

AIR SAMPLING AND ANALYSIS FOR GASES AND VAPORS

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Exposure to airborne contaminants in the work environment has been linked to a wide spectrum of occupational diseases. A serious problem has existed over the years in occupational health in that much of the medical and epidemiological research data collected on workers has not had companion occupational environmental data collected in the time interval over which exposures occurred. The evaluation of worker exposure to potentially hazardous agents in the workplace is essential to establishing cause/effect relationships between an occupationally related illness and a specific agent(s). Existing gaps in worker exposure data have greatly limited the establishment and promulgation of proper occupational health standards for our nation's work force.

The purpose of this chapter is to describe current procedures and methods employed by industrial hygienists to assess, measure, and characterize worker exposure to potentially hazardous contaminants in the occupational environment. The chapter is divided into two sections: sampling techniques for gases and vapors and techniques for particulate sampling.

INTRODUCTION

Air sampling for gases and vapors in the occupational environment is less difficult than for aerosols because at ordinary temperatures and pressure they follow the ideal gas law, they mix freely with ambient air, and in a short time can reach a state of equilibrium. Although the terms "gases" and "vapors" are frequently used synonymously, there are differences that should be acknowledged. For industrial hygiene purposes, a substance is a gas if, at standard conditions (70°F and 760 mm Hg), its normal physical state is gaseous. A vapor is a gaseous form of a substance which under standard conditions may exist as a solid or a liquid in equilibrium with its vapor. Because gases and vapors exist in a similar physical state, the term gas or gaseous substance will be used to include both gases and vapors and they can be collected with the same air sampling devices. The only exception to this is the rare circumstance where vapors at supersaturated concentrations may co-exist as liquids or mists.

Two kinds of air sampling instrumentation are employed to measure worker exposure to gaseous substances: (1) methods requiring laboratory analysis of collected samples, and (2) direct reading instrumentation capable of sam-

pling a volume of air, performing immediate analysis internally, and displaying results visually.

METHODS REQUIRING LABORATORY ANALYSIS OF COLLECTED SAMPLES

Basically, two air sampling methods are employed in industrial hygiene to collect gaseous samples from ambient work atmospheres for subsequent analysis. The first is the grab (instantaneous or short-term) sample in which a volume of air containing a gaseous contaminant is collected over a short period of time, usually from seconds to less than two minutes. Results of the sample's analysis are representative of the airborne concentration of the contaminant, at the sampling location at that point in time. The second is the integrated (average or long-term) sample in which a known volume of air is metered through an appropriate absorbing or adsorbing medium to remove the gaseous contaminant from the sampled airstream. Depending on the circumstances, the sample period may vary from a partial period sample of less than one hour to a full eight-hour sample. Analysis of these samples yield integrated, average, or long-term exposure levels reflecting the workers' overall exposure for that sample period.

Several important criteria that must be considered in the selection of a sampling method are: the solubility, volatility, and reactivity of the contaminant; the sensitivity of the analytical method (77); and the kind of information sought (e.g., peak concentrations or integrated exposure levels).

Grab—Instantaneous or Short-Term Samples

Grab sampling is best employed in monitoring several phases of a cyclic process and for determining peak concentrations where working levels of a contaminant generated by an industrial process vary over time. A wide spectrum of gas collection devices have been used to collect grab samples, including evacuated flasks or metal cylinders, syringes, plastic bags, and gas and liquid-displacement containers.

