous pump at a very low flow rate for periods as long as eight hours to give time-weighted average (TWA) concentrations. No pump is required by passive types that rely upon diffusion of the analyte from air into the sensing absorbent. Original types of sensing absorbents exhibited a change in color tint. More accurate results are obtained with absorbents producing a length of stain that is related to analyte concentration. These characteristics are listed in Table TI-1 for the instruments that are described. Table TI-2 is an index of contaminants showing applicable instruments and their characteristics for each analysis. Table TI-8 lists the commercial sources for the instruments described. All tables pertaining to this instrument section can be found at the end of the actual instrument descriptions.

T-1 Carbon Monoxide Dosimeter
Advanced Chemicals Sensors, Inc.

The Advanced Chemicals Sensors, Inc., CO Monitor is designed to measure carbon monoxide. A CO tube is



INSTRUMENT T-1. Carbon Monoxide Dosimeter Schematic.

exposed for 4 to 24 hours. The length of the dark column in the tube is related to the average CO concentration. This instrument consists of a plastic holder into which the detector tube, with calibrated scale, is inserted. The tubes are not reusable.

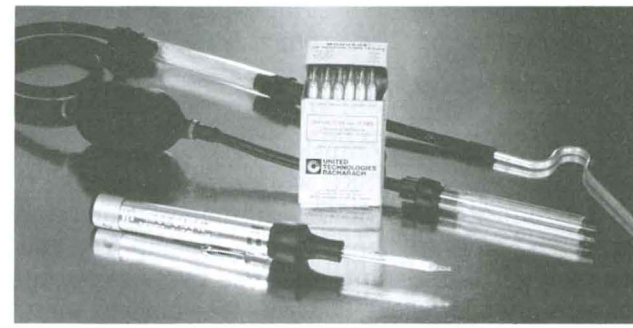
T-2 Bacharach Gas Hazard Indicator
Bacharach, Inc.

The Bacharach Gas Hazard Indicator is a portable instrument for the detection of concentrations of CO_2, CO, H_2S, SO_2, and Cl_2. Used by safety engineers and industrial hygienists, it finds applications in process industries, refineries, mines, tunnels, sewers, natural gas fields, and confined areas. Hazardous gas content in ppm is determined by measuring the length of the stain or bleach. Air is sampled with a hand-held sampling pump that has interchangeable scales and calibrated tubes. Measurements are read directly from the length of stain, and no color comparison charts or calibration curves are necessary. The ranges of the various tubes are shown in Table TI-3.

INSTRUMENT T-2. Gas Hazard Indicator.

T-3 Monoxor® Carbon Monoxide Detector
Bacharach, Inc.

The Monoxor® Detector (No. 19-7021) is a pocket-sized instrument for detecting dangerous CO concentrations; it is not intended for precise measurements of CO percentages. Sealed Monoxor Indicator tubes contain a short length of yellow CO-sensitive chemical, protected on both ends by a guard gel. This guard gel is unaffected by CO and renders the yellow indicating chemical insensitive to smoke, fumes, gases, and vapors other than CO. When exposed to CO, a brownish-gray stain appears at the end of the yellow chemical. The Monoxor Detector has a push-button aspirator pump with a diameter of 3 cm (1⅛ in.) and a length of 16½ cm (6½ in.). If, after one pump stroke, the stain forms only at the edge of the gel, the concentration is approximately 300 parts CO per million parts of air, but the CO concentration is much higher as the stain extends over the entire length of the gel. If the stain appears after the second stroke, the CO concentration is in the range of 100 to 300 ppm.



INSTRUMENT T-3. Monoxor® Carbon Monoxide Detector, No. 19-7021.

T-4 Monoxor® Carbon Monoxide Indicator
Bacharach, Inc.

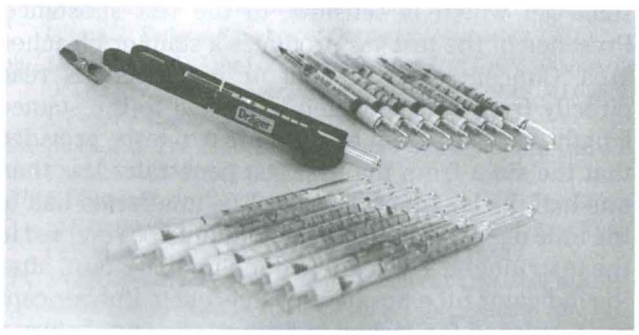
A hand-operated pump is used to pass an air sample through an indicator tube containing an impregnated silica gel which is sensitive to the test substance. Presence of the test gas produces a stain or bleached area. Concentration in ppm or in percent is read directly from a scale which is applied to the stained length. Each tube can be used for two tests, provided that the stain from the first test penetrates less than one-half the length of the tube. The unaffected half of the tube used for the second test should be reversed in the instrument. This can be done up to 6 hours after the indicator tube tips have been broken. Rubber caps are furnished for sealing indicator tube ends between tests. The Monoxor® Carbon Monoxide Indicator Kit

consists of one sampler Model CDE, one double-sided scale with appropriate ranges, one carton containing 12 Monoxor CO indicator tubes, one Allen wrench, and 6 indicator tube caps, all contained in a steel carrying case 10 cm × 17 cm × 7 cm (7 in. × 6½ in. × 2¾ in). Total weight: 1.1 kg (2.5 lbs). Tubes are available in two ranges: 0 to 2000 ppm and 0 to 5000 ppm. The CO indicator tubes will not be affected by 10,000 ppm oxides of nitrogen, 500,000 ppm carbon dioxide, 20,000 ppm sulfur dioxide, 200 ppm methane, and concentrations ordinarily found under industrial working conditions of hydrogen cyanide, trichloroethylene, ammonia, and methylene chloride. A reading 5% above nominal is obtained with 5000 ppm hydrogen and 10,000 ppm ethylene. Stains similar to those produced by CO will be produced by hydrogen sulfide and acetylene. Comparatively, the indications are only slightly affected by the indicator tube temperature. The readings should be multiplied by the correction factor indicated in parentheses to give the true value: -40°F (0.8), 13°F (0.9), 60°F (1.0), 85°F (1.1), 104°F (1.2), 117°F (1.3). There is also a correction factor for altitude: 5000 ft (1.21), 10,000 ft (1.44), 15,000 ft (1.75), 20,000 ft (2.15).

T-5 Diffusion Tubes

National Draeger, Inc.
SKC, Inc.

The direct-reading diffusion detector tubes from National Draeger and SKC work on the principle of gaseous diffusion to give long-term, time-weighted average (TWA) measurements without a pump. The contaminant gas diffuses into the tube by means of the concentration gradient between the ambient atmosphere and the interior of the tube. The diffusion tubes have been calibrated in ppm × hours and volume % × hours with the calibrated scale printed directly on the tube. This system consists of a tube holder and a diffusion tube which may be attached to a pocket or lapel. The range of measurement for various Draeger Diffusion Tubes is given in Table TI-4.

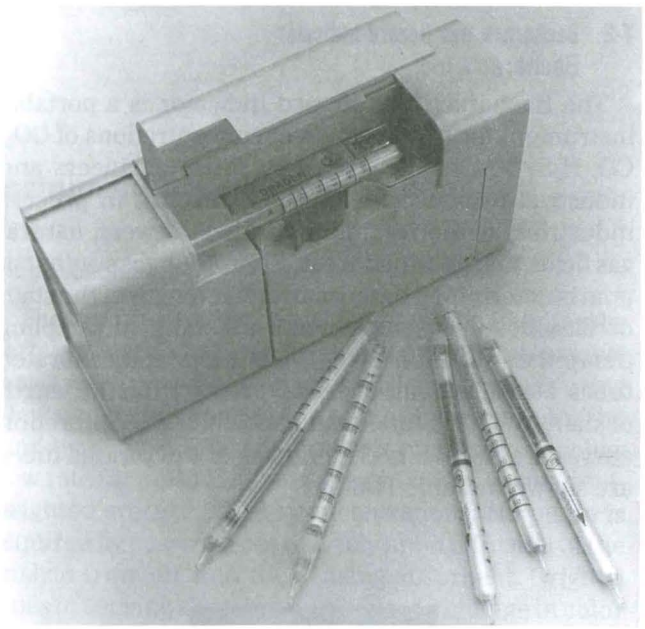


INSTRUMENT T-5. Draeger diffusion tubes and holder.