Evacuated Containers

Evacuated containers are usually heavy walled, glass containers ranging in size from 200 to 1000 cc in which the air has been partially or completely removed. These air collection devices have been successfully used for many years in the mining industry by the Bureau of Mines (BOM) (5)(77)(100) and more recently by the Mine Safety and Health Administration (MSHA) compliance officers to test underground work atmospheres for toxic and explosive gases (101). Containers currently used are 50 cc or 250 cc glass bulbs that have been evacuated with a vacuum pump and the neck sealed by heating and drawing the open end to a tip during the final stages of evacuation. To collect an air sample, the etched tip of the bulb is broken; the surrounding atmosphere enters and fills it to atmospheric pressure. The container is then resealed and submitted to the laboratory for analysis. A lightweight, steel evacuated container (Figure I-1) lined with a nonabsorbing interior surface has reportedly been used with success for a number of years (61). Designed and used initially as a breath alcohol tester in forensic applications (84), its use has been extended to air sampling for a variety of organic vapors including benzene, methyl ethyl ketone, styrene, and vinyl chloride. Sample collection is achieved by pressing a button which activates the sampler. After the sample has been collected, the sampler

is submitted to the laboratory for analysis.

With the availability of more sensitive analytical instrumentation, smaller sample volumes have been found to be adequate. This led to the use of 10 cc *vacutainer syringe systems* (31)(32)(33)(101) by the BOM and MSHA for routine sampling of mine gases except for those which are highly reactive. Similar to conventional hypodermic syringes, the vacutainer system is an evacuated glass test tube-shaped vessel, capped with a self-sealing butyl rubber septum (Figure I-2). To draw a sample, the tube is inserted into a holder equipped with a needle which punctures the rubber septum allowing air from the surrounding atmosphere to be drawn into the tube. After the sample is drawn, the glass tube is removed from the holder and the septum self-seals. Advantages of the vacutainer system are that the syringes are small, light-weight, economical, convenient, and simple to use. The use of conventional *hypodermic syringes for sampling* gases and vapors has been previously reported (34)(47).

Gas Sampling Bags

Gas sampling bags have been used successfully for a number of years to collect air samples containing organic and inorganic gases (19)(20)(21)(53)(75)(87)(95)(98)(102) and as a static system for the preparation of known concentrations of gases for the calibration of air sampling instrumentation (7)(10)(95). Grab bag sampling provides a simple, uncomplicated, and relatively economical means of collecting and transferring air samples to a laboratory for analysis.

An important feature of plastic bag sampling is that it offers the option of short-term sampling or sampling for a full work shift, depending on the size of the bag and the pump flow rate. Common field application of this technique is the use of a single portable analytical instrument to analyze multiple samples on site (where they are collected by an industrial hygiene team). Immediate on-site testing of a gas has an important advantage in that it greatly reduces the possibility of gas decomposition before analysis.

Plastic bags are commercially available and come in a variety of sizes and shapes with the 1-15 liter volume appearing to be the most useful for grab or short-term sampling and up to 170 liters for full-shift sampling. In addition, most

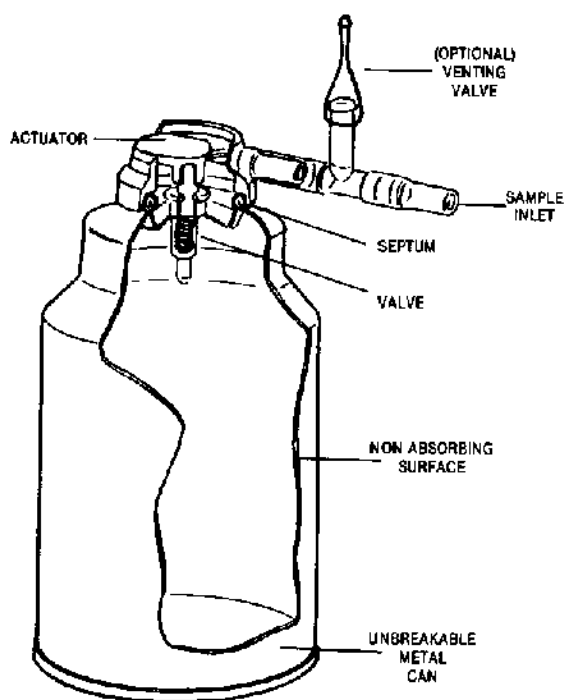


Figure I-1. Steel Evacuated Air Sampler (Vaccu-Sampler)