T-6 Long-Duration Detector Tubes and Polymeter

National Draeger, Inc.
SKC, Inc.

The Draeger Long-Term Detector Tubes and the Draeger Polymeter measure the mean value of the contaminant concentration over periods of up to eight hours. The Polymeter is a battery-powered peristaltic pump which provides a continuous flow at 10 to 20 ml/min. The Long-Term Detector tubes are calibrated in units of microliters, and the time-weighted average (TWA) concentration in parts per million is calculated by dividing the detector tube indication by the sample volume in liters. The Polymeter has a flow rate of approximately 15 ml/min and is powered by a rechargeable storage cell. The unit is supplied in a leather carrying bag with a shoulder strap. Extension hoses are available. Table TI-5 indicates the measuring range and usage of Draeger Long-Duration tubes.



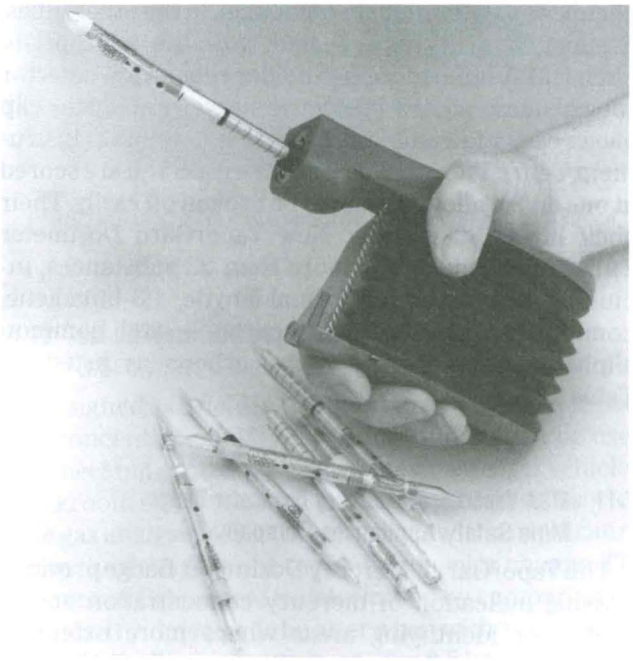
INSTRUMENT T-6. Draeger Long-Duration Tubes and Polymeter-22.

T-7 Multi-Gas Detectors and Quantimeter®-1000

National Draeger, Inc.
SKC, Inc.

The National Draeger Multi-Gas Detector is a portable gas analyzer for use in measuring concentrations of various gases and vapors. Draeger Detector Tubes are available for approximately 100 air contaminants and for technical gas analysis. Table TI-2 lists detector tubes that are available. This instrument consists of the Draeger Bellows Pump and the Draeger Detector Tubes suitable for the gas or vapor to be measured (Instrument T-7). The pump delivers 100 ml of sample air with each pump stroke. After a prescribed number of pump

strokes, the stain length or the discoloration of the tube gives a direct measure of the gas or vapor concentration. Calibration scales are printed directly on most types of tubes. An automatic stroke counter is available as an accessory. The Quantimeter–1000 is a programmable, battery-operated bellows pump with the same flow characteristics as the hand-operated pump. The complete Draeger Model 31 Multi-Gas Detector Kit with a spanner wrench, a screwdriver, break-off husk, and spare parts kit is contained in a vinyl carrying case and weighs approximately 1.4 kg (3 lbs). The detector tube for a particular gas or vapor is essentially specific for that gas or vapor. This is achieved not only by the use of specific and stable reagents but also by the use of precleansing layers placed in front of the actual reactive layer to selectively absorb interfering components that may be contained in the gas or vapor sample. The reading deviations are not more than ± 25% from the true value.



INSTRUMENT T-7. Bellows pump, Model 31, and detector tubes.

T-8 Kitagawa Precision® Gas Detector Kit
Matheson Gas Products
Enmet Corporation

The Model 8014 Precision Gas Detector is used for rapid determination of atmospheric concentrations of toxic gases and vapors. Calibrated detector tubes are available for 31 different gases and vapors as shown in Table TI-2. For many gases and vapors, tubes are available for more than one concentration range, bringing the total number of individual tubes currently available

INSTRUMENT T-8. Kitagawa Precision Gas Detector, Model 8014-400A, and detector tubes.

to 200. For sampling, a detector tube is inserted in the piston pump inlet. When the pump handle is withdrawn, a 100-cc air sample is drawn through the tube. A single pump stroke is sufficient to produce a color stain, which is proportional to the concentration of the gas or vapor. The detecting reagents are absorbed on particles, hermetically sealed in the glass detector tubes. The very fine grain size ensures uniform distribution of air flow through the tubes and provides sharp demarcation lines on all length-of-stain tubes and uniform color changes in color intensity tubes. Typically, the concentration is read directly off the scale etched on each tube. The Gas Detector Kit (Instrument T-8) includes a piston pump, spare parts, and carrying case with room for seven boxes of tubes. The weight of the pump is 0.6 kg (1.25 lbs); it is 7.3 cm (1.5 in.) in diameter and 20 cm (8 in.) long. The complete unit weighs 1.4 kg (3.5 lbs). Table TI-2 lists the detector tubes available. When used within their expiration date, the readings at 20°C (68°F) are designed to be within 5% to 10% of the true concentration. Temperature corrections for operating at other temperatures are normally unnecessary but are provided with those tubes requiring it.

T-9 Samplair™ Pump, Model A, and Detector Tubes
Mine Safety Appliances Company

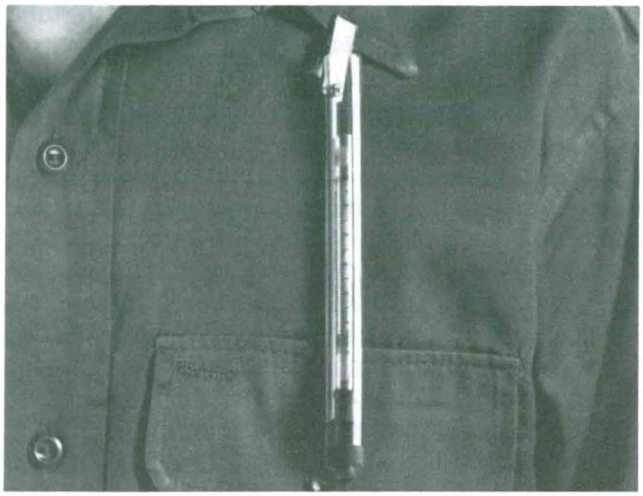
The Samplair™ Pump, Model A, is used with the MSA detector tubes listed in Table TI-2 for manual sampling of approximately 150 toxic gases, vapors, and mists in the threshold limit value ranges. A measured volume of air sample is drawn through the detector using a Samplair Pump; in individual kits, a Samplair Pump or special rubber bulb aspirator assembly is used. A pyrolyzer accessory is utilized in sampling most halogenated and nitrogenated organic contaminants. The Model A is a variable-volume, piston-type pump which draws an accurate sample of ambient air through a

detector tube affixed to its intake end. The operator draws the handle of the pump to the preset position which controls volume at four levels (25, 50, 75, or 100 ml) and notes the reaction in the detector tube being exposed. The Samplair Pump Kit includes: pump, carrying case, spare parts vial, and maintenance sheet. The case has sufficient space for two packages of detector tubes. The measurable ranges of concentrations include the threshold limit value. Allowance should also be made for possible interference from other contaminants. All detector tubes and reagent kits are packaged to have a shelf life of two years. The detector tubes, which are prepared and filled by the user before use, are stable for several days or weeks. Temperature corrections are listed for the determination of various halogenated hydrocarbons.