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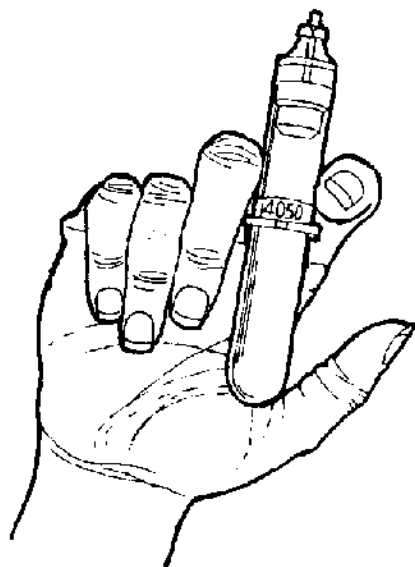


Figure I-2. Vacutainer syringe system used in the collection of mine atmosphere gases.

Source: *Mine Gases*, Safety Manual No. 2, U.S. Department of Interior, Mine Enforcement and Safety Administration.

plastic air sampling bags can be obtained with a number of convenient accessories, such as twist-lock open and shut-off valves, through which air can be easily sampled or discharged, and special permanent or replaceable rubber septums, through which air samples can be removed with a syringe.

Gas sampling bags are constructed from a number of materials including polyester, polyvinylidene chloride, teflon, and fluorocarbons (77). The selection of a bag constructed of a given material cannot be extended for use in collecting a broad range of gases because of the possible reactive nature of the gas with the bag. It is, therefore, necessary to know the type of material from which the bag is fabricated as well as its reactive, adsorptive, absorptive, and diffusive properties to the gaseous contaminant. Information on the storage properties of gases and vapors in plastic containers has been published (4)(6)(12)(23)(39)(54)(74)(83)(92).

Gas or Liquid Displacement Collectors

Gas or liquid displacement collectors (6)(77)(101) are primarily 250-300 ml *glass aspirator bulbs* fitted with end tubes which can be conveniently opened and closed with greased stop-cocks. Air samples are collected by aspirating the test atmosphere through the sample container with a suitable source of suction (bulb aspirator, hand pump, battery, or electrically operated vacuum pump) until its original content of air is replaced. Larger *aspirator vessels* can be used where large volumes of the test atmosphere or longer term sampling is required. Air samples can also be collected by liquid displacement. This method entails filling the container with a suitable liquid (usually water) and allowing it to drain out at the sampling location, whereupon the test atmosphere enters the container as the liquid is displaced. Application of this method is limited to gases which are insoluble or nonreactive with the displaced liquid. Although these methods were once routinely used for collecting air samples in work atmospheres and in laboratory studies, they receive little use today because of more convenient and accurate methods.

Because the quantity of material collected with gas sampling devices is often small, sensitive analytical methods are required to detect and measure concentrations of the gaseous contaminant collected. This has been a limiting factor

in using the grab sample in the past. Consequently, grab sampling has, to a large extent, been restricted to the collection of gross quantities of gases in air such as methane, oxygen, carbon monoxide, carbon dioxide, and nitrogen. However, the use of grab samples for the collection of low levels of gaseous contaminants has been greatly extended by advances in the refinement of sensitive analytical procedures and instruments based on chromatography and spectrophotometry.

Grab samplers should not be used to collect reactive gases (hydrogen sulfide, oxides of nitrogen, sulfur oxides, etc.) unless the samples can be analyzed within a short time after collection. Without prompt analysis, these gases can react with dust particles, moisture in the stopper, sealant compounds, and the glass container to alter a sample's chemical composition and result in an erroneous estimate of the concentration. This problem can sometimes be overcome by collecting the reactive gas in a conventional vacuum-type (evacuated) sample container prepared with an appropriate absorbing reagent to stabilize and preserve the sample until analysis can be accomplished (5)(14)(100).

An important feature of grab sampling is that the collection efficiency is normally 100%. However, sample decay can occur for several reasons. To limit or avoid this source of error, after introducing the sample of contaminated air into the container, it should be properly sealed to prevent sample loss and analyzed immediately in the field or submitted to the laboratory as soon as possible.

Unlike conventional liquid and solid sorbent sampling, gas flow measurements are not necessary with grab sampling devices because the air sample collected can be metered directly from the sample container into the analytical instrument, or measured volumes of the air sample can be drawn from the sampling device with a syringe and injected directly into the injection port of the analytical instrument. However, it is necessary to include the temperature and pressure (normally 25°C and 760 mm mercury) at which the air sample was collected in order that results of the sample analysis can be reported in terms of standard conditions.

Integrated—Average or Long-Term Sampling

Integrated sampling for airborne gaseous

agents is employed when (a) concentrations of the contaminant(s) to which the worker is exposed vary significantly over a work shift, (b) when ambient concentrations of the contaminant(s) are low and sampling over an extended period of time is required to satisfy the sensitivity requirements of the analytical method, and/or (c) to obtain a reliable estimate of the worker's exposure over a full work shift, in order to establish compliance or noncompliance with an 8-hour, time-weighted-average occupational health standard.

The collection of integrated samples usually involves the extraction and concentration of gaseous contaminants from a sample's airstream, employing the principles of *absorption*, *adsorption*, or *condensation*.

Absorption

In this method the gaseous contaminant is extracted from the sampled air stream and concentrated in solution by drawing it through an absorbing liquid or reacting it with an absorbing reagent. Four basic absorbers have been used: *simple gas wash bottles*, *spiral or helical absorbers*, *fritted bubblers*, and *glass beaded columns*. The selection of an appropriate absorbing device depends upon the solubility and reactivity of the gaseous agent being collected.

Simple gas wash bottles such as the Greenberg-Smith (35)(37) and midget impinger (24)(52)(56)(63) are suitable for sample collection of nonreactive gases and vapors that are highly soluble in absorbing liquids and form near perfect solutions such as methanol in water and esters in alcohols. High collection efficiency can also be achieved by utilizing specific absorbing reagents which react rapidly with the gaseous contaminant, chemically changing it to a more stable form. Examples of these are 2,4-toluene diisocyanate (TDI) hydrolyzed by an absorbing reagent solution to a corresponding toluenediamine derivative (64), and p,p diphenylmethane diisocyanate (MDI) hydrolyzed to methylene dianiline (65).

The midget impinger (Figure I-3) has been the most widely used gas washing bottle for sampling of gases and vapors in the occupational environment. They can be used to collect general area air samples from a stationary position; they can be hand held to collect worker breathing zone samples; or they can be attached to the worker's clothing for a personal sample. A

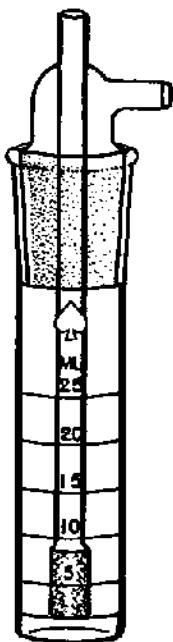


Figure I-3. Midget Impinger

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serious problem often encountered in the field is accidental spillage of the absorbent liquid by the worker bending over and inverting the impinger. However, spillproof impingers have been developed and are commercially available (38). The collection efficiency can be increased by entraining two or more impingers in series (25)(26).

Spiral Type Absorbers—(Figure I-4) are examples of gas wash bottles that can be used to collect gaseous substances that are only moderately soluble or slow reacting with reagents in the absorbing medium. These absorbers are essentially the same as those for simple gas wash bottles except that the spiral or helical structure design provides for higher collection efficiency by forcing the air sample to travel a spiral or helical path through the liquid. This takes five to ten times longer than does the simple wash bottle; allows a longer residence time within the tube; and results in longer contact between the sampled air and the absorbing solution.