INSTRUMENT T-9. Samplair™ Pump Kit.

T-10 VaporGard® Vapor Dosimeter Tubes
Mine Safety Appliances Company

VaporGard® inorganic and organic vapor dosimeter tubes are designed to measure worker exposure to the toxic vapors of inorganic compounds such as CO, H_2S, SO_2, NH_3, NO_2, CO_2, HCN, Cl_2, and HCl as shown in Table TI-6a and b. VaporGard tubes are passive dosimeters that work by diffusion; no pumps are required. The user breaks off one end of the detector tube, inserts the tube into the holder, and attaches the holder to his/her clothing. The tube can then be used to sample the atmosphere for up to eight hours. If the gas of interest is present, the VaporGard tube will change color. To determine the gas concentration, the user measures the length of the color stain in millimeters from the scale printed on the tube. A graph gives the average gas concentration as a function of stain length and sampling time. No separate readout device is required.



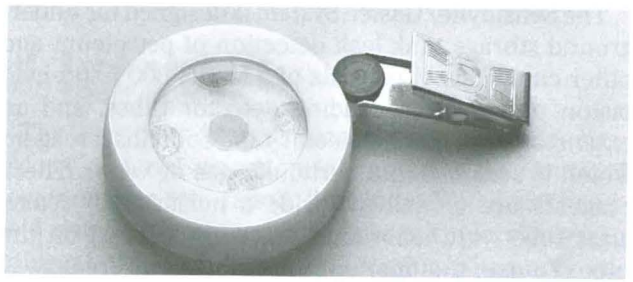
INSTRUMENT T-10. VaporGard® vapor dosimeter tube and holder.

VaporGard tubes use two different methods to contain the colorimetric chemical. In the CO and CO_2 tubes, the chemical is an impregnated silica gel. In the other tubes, a paper strip is impregnated with the appropriate chemical. A molded rubber holder retains the detector tube inside a Lucite® protective sleeve; an alligator clip allows easy attachment to the worker's clothing (Instrument T-10). The tubes are made of glass and are scored at one end to allow the end to be broken off easily. Their shelf life is 30 months. New VaporGard Dosimeter Tubes are available for more than 33 substances, including new tubes for formaldehyde, 1,3-butadiene, common halogenated hydrocarbons, and common aliphatic and aromatic hydrocarbons as listed on Table TI-5.

T-11 MSA VaporGard® Mercury Dosimeter Badge
Mine Safety Appliances Company

The VaporGard® Mercury Dosimeter Badge provides a visual indication of mercury concentration and is useful for identifying areas where more extensive monitoring may be desired. The VaporGard Mercury Dosimeter is a passive dosimeter that works by diffusion; no pumps or other external collection apparatus are necessary. The badge may be clipped to shirt or lapel near the test subject's breathing zone. If mercury vapors are present, the cuprous iodine-impregnated colorimetric indicator inside the badge will change color from off-white to light orange. The color change is in direct relation to the concentration of mercury vapor in the air, i.e., the higher the concentration, the darker the color. There is negligible interference from airborne contaminants or organic vapors. To obtain an estimate of the mercury concentration, the user compares the badge color to the color standard chart supplied with each carton of badges. A graph of color

standard vs. exposure time is then used to estimate the vapor concentration. The badge itself is made up of a windshield, a colorimetric indicating disk, and a cloth support for the disk, all contained in a lightweight plastic case with an alligator clip. The windshield ensures proper diffusion of the sample into the case (Instrument T-11). The VaporGard Mercury Dosimeter measures mercury up to 0.25 mg/m^3, depending upon the length of sampling period. The length of the dosimetry test (in hours) times the concentration (in mg/m^3) should not exceed 0.40. For example, in areas where the average mercury concentration is 0.10 mg/m^3, the dosimetry test should last at most four hours; or, in areas where the average concentration in 0.05 mg/m^3, the dosimetry test can last up to eight hours.



INSTRUMENT T-11. VaporGard® Mercury Dosimeter Badge.

T-12 Saf-CO-Meter (Carbon Monoxide Indicator)
U.S. Safety, Division of Parmelee Industries, Inc.

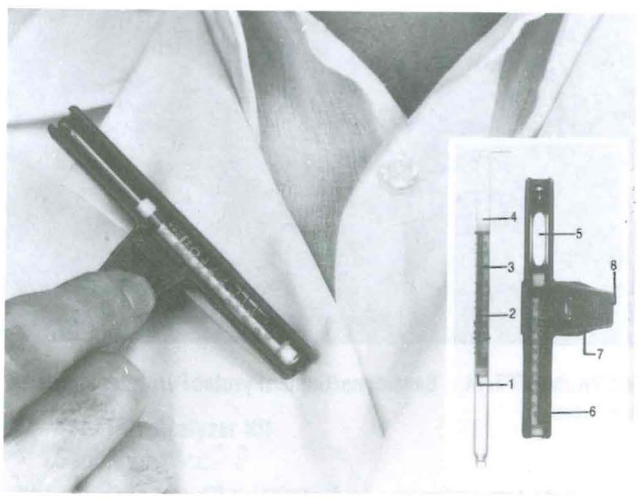
Designed as a field instrument to detect and estimate the concentration of CO, this instrument can be used for checking garages, aircraft, mines, passenger vehicles, workroom environments, and with special accessories, flue gas analysis. CO in the air reacts with an indicating gel in the detector tube to produce a color change. The amount of CO present is determined by comparing the color in the detector tube after a test with a color chart furnished with the instrument. The 0.5 kg (1 lb.) unit is 15 cm (6 in.) high and 8.4 cm (3$\frac{5}{16}$ in.) in diameter. The full unit (Instrument T-12) consists of 12 indicating tubes, 12 end caps for tubes, a tip breaker, aspirator bulb, and color comparison chart. These are contained in a lightweight metal carrying case with shoulder strap. The tubes are made under a license agreement with the U.S. Secretary of Commerce, and they are required to meet quality and accuracy standards set up by the U.S. Bureau of Standards. The five standard colors on the chart represent: 0, 0.005, 0.01, 0.02, and 0.04% CO (50, 100, 200, and 400 ppm) for one bulb squeeze; for five bulb squeezes, the same colors represent: 0, 0.001, 0.002, 0.004, and 0.008% CO (10, 20, 40, and 80 ppm). The readings are multiplied by the factors provided in

INSTRUMENT T-12. Saf-CO Meter.

parentheses to correct for high altitudes: altitude 5000 ft (1.2), 10,000 ft (1.5), 20,000 ft (2.2), 30,000 ft (3.5), 40,000 ft (5.4). The standardization is reliable in the temperature range of 65° to 85°F (18° to 29°C). Activated carbon tubes are recommended for use in flue gas analysis but are not needed for testing for CO under normal circumstances. NO_2 counteracts the normal development of color in the CO colorimetric indicating tube with a resulting variation in color which makes readings inconsistent.

T-13 Sensidyne/Gastec Dosimeter Tubes
Sensidyne, Inc.

The Sensidyne/Gastec dosimeter tubes contain a reagent which is sensitive to a particular vapor or gas.