Fritted Bubblers—(Figure I-5) are the most commonly used absorbing devices in the field today for sampling gaseous air contaminants in ambient work atmospheres. They are more efficient collectors than simple gas wash bottles

and can be used to collect gases and vapors that are only slightly soluble or reactive with the absorbing liquid medium. The principle involves drawing the air sample through a sintered or fritted glass bubbler which is submerged in an absorbing solution or reagent. As the sampled air is drawn through the fritted bubbler, many small bubbles and a heavy froth develop, increasing the surface area and contact time between the gaseous contaminant and the absorbing solution. Air bubble size is dependent upon the nature of the absorbing liquid and diameter of the orifices from which the bubbles emerge.

Frits are classified as fine, coarse, and extra coarse depending on the number of openings per unit area. Coarse frits are used when a rapid sample rate is desired and when the gaseous contaminant sampled is appreciably soluble and/or reactive in the absorbing liquid medium. Medium porosity frits are used for gases and vapors that are more difficult to collect, and fine porosity frits are used for highly volatile gaseous substances that are extremely difficult to collect. In general, smaller bubbles and greater generated froth effectuate greater surface area and contact

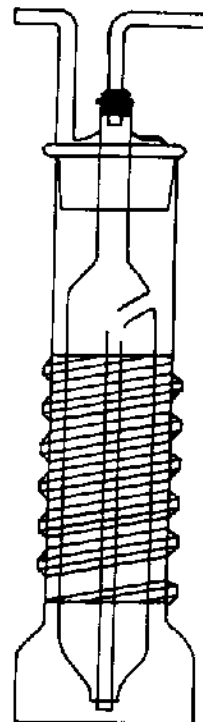


Figure I-4. Spiral Absorber

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time between the gaseous contaminant and the absorbing solution—hence, greater collection efficiency.

Columns packed with glass pearl beads (Figure I-6) coated with an appropriate absorbing medium are used in special situations where concentrated solutions of a gaseous contaminant is required. The beads provide a large surface area for collection of the gaseous contaminant. This absorption method has been used successfully in the past to collect benzene and other aromatic hydrocarbon vapors in nitric acid (91).

Adsorption

The most common air sampling method used today to collect trace quantities of insoluble or nonreactive gases and vapors in the workplace is adsorption with solid sorbents. Several solid sorbents have been successfully used such as activated alumina (11), molecular sieves (2) (11), porous polymer beads (22)(48)(59)(60), silica gel (16), and activated charcoal (28)(29) (30)(76) (93)(103)—with the latter two being the most widely used. The principle of adsorption involves drawing a known volume of air at a controlled flow rate through a small tube packed with an appropriate sorbent material. As the air passes through the tube, the molecules of the contaminant are adsorbed onto the surface of the sorbent chemically and physically unchanged. The contaminant is then desorbed (extracted) from the sorbent by a liquid solvent or thermal desorption for subsequent analysis.

Solvent desorption (28)(72)(76)(103) has been considered the standard method for sample recovery. However, the use of thermal desorption (22)(59)(82)(93) is becoming more widely used because the entire sample can be removed from the sorbent and analyzed at once, increasing the sensitivity of the analytical method.

The adsorbing properties of activated sorbents are entirely determined by the nature and extent of their surfaces and may be classified as either electrically polar or nonpolar (2).

The polar adsorbents have an affinity for polar as well as nonpolar molecules, but prefer polar substances, such as water vapor. Polar adsorbents such as silica gel can, therefore, be used either for short duration sampling of atmospheres that contain relatively high concentrations of contaminants or in atmospheres that are sufficiently low in moisture content so that the ad-

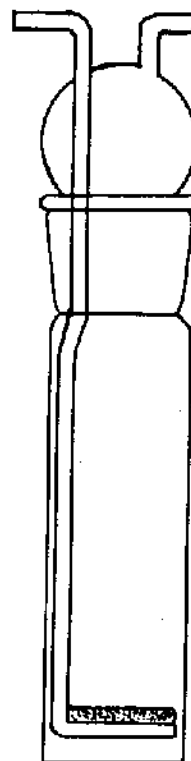


Figure I-5. Fritted Bubbler

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sorbent does not become saturated with water vapor before sampling is complete (2).

Silica gel, an amorphous form of silica, is formed from reacting sodium silicate with sulfuric acid. It is electrically polar and therefore attracts partially charged (polar) molecules to active sites on its surfaces. Among the important advantages of using silica gel are: (1) desorption of contaminants can be easily accomplished with a variety of common solvents such as alcohols, ethers, and water; (2) it can be used to collect certain inorganic substances for which charcoal is unsuitable. A disadvantage is that being highly polar, water remains tightly bound to the surface of silica gel, and if sampling is continued long enough, moisture will displace relatively nonpolar organic solvents already collected. Beginning with water vapor, the descending order of polarizability of specific homologous chemical groups are: alcohols, aldehydes, ketones, esters, aromatic hydrocarbons, olefins,

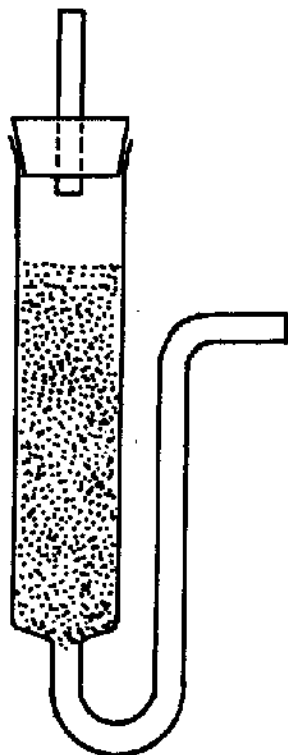


Figure I-6. Column packed with glass beads.

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and paraffins (78). Silica gel is currently the standard method recommended by NIOSH for aromatic (67) and aliphatic amines in air (66).

Charcoal (an amorphous form of carbon formed by burning wood, nutshells, animal bones, and other carbonaceous materials) is the most common solid sorbent in current use for sampling for airborne concentrations of organic solvent vapors. Because of its electrically non-polar character, it adsorbs organic vapors and gases in preference to atmospheric moisture.

The activated carbon currently recommended is coconut shell charcoal, manufactured to NIOSH specifications (11)(72). The advantage of using charcoal is that it has an extensive internal surface area, as large as 10,000 sq. ft. per gram of material (77), which greatly enhances its adsorption capacity.

Experience has shown that organic solvent vapors are usually encountered in the industrial environment as mixtures and not in a single pure form. Therefore, an air sampling and analytical

technique is desirable which is capable of collecting, separating, identifying, and determining the concentrations of each individual constituent of a mixture of airborne solvent vapors. The method that fulfills this requirement is the Charcoal Tube-Gas Chromatographic Method (28)(30)(56)(85)(86)(93)(103)(104)(Figure I-7). The method entails adsorption of organic vapors onto activated charcoal during sampling, desorption of the material from the charcoal with carbon disulfide, and subsequent analysis with flame ionization or electron capture gas chromatography. This is presently the air sampling and analytical method recommended for organic solvents in air by NIOSH (72).

Disadvantages of this method are that solvent desorption of the contaminant(s) from the charcoal is not always 100%, dilution of the sample occurs from solvent extraction resulting in a lowered sensitivity for analysis, and the carbon disulfide solvent used for desorption is extremely toxic and flammable.