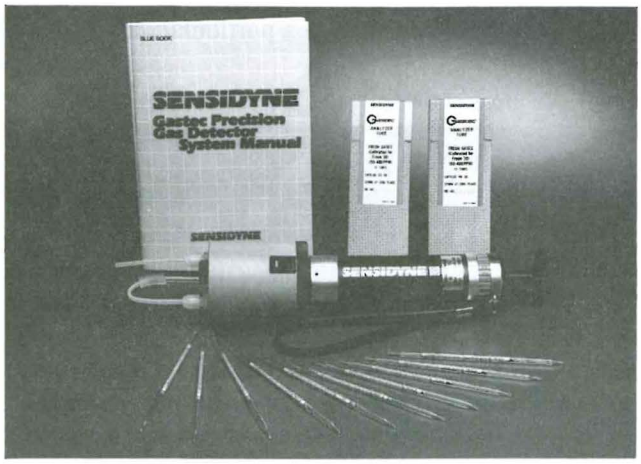


INSTRUMENT T-13. Sensidyne/Gastec dosimeter tube and holder. Insert key: indicating layer support 1; indicating layer 2; calibration marks 3; prescored break-off area 4; access hole for tube removal 5; tube holder 6; clip 7; string attachment 8.

To operate, snap off the breakaway, prescored end of the tube and insert it in the tube holder. The gas or vapor to be measured immediately enters the tube by diffusion and reacts with the absorbing medium quantitatively to produce a length-of-stain indication. The two-layer construction provides a distinct line of demarcation. The dosimeter tube is read in ppm-hours. At the end of the sampling period, the ppm-hour calibration mark on the tube at the point where the color stain stops is divided by the number of hours in the sampling period to obtain the TWA ppm concentration. The tube holder is made of corrosion-resistant, high-impact plastic and conveniently clips to the worker's collar or shirt, thus preventing the tube holder from dangling far in front of the worker. The dosimeter tube can be read while in the tube holder. A string attachment, secured to the holder and worn around the user's neck, eliminates the possible contamination from a dropped tube. All Sensidyne/Gastec dosimeter tubes are direct-reading.

T-14 Sensidyne/Gastec Pyrotec Pyrolyzer
Sensidyne, Inc.

The Pyrotec Pyrolyzer is used in conjunction with Sensidyne/Gastec's Model 800 sampling pump and Freon® detector tube. These detector tubes are the direct-reading type, with a single calibration scale printed on each tube, so measurements can be made simply and reliably. The method of detection is to first

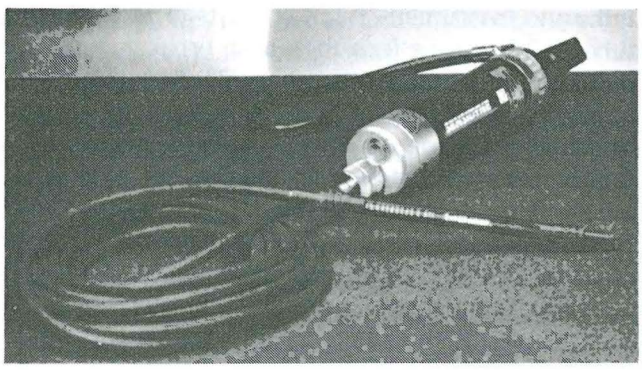


INSTRUMENT T-14. Sensidyne/Gastec Pyrotec Pyrolyzer and detector tubes.

pyrolyze (decompose by heat) the Freon sample, then measure the level of combustion by-products via a length-of-stain detector tube. The concentration of the by-products of combustion is directly proportional to the concentration of Freon in the air. The calibration scale printed on the Freon detector tube provides a direct-reading for Freon-30. Conversion for other common Freons are shown in Table TI-6. To sample, the operator snaps off both breakaway ends of the tube; inserts the tube into the Pyrotec tube holder, turns the Pyrotec on, and pulls the pump handle out. Construction: high-impact plastic; dimensions: 8.3 cm × 6.3 cm (3.25 in. × 2.5 in.); weight 200 g (7 oz). It screws onto the front of the Model 800 pump. Four standard AA batteries power the instrument for hours of continuous operation. Tube No. 50 (the Freon tube) is the only Sensidyne/Gastec tube that requires the Pyrotec Pyrolyzer (see Table TI-7).

T-15 Sensidyne/Gastec System
Sensidyne, Inc.

The Sensidyne/Gastec System is designed for underground storage tank leak detection of petroleum and other chemicals. It consists of a Model 800 hand-held piston pump, direct-reading detector tubes, and an extension hose. Each detector tube contains a reagent which is sensitive to a particular gas or vapor. These reagents are contained inside a hermetically-sealed glass tube with calibration markings printed on the tube. To use, the operator snaps off both breakaway ends of a tube; inserts it into the extension hose; drops the extension hose into the interstitial cavity of a double-walled tank, into a bore hole, or into a groundwater monitoring well above the water level; and pulls the pump handle. As the handle is pulled, a measured volume of air is drawn inside the tube where it contacts the reagent to produce a length-of-stain indication. The pump weighs 260 g (9.25 oz), and tubes may be shipped without special approvals. The system does not require electrical power; it may safely be used in the presence of explosive or flammable gas. It is capable of monitoring 200 gases and can discriminate between acids and petroleum products. Gasoline vapors can be detected as low as 3 ppm. Table TI-2 lists detector tubes available.



INSTRUMENT T-15. Sensidyne/Gastec System.

INSTRUMENT T-16. Standard HazMat Kit with accessories (Model 800 pump).

T-16 Sensidyne HazMat Kit
Sensidyne, Inc.

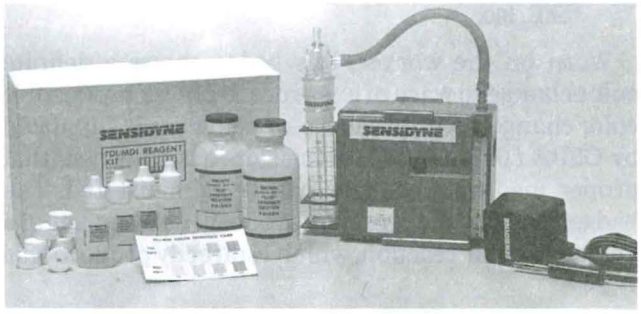
The Sensidyne/Gastec Hazmat Kit is a portable hazardous material detection kit requiring no electrical power or user calibration. It uses the Model 800 hand-held piston pump, extension cable and incorporates 13 different types of detector tubes for commonly encountered substances, as shown in Table TI-2. The kit includes a leather shoulder bag and a laminated sampling logic chart. The Deluxe HazMat Kit incorporates all of these elements plus an air flow indicator, smoke tube kit, and 13 to 24 boxes of detector tubes. This system is capable of measuring over 200 gases. See Table TI-2 for a list of gas detector tubes available.

T-17 Sensidyne Precision Gas Detector System
Sensidyne, Inc.

Over 200 gases and vapors can be measured with the High-Precision Gas Sampling System using the detector tubes listed in Table TI-2. The two major components are 1) direct-reading detector tubes and 2) the high-precision, piston-type volumetric pump. Each detector tube contains a reagent which is specifically sensitive to a particular vapor or gas. These reagents are contained on fine-grain silica gel, activated Alumina, or other adsorbing media (depending upon application requirements), inside a constant-inner-diameter, hermetically-sealed glass tube. To sample, the operator snaps off both breakaway ends of a tube, inserts the tube into the hand-held pump, and pulls the pump handle out. A measured volume of ambient air is drawn inside the tube. The reagent changes color instantly and reacts quantitatively to provide a length-of-stain indication. The farther the color stain travels along the tube, the higher the concentration of gas. The calibration mark on the tube at the point where the color stain stops gives the concentration. Calibration scales for the detector tubes are printed on the basis of individual production lots. Calibration scales are in ppm, mg/L, or percent, depending on the substance to be measured and the desired measuring range. Every tube and tube box carries the quality control number, chemical symbol, and the expiration date. Expandable Measuring Range: concentrations can be measured above or below the printed scale, simply by increasing or decreasing pump strokes.

T-18 TDI/MDI Analyzer Kit
Sensidyne, Inc.

The Sensidyne TDI/MDI Analyzer Kit provides a rapid method for field determination of toluene diisocyanate and methylene bis(4-phenylisocyanate) in air. A sample is drawn through a special absorbing solution using the BDX 55 pump and a midget impinger at 0.1 cfm (2.8 L/min) for 10 minutes. The solution is transferred to a test tube and a series of reagents added to produce a blue-red color. The color is compared to a color reference card graduated in ppm by volume. Results within 0.01 to 0.35 ppm limits can be obtained in about 30 minutes directly in the work environment. It offers accuracy of ± 0.01 ppm when used in accordance with kit instructions. The BDX 55 Super Sampler pump is Factory Mutual-approved for Class I, II and III, Division 1 hazardous locations. It is powered by rechargeable Ni-Cd batteries.



INSTRUMENT T-18. TDI/MDI Analyzer Kit.

T-19 TEL/TML Analyzer Kit
Sensidyne, Inc.

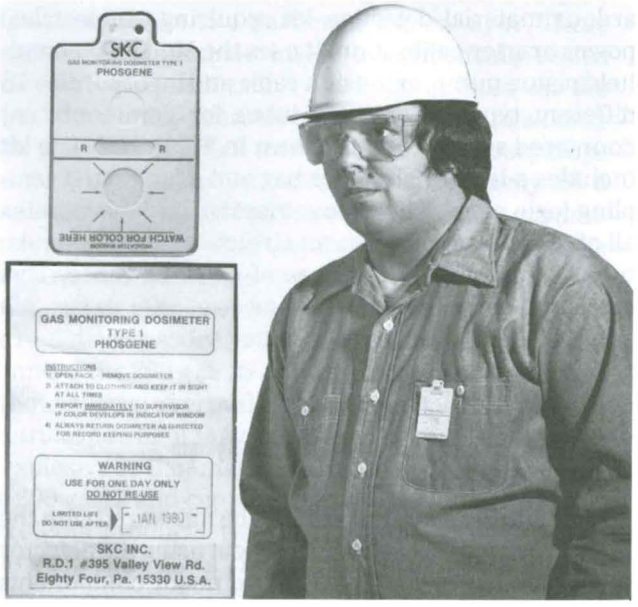
The Sensidyne TEL/TML Analyzer Kit is used for field sampling of tetraethyl lead or tetramethyl lead in air and for confined space entry testing in gasoline storage tanks. A sample is drawn through a cyanide solution using a BDX 55 pump and midget impinger.

INSTRUMENT T-19. Sensidyne TEL/TML Analyzer Kit.

The solution is transferred to a comparator tube and reagents are added to form a red color. The color is compared to standard colors in a comparator viewer. The concentration is read directly in $\mu g/ft^3$ (conversion to mg/m^3 is: $\mu g/ft^3 \times 0.035 = mg/m^3$) of lead in air. The performance data on the TEL/TML kit are: measuring range: 1 to 20 $\mu g/ft^3$ (= 0.035 to 0.7 mg/m^3); accuracy: ± 1 μg; duration of test: about 30 min. The BDX 55 Super Sampler pump may be used in other applications by simply adding appropriate accessories. Factory Mutual-approved for intrinsic safety in Class I, II, and III, Division 1 hazardous locations, the pump may be used for up to eight hours continuously using rechargeable Ni-Cd batteries.

T-20 Gas Monitoring Dosimeter Badge Type I — Phosgene
SKC, Inc.

Worn on the worker, this badge shows a definite color change to warn of exposure to phosgene. Positive color change occurs at, above, or below levels stipulated by OSHA (0.5 mg/m^3). Precise dose is shown so that proper medical treatment can be administered. The badge indicates the presence of phosgene by means of a chemical color reaction, which is directly proportional to the amount of phosgene in the atmosphere and the length of exposure. Because the chemical reaction is immediate, the dosimeter provides: 1) immediate warning of hazardous phosgene concentration and 2) the ability to measure the total exposure, either immediately or after a full work shift. The badge uses two readout systems: 1) *Color Dose Determinator* — a color wheel permits the determination of the exposed dose directly on site and 2) *Instrument Readout* —a dedicated, special purpose colorimeter gives the concentration/dose of the phosgene directly in ppm-min. The threshold sensitivity is 1 ppm-min. It is unaffected by humidity, temperature, or HCl fumes. The phosgene dosimeter is a disposable, lightweight monitor designed to be worn on the clothing. The dosimeter is supplied in a sealed pouch and has a defined shelf life which is indicated by an expiration date on the pouch. Dosimeters are intended for use during one day (up to 12 hours) only.



INSTRUMENT T-20. Gas Monitoring Dosimeter Badge Type I — Phosgene.

TABLE TI-1. Index of Instruments and Characteristics

Instrument		Characteristic				
		Aspiration	Diffusion	Color Change	Length of Stain	Long-Term
T-1	Advanced Chemical Sensors Carbon Monoxide Monitor		X		X	X
T-2	Bacharach Gas Hazard Indicator	X			X	
T-3	Bacharach MONOXOR® Carbon Monoxide Detector	X		X		
T-4	Bacharach MONOXOR® Indicator	X		X		
T-5	Draeger Diffusion Tubes		X	X	X	X
T-6	Draeger Long-Duration Detector Tubes & Polymeter®	X			X	X
T-7	Draeger Multi Gas Detectors & Quantimeter®-1000	X		X	X	
T-8	Kitagawa Precision® Gas Detector	X			X	X
T-9	MSA Samplair™ Pump, Model A, and Detector Tubes	X		X	X	
T-10	MSA VaporGard® Vapor Dosimeter Tubes		X		X	X
T-11	MSA VaporGard® Mercury Dosimeter Badge		X		X	X
T-12	Saf-CO-Meter (Carbon Monoxide Indicator)	X		X		
T-13	Sensidyne/Gastec Dosimeter Tubes		X		X	X
T-14	Sensidyne/Gastec Pyrotec Pyrolyzer	X			X	
T-15	Sensidyne/Gastec System	X			X	
T-16	Sensidyne HazMat Kit	X			X	
T-17	Sensidyne Precision Gas Detection System	X			X	
T-18	Sensidyne TDI/MDI Analyzer Kit	X		X		X
T-19	Sensidyne TEL/TML Analyzer Kit	X		X		
T-20	SKC Gas Monitoring Dosimeter Type I — Phosgene		X	X		X