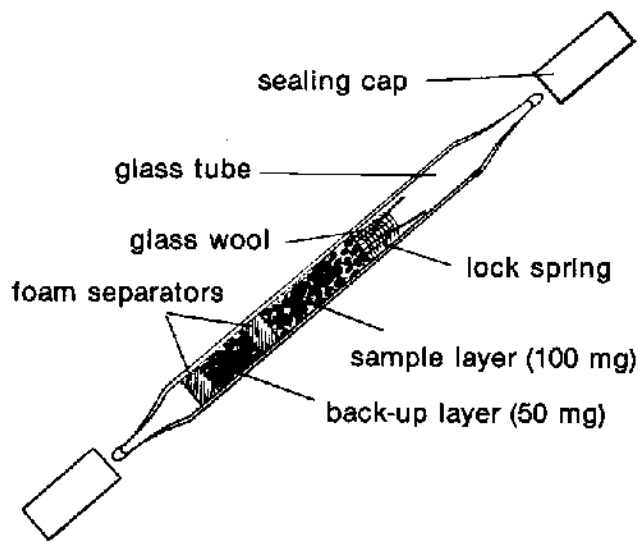


Figure I-7. Activated Charcoal Sampling Tube

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Inorganic compounds such as ozone, nitrogen dioxide, chlorine, hydrogen sulfide, and sulfur dioxide react chemically with activated charcoal and cannot be collected for analysis by this method (77). In addition, chemical substances such as the amines and particularly the aromatic amines (aniline, o-anisidine, p-anisi-

dine, N, N-dimethylaniline, p-nitroaniline, o-toluidine, and 2,4-xylidine) are not easily removed from charcoal and must be collected with other collecting media such as silica gel.

Impregnated Solid Sorbents—Until recently, the use of solid sorbents in air sampling has been restricted to the collection of nonpolar, insoluble, nonreactive gases. The development of ion chromatography (36)(97) as an analytical tool for the analysis of ionic forms of gaseous agents, and the subsequent development of solid sorbent tubes impregnated with absorbing reagents, has led to the successful collection and analysis of reactive (45)(71) and other gases (15) which previously could only be collected by wet impingement methods (71)(89) or for which no suitable method existed (62).

Any gas or vapor that can be quantitatively converted to an ionic form can be analyzed by ion chromatography. First, the sample is passed through an ion exchange column where the contaminant is retained. Second, the background ionic level of the eluent is suppressed by a second ion-exchange column which cancels the unwanted ions of eluent but does not affect the eluting ions. The eluting ions are detected by a conductivity detector.

The principle of sampling with impregnated solid sorbents involves the collection of a gaseous contaminant in standard solid sorbent tubes (69) impregnated with an appropriate absorbic reagent which changes the collected gas to a more stable ionic form. This is achieved by drawing the air through the sorbent tubes at a controlled flow rate for a known period of time. The sample is then desorbed with an appropriate solvent, followed by ion chromatography analysis.

Impregnated solid sorbent tubes using charcoal as the sorbent material, have been recently developed and tested for sulfur dioxide (96) and formaldehyde (45). These contaminants have traditionally been collected by wet chemical methods that require the use of liquid impingers. The overall recovery rates for sulfur dioxide and formaldehyde were reported as 94.6% and 100% respectively.

Impregnated solid sorbent tube sampling has significant advantages over the use of midge impingers. (1) It facilitates the collection and analysis of certain gaseous agents which do not lend themselves to more conventional methods; (2) the tubes are easily handled in the field; (3) they cannot be spilled; and (4) due to their small

size, they can be easily packed for safe transportation to the laboratory.

The combination of impregnated sorbent tubes and ion chromatography promises superior sampling and analytical methods for the collection and analysis of reactive gases and vapors. Further developmental work on impregnated solid sorbent tubes should result in tubes designed specifically for reactive gases such as ozone, nitrogen dioxide, chlorine, and hydrogen sulfide, as well as other inorganic and organic gases and vapors. Not only will sampling be simplified, but the analytical method itself will be more precise, accurate, and less expensive than most of the currently available methods.

Passive Dosimeters—Passive dosimetry is a new and innovative concept for sampling both organic and inorganic vapors that promises a simpler sampling future for the industrial hygienist. The method requires no air sampling pump, has a low unit and capital cost, can be used to monitor organic vapors currently being sampled by solid sorbent tube methods, and the samples can be analyzed using standard GC techniques. Inorganic vapors such as NO₂, SO₂, and NH₃ can be determined using the passive dosimeter in combination with photometry, chromatography, or colorimetry. The passive dosimeters produce an integrated sample for periods as low as 15 minutes and as long as 8 hours.

The process of passive dosimetry is based on Fick's first law of diffusion. The basic requirement is that complete collection efficiency occurs such that the concentration of contaminant at the collection surface is zero. The concentration of contaminant at the badge face is the ambient concentration. This results in a concentration gradient through which contaminant molecules diffuse at a constant rate.

Two mechanisms exist for collection of contaminant material. One is adsorption of the contaminant into a bed of uncoated solid sorbent such as charcoal or silica gel. The other method is to react the contaminant with a chemical coating on the collection surface. Both methods are currently used, with charcoal being used for nonpolar organics, silica gel for polar gases, and chemical coatings for reactive gases.

Development of dosimeters for NO_x and NO₂ (Figure I-8) has been carried out primarily by Palmes et al. (79)(80)(81). Field tests of two types of NO₂ dosimeters have been conducted by Jones et al. (41). Evaluation of passive dosi-

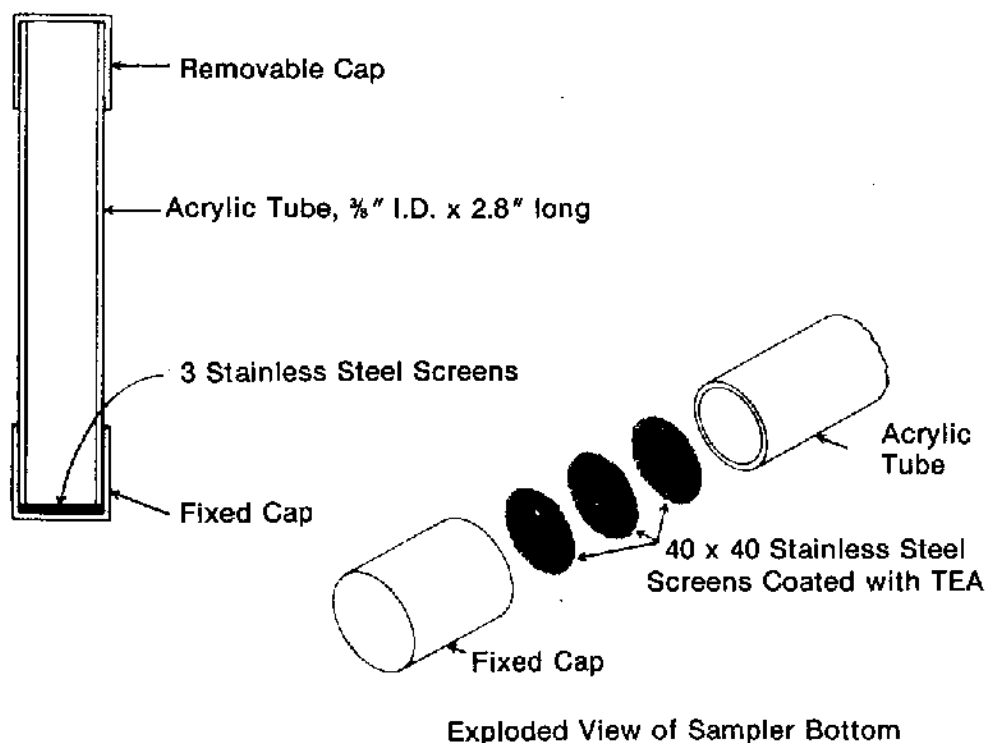


Figure I-8. Palmes Passive NO₂ Dosimeter

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meters for organic vapors have been conducted by Bamberger (13).

Commercial versions of the passive dosimeter have only recently begun to appear on the market. The industrial hygiene community has not yet had time to gain sufficient field experience in their use to fully evaluate the devices. However, the advantages of passive dosimeters are such that a great deal of effort is currently being put into their development and field evaluation.

Passive dosimeters are commercially available for SO₂ (99), NO₂ (99), mercury vapor (57), and aniline vapors (18), as well as several other gases (46)(49). The dosimeters are desorbed and analyzed by standard gas chromatography or other analytic methods.

A recently developed