TABLE TI-2. Index of Contaminants and Applicable Commercial Instruments

Contaminant	Commercial Instruments (see footnotes for symbol descriptions)
Acetaldehyde	7,8,9,15,16,17
Acetic acid	5*†
Acetic anhydride	15,16,17
Acetone	5*†,6*,7,8,9,15,16,17
Acetone cyanohydrin	15,16,17
Acetonitrile	9
Acetylene	7,8,9,15,16,17
Acid compounds	7
Acrolein	8,15,16,17
Acrylonitrile	6*,7,8,9,15,16,17
Aliphatic hydrocarbons	7
Allyl alcohol	8
Allyl chloride	9
Ammonia	5*†,6*,7§,8*§,9§,10*†, 13*†, 15§, 16§,17§
n-Amyl acetate	8,15,16,17
n-Amyl alcohol	9,15,16,17
Amyl alcohol (sec. & tert.)	9
Amyl mercaptan	9
Aniline	7,8,15,16,17
Aromatics	7,10†*
Arsenic trioxide	7
Arsine	7,8,9,15,16,17
Arsine compounds (organic)	7
Basic compounds	7
Benzene	6*,7§,8§,9§,15§,16§,17§
Benzyl bromide	15,16,17
Benzyl chloride	15,16,17
Bromine	7,8,9,15,16,17
Bromobenzene (mono)	9
Bromoform	15,16,17
Butadiene	5*†,8,9,10*†,15,16,17
Butane	7,8,9,10*†,15,16,17
Butyl acetate	8,15,16,17
Butyl acrylate	8
Butyl alcohol (n, sec. & tert.)	8,9,15,16,17
n-Butylamine	9,10*†,15,16,17
Butyl Cellosolve	8,9,15,16,17
Butylene	7
Butyl mercaptan	8,9
Carbon dioxide	2,5*†,6*,7§,8§,9§,10*†, 15§,16§,17§
Carbon disulfide	6*,7,8,9,15,16,17
Carbon monoxide	1*†,2,3,4,5*†,6*,7§,8*,9§, 10*†,12,13*,15§,16§,17§
Carbon tetrachloride	7,8,9,15,16,17
Carbonyl sulfide	15,16,17
Cellosolve	9,15,16,17
Chlorine	2,6*,7§,8§,9§,10*†,15§, 16§,17§
Chlorine dioxide	8,9,15,16,17
Chlorobenzene	7,8,9,10*†,15,16,17
Chlorobromomethane	9,15,16,17
Chlorodifluoroethane (Genetron 142B)	9
Chlorodifluoromethane (Freon 22)	9,14,15,16,17
Chloroform	7,8,9,15,16,17
Chloroformates	7
Chloronitropropane	9
Chloropentafluoroethane (Freon 115)	9
Chloropicrin	8,15,16,17
Chloroprene	6*,7,8
Chlorotrifluoromethane (Freon 13)	9
Chromic acid	7,9
Cresol	8,15,16,17
Cumene	9,15,16,17
Cyanide ion	7
Cyanogen	9
Cyanogen chloride	7
Cyclohexane	7,8,9,10*†,15,16,17
Cyclohexanol	8,9
Cyclohexanone	8,15,16,17
Cyclohexene	15,16,17
Cyclohexylamine	7,9,10*†,15,16,17
Decaborane	9
Demeton	7
Diacetone alcohol	8
Diborane	7,9
Dibromoethane (ethylene dibromide)	8,9,15,16,17
1,1-Dibromoethane	15,16,17
Dichlorobenzene (ortho)	8,9,10*†,15,16,17
Dichlorodifluoromethane (Freon 12)	9,14,15,16,17
1,1-Dichloroethane	9
Dichloroethane (ethylene dichloride)	9,10*†,15,16,17
Dichloroethylene (cis and trans)	8,9,10*†,15,16,17
Dichloroethyl ether	8,9
Dichloromethane (methylene chloride)	6*,8,9,10*†,14,15,16,17
Dichloronitroethane	9
Dichloropropane	8,15,16,17
Dichlorotetrafluoroethane (Freon 114)	9,14,15,16,17
Diethylamine	8,9,10*†,15,16,17
Diethylbenzene	15,16,17
Diethylenetriamine	15,16,17
Diethylether (ethyl ether)	7,8,15,16,17
Diethyl sulfate	9
Diisopropylamine	15,16,17
Dimethyl acetamide	7,9,15,16,17
Dimethylamine	9,10*†,15,16,17
Dimethylaniline	15,16,17
Dimethyl ether (methyl ether)	8,15,16,17
Dimethylformamide, N,N-	7,8,9,15,16,17
Dimethylhydrazine (uns) (UMDH)	9
Dimethylsulfate	7,9
Dimethylsulfide	7
Dimethylsulfoxide	9
Di-n-propylamine	9,10*†
Dioxane	8,15,16,17
Epichlorohydrin	7,8,15,16,17
Ethanolamine (mono)	8,15,16,17
2-Ethoxyethanol (Cellosolve)	8,9
Ethyl acetate	5*†,6*,7,8,15,16,17
Ethylacrylate	8,15,16,17
Ethyl alcohol (ethanol)	5*†,6*,7,8,9,15,16,17
Ethylamine	8,9,10*†,15,16,17
Ethyl benzene	7,8,9,10*†,15,16,17
Ethyl bromide	9,15,16,17
Ethyl chloride	9,15,16,17
Ethyl chloroformate	15,16,17
Ethyl cyanide (propionitrile)	15,16,17
Ethylene	7,8,9,15,16,17

TABLE TI-2 (con't). Index of Contaminants and Applicable Commercial Instruments

Contaminant	Commercial Instruments (see footnotes for symbol descriptions)
Ethylene diamine	15,16,17
Ethylene dibromide	8
Ethylene dichloride (dichloroethane)	9,10*†
Ethylene imine	9,15,16,17
Ethylene glycol	7,15,16,17
Ethylene oxide	7,8*,9,15,16,17
Ethyl ether (diethyl ether)	7,8,15,16,17
Ethyl glycol acetate	7
Ethyl mercaptan	8,9,15,16,17
N-Ethylmorpholine	9,10*†
Fluorotrichloromethane (Freon 11)	9,14
Formaldehyde	7,8,9,10*†,15,16,17
Formic acid	7,8,15,16,17
Freons	15,16,17
Furan	8
Furfural	8,15,16,17
Furfuryl alcohol	9
Gasoline (hydrocarbons)	7,8,9,15,16,17
Halogenated hydrocarbons	10*†
Heptane	8,9,10*†,15,16,17
Hexane	7,8,9,10*†,15,16,17
Hydrazine	6*,7,8,9,15,16,17
Hydrocarbons	6*,7,8,10*†,15,16,17
Hydrogen	8,15,16,17
Hydrogen bromide	15,16,17
Hydrogen chloride (hydrochloric acid)	5*†,6*,7,8,9,10*†,15,16,17
Hydrogen cyanide (hydrocyanic acid)	5*†,6*,7§,8§,9§,10*†,13*†, 15§,16§,17§
Hydrogen fluoride	6*,7,8,9,15,16,17
Hydrogen peroxide	7
Hydrogen selenide	8
Hydrogen sulfide	2,5*†,6*,7§,8*,9§,10*†, 13*†,15§,16§,17§
Iodine	15,16,17
Isoamyl acetate	8
Isoamyl alcohol	8,9
Isobutane	8
Isobutyl acetate	8,15,16,17
Isobutyl acrylate	8
Isobutyl alcohol	8,9,15,16,17
Isooctane	9,10*†,15,16,17
Isopropyl acetate	8,15,16,17
Isopropyl alcohol	8,15,16,17
Isopropylamine	9,10*†,15,16,17
Kerosene	9,15,16,17
Lead (inorganic)	9
Lead, tetraethyl	19*
Lead, tetramethyl	19*
LP gas	15,16,17
MDI (methylene bis (4-phenylisocyanate)	18,18*
Mercaptan	7,8
Mercury	7,8,9,11*†,15,16,17
Mesityl oxide	8
Methacrylonitrile	7,9,15,16,17
Methane (natural gas)	7
Methyl acetate	8,15,16,17
Methyl acrylate	7,8
Methyl acrylonitrile	7
Methyl alcohol	7,8,9,15,16,17
Methyl amine	8,9,10*†
Methyl bromide	7,8,9,15,16,17
Methyl Cellosolve	8,15,16,17
Methyl Cellosolve acetate	15,16,17
Methyl chloride	9
Methyl chloroform (trichloroethane)	7,8,9,15,16,17
Methyl chloroformate	15,16,17
Methyl cyclohexanol	8,9
Methyl cyclohexanone	8
Methylene chloride	6*,7,8,9,10*†,14,15,16,17
Methyl ether (dimethyl ether)	8,15,16,17
Methyl ethyl ketone (MEK)	8,15,16,17
Methyl iodide	8
Methyl isobutyl ketone	8,15,16,17
Methyl isobutyl carbinol (methyl amyl carbinol)	9
Methyl mercaptan	8,9,15,16,17
Methyl methacrylate	7,8,15,16,17
Methyl styrene	8
Mineral spirits	15,16,17
Monochlorobenzene	7,8,9,10*†,14,15,16,17
Monoethylamine	15,16,17
Monomethylamine	15,16,17
Monomethyl aniline	15,16,17
Monomethyl hydrazine	9
Monostyrene	6*,7,8,9,15,16,17
Morpholine	15,16,17
Naphthalene	8
Natural gas	7
Nickel	7
Nickel carbonyl	7,8,15,16,17
Nitric acid	7,15,16,17
Nitric oxide	7,9,15,16,17
Nitroethane	9
Nitrogen dioxide	2,5*†,6*,7§,8§,9§,10*†, 15§,16§,17§
Nitrogen oxides	8,15,16,17
Nitroglycol	7
Nitromethane	9
Nitropropane (1- & 2-)	9
Nitrous fumes	6*,7
Nonane	9
Octane	7,9,10*†,15,16,17
Oil mist	7
Olefins	5*†,7
Organic basic nitrogen	7
Organic compounds	8
Oxygen	7,8,15,16,17
Ozone	7,8,9,15,16,17
Pentaborane	9
Pentane	7,8,9,10*†,15,16,17
Pentenenitrile	15,16,17
Perchloroethylene (tetrachloroethylene)	6*,7,8,9,10*†,15,16,17
Petroleum ether	15,16,17
Petroleum hydrocarbons	7,15,16,17
Phenol	7,8,15,16,17
Phosgene	7,8,9,15,16,17,20*†
Phosphine	6*,7,8,9,15,16,17
Phosphoric acid esters	7
Propane (see hydrocarbons)	7,8,9,10*†,15,16,17
Propyl acetate	8,15,16,17

TABLE TI-2 (con't). Index of Contaminants and Applicable Commercial Instruments

Contaminant	Commercial Instruments (see footnotes for symbol descriptions)	Contaminant	Commercial Instruments (see footnotes for symbol descriptions)
Propyl alcohol	7,9,15,16,17	Tetrahydrofuran	8,10*†,15,16,17
Propylene	7,8,9,15,16,17	Tetrahydrothiophene	7
Propylene dichloride	9	Tetramethyl lead	19
Propylene imine	9,15,16,17	Thioether	7
Propylene oxide	8,9,15,16,17	Toluene	5*†,6*,7,8*,9,10*†,15,16,17
n-Propyl mercaptan	9	Toluene diisocyanate (TDI)	7,18,18*
Propyl nitrate	8,9	Toluidine (ortho)	7,15,16,17
Pyridine	7,9,15,16,17	Trichloroethane (methyl chloroform)	7,8,9,15,16,17
Screening tube	7	1,1,2-Trichloroethane	8,9
Sec-amyl alcohol	9	Trichloroethylene	6*,7§,8§,9§,10*†,15§,16§,17§
Sec-butyl alcohol	9,15,16,17	Trichlorofluoromethane (Freon 11)	14,15,16,17
Stibine	9	Trichloropropane	9,10*†
Stoddard solvent	15,16,17	Trichlorotrifluoroethane (Freon 113)	9,14,15,16,17
Styrene (monomer)	6*,7,8,9,15,16,17	Triethylamine	7,8,9,10*†,15,16,17
Sulfur dioxide	2,5*†,6*,7§,8*,9§,10*†,13*†, 15§,16§,17§	Trifluoromonobromomethane (Freon 13B1)	9
Sulfuric acid	7	Trimethylamine	9,10†,15,16,17
Systox™	7	Vinyl acetate	15,16,17
Tert-amyl alcohol	9	Vinyl chloride	6*,7,8,9,15,16,17
Tert-butyl alcohol	9,15,16,17	Vinylidene chloride	9,15,16,17
Tert-butyl mercaptan	9,15,16,17	Vinyl pyridine	9
1,1,2,2-Tetrabromoethane	9	Water vapor	5*,7,8,15,16,17
1,1,2,2-Tetrachloroethane	9,15,16,17	Xylene (o-, m-, and p- isomers)	7,8,9,10*†,15,16,17
Tetrachloroethylene	6*,7,8,9,10*†,15§,16§,17§		
1,1,3,3-Tetrachloropropene	9		
Tetraethyl lead	19		

As listed by manufacturers, each number refers to a specific instrument (Table TI-1).
* Indicates long-term device.
† Indicates diffusion tube or badge.
§ Indicates Tube Certified by Safety Equipment Institute as of May 1988.

TABLE TI-3. Bacharach — Ranges of Various Tubes

Bacharach Code Complete Kit	Gas Type	Range
19-0247	H_2S	0–650 ppm
19-0248	SO_2	0–2700 ppm
19-0249	CO_2	0–4%
19-0250	NO_2	0–50 ppm
19-0251	Cl_2	0–20 ppm
19-0240	CO	0–0.2%
19-0241	CO	0–0.5%

TABLE TI-4. Draeger Diffusion Tube Ranges (Instrument T-5)

Diffusion Tubes with Direct Indication	Draeger Reference Number	Range of Measurement in Absolute Units	Range of Measurement for Maximum Periods of Use (8 hours)
Acetic acid 10/a-D	81 01071	10 - 200 ppm-hr	1.3 - 25 ppm
Acetone 1000/a-D	81 01291	1000 - 30,000 ppm-hr	125 - 3700 ppm
Ammonia 10/a-D	67 33061	10 - 500 ppm-hr	1.3 - 62 ppm
Butadiene 10/a-D	81 01161	10 - 300 ppm-hr	1.3 - 40 ppm
Carbon dioxide 500/a-D	81 01381	500 - 20,000 ppm-hr	65 - 2500 ppm
Carbon dioxide 1%/a-D	81 01051	1 - 30 Vol. % h	0.13 - 3.8 Vol. %
Carbon monoxide 50/a-D	67 33191	50 - 600 ppm-hr	6.3 - 75 ppm
Ethanol 1000/a-D	81 01151	1000 - 25,000 ppm-hr	125 - 3100 ppm
Ethyl acrylate 500/a-D	81 01241	500 - 10,000 ppm-hr	63 - 1250 ppm
Hydrochloric acid 10/a-D	67 33111	10 - 200 ppm-hr	1.3 - 25 ppm
Hydrocyanic acid 20/a-D	67 33221	20 - 200 ppm-hr	2.5 - 25 ppm
Hydrogen sulfide 10/a-D	67 33091	10 - 300 ppm-hr	1.3 - 38 ppm
Nitrogen dioxide 10/a-D	81 01111	10 - 200 ppm-hr	1.3 - 25 ppm
Olefin 100/a-D	81 01171	100 - 2000 ppm-hr	12.5 - 250 ppm
Sulfur dioxide 5/a-D	81 01091	5 - 150 ppm-hr	0.63 - 18 ppm
Toluene 100/a-D	81 01421	100 - 3000 ppm-hr	13 - 380 ppm
Water vapor 5/a-D	81 01391	5 - 100 mg/L-hr	0.6 - 12.5 mg/L
Diffusion tube holder	67 33014	Package of three	—

TABLE TI-5. Draeger Long-Duration Tubes and Ranges

Long-Duration Tubes	Draeger Reference Number	Measuring Range (ppm)	Relative Standard Deviation (%)	Threshold Limit Value (ACGIH 1989-90) (ppm)	Maximum Usage (hrs)
Acetic acid 5/a-L	67 33041	1.3 - 40	15 - 10	10	4
Acetone 500/a-L	67 28731	62.5 - 10,000	15 - 10	750	8
Acrylonitrile 2/a-L	67 28721	0.25 - 40	15 - 10	2,A2[B]	8
Ammonia 10/a-L	67 28231	5 - 100	15 - 10	25	4
Benzene 20/a-L	67 28221	10 - 200	20 - 15	10,A2	4
Carbon dioxide 1000/a-L	67 28611	500 - 6000	15 - 10	5000	4
Carbon disulfide 10/a-L	67 28621	1.25 - 50	15 - 10	10	8
Carbon monoxide 10/a-L	67 28741	2.5 - 100	10 - 5	50	4
Carbon monoxide 50/a-L	67 28121	5 - 500	10 - 5	50	8
Chlorine 1/a-L	67 28421	0.1 - 20	15 - 10	0.5	8
Chloroprene 5/a-L	67 28431	1 - 100	15 - 10	10	4
Ethanol 500/a-L	67 28691	62.5 - 8000	20 - 15	1000	8
Ethyl acetate 1000/a-L	67 28771	125 - 9000	20 - 15	400	8
Hydrazine 0.2/a-L	67 28641	0.05 - 3	15 - 10	0.1,A2[C]	4
Hydrocarbons 100/a-L	67 28571	50 - 3000	15 - 10	—	4
Hydrochloric acid 10/a-L	67 28581	2 - 50	15 - 10	C 5	8
Hydrocyanic acid 10/a-L	67 28441	1 - 120	15 - 10	C 10	8
Hydrogen fluoride 2/a-L	67 28841	0.25 - 30	15 - 10	C 3	8
Hydrogen sulfide 5/a-L	67 28141	0.5 - 60	10 - 5	10	8
Methylene chloride 50/a-L	67 28881	12.5 - 800	20 - 15	50,A2	4
Monostyrene 20/a-L	67 28711	10 - 250	15 - 10	50	2
Nitrogen dioxide 10/a-L	67 28281	1 - 100	20 - 15	3	8
Nitrous fumes 5/a-L	67 28911	1.25 - 50	15 - 10	3 (NO_2)	4
Nitrous fumes 50/a-L ($NO + NO_2$)	67 28191	10 - 350	20 - 15	3 (NO_2)	2
Perchloroethylene 50/a-L	67 28671	12.5 - 300	15 - 10	50	4
Phosphine 0.1/a-L	81 01261	0.025 - 1.5	15 - 10	0.3	4
Sulfur dioxide 2/a-L	67 28921	0.5 - 20	15 - 10	2	4
Sulfur dioxide 5/a-L	67 28151	1 - 50	15 - 10	2	4
Toluene 200/a-L	67 28271	20 - 4000	15 - 10	100	8
Trichloroethylene 10/a-L	67 28291	5 - 200	15 - 10	50	4
Vinyl chloride 10/a-L	67 28131	1 - 50	15 - 10	5,A1[D]	8

[A] TWA unless preceded by a "C" indicating a ceiling limit.
[B] A2 = Suspected Human Carcinogen.
[C] Hydrazine appears on the "Notice of Intended Changes for 1989-90" at a proposed TWA of 0.01 ppm and retaining the A2 designation.
[D] A1 = Confirmed Human Carcinogen.

TABLE TI-6. VaporGard® Dosimeter Tubes — A. Inorganic Tubes (relative humidity 10-90%, accuracy ± 25%)

Substance	Range ppm or %	Temperature Range °C(°F)	Interferences
Ammonia[A]	0–125	4–32 (40-90)	Amines,[A] acid gases[B]
Carbon dioxide	0–4%	0–49 (32–120)	
Carbon monoxide	0–250	-18–52 (0–125)	C_2H_4, H_2S, strong reducing gases
Hydrogen cyanide	0–25	4–38 (40–100)	NO_2, H_2S[B]
Hydrogen sulfide	0–50	0–49 (32–120)	
Nitrogen dioxide	0–20	0–49 (32–120)	Halogens
Sulfur dioxide	0–25	4–32 (40–90)	Acid gases

[A]Also measures n-butylamine, diethylamine, dipropylamine, N-ethylmorpholine, methylamine, trimethylamine, cyclohexylamine, dimethylamine, ethylamine, isopropylamine, and triethylamine.
[B]Decreases stain length. (All others increase stain lengths.)

TABLE TI-6. VaporGard® Dosimeter Tubes — B. Organic Tubes

	Measurable Range (ppm)
Detectable Compounds with the Hydrocarbon Dosimeter Tubes — Group A	
Propane	200- 800
Butane	200–1000
Pentane	100–1000
Hexane	25- 200
Heptane	50- 500
Cyclohexane	100–1000
Tetrahydrofuran	50- 400
Detectable Compounds with the Hydrocarbon Dosimeter Tubes — Group B	
Heptane	500- 800
Toluene	50- 500
n-Octane	100–1000
iso-Octane	100–1000
Ethyl benzene	50- 500
Xylene	50- 500
Detectable Compounds with Halogenated Hydrocarbon Dosimeter Tubes	
1, 2-Dichloroethylene	25- 300
Methylene chloride (Dichloromethane)	25- 300
Perchloroethylene	25- 300
Trichloroethylene	25- 300
1,2,3-Trichloropropane	25- 500
o-Dichlorobenzene	50- 300
Monochlorobenzene	25- 200
1,2-Dichloroethane (Ethylene dichloride)	20- 200

TABLE TI-7. Freon® Gases Analyzed by Pyrotec Pyrolyzer

Specifications — Tube No. 50				
Contaminant	Measuring Range (ppm)	Multiplication Factor	Pump Strokes	Shelf Life
Freon 11	38–300	0.75	3	3 yrs
Freon 12	50–400	none	3	3 yrs
Freon 22	175–1400	3.5	3	3 yrs
Freon 30	50–400	none	3	3 yrs
Freon 113	38–300	0.75	3	3 yrs
Freon 114	125–1000	2.5	3	3 yrs

*Freon® is a trade name of the E.I. duPont deNemours and Company for a group of polyhalogenated hydrocarbons.

TABLE TI-8. Commercial Sources of Colorimetric Indicators

ACS Advanced Chemical Sensors, Inc.
350 Oaks Lane
Pompano Beach, FL 33060
(305) 979-0958

BAC Bacharach, Inc.
625 Alpha Drive
Pittsburgh, PA 15238
(412) 963-2000

ENM Enmet Corporation
2308 S. Industrial Way
P.O. Box 979
Ann Arbor, MI 48106-0979
(313) 761-1270

MGP Matheson Gas Products
30 Seaview Drive
Secaucus, NJ 07094
(201) 933-2400

MSA Mine Safety Appliances Company
600 Penn Center Boulevard
Pittsburgh, PA 15235
(412) 967-3000

NDI National Draeger, Inc.
P.O. Box 120
101 Technology Drive
Pittsburgh, PA 15230
(412) 787-8383

SEN Sensidyne, Inc.
12345 Starkey Road, Suite E
Largo, FL 34643
(800) 451-9444; (813) 530-3602 in FL

SKC SKC Inc.
339 Valley View Road
Eighty Four, PA 15330-9614
(412) 941-9701

USS U.S. Safety Company
Division of Parmalee Industries, Inc.
P.O. Box 417237
Kansas City, MO 64141-2737
(816) 842-8500

AIR SAMPLING INSTRUMENTS

for evaluation
of atmospheric
contaminants

7th edition 1989

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Technical Editor

American Conference
of
Governmental Industrial Hygienists
Cincinnati, Ohio

First Edition 1960
Second Edition 1962
Third Edition 1967
Fourth Edition 1972
Fifth Edition 1978
Sixth Edition 1983
Seventh Edition 1989

Second Printing

Library of Congress Catalog Card Number 83-70265

ISBN: 0-936712-82-1

Published in the United States of America by

American Conference of Governmental Industrial Hygienists, Inc.
6500 Glenway Avenue, Building D-7
Cincinnati, Ohio 45211-4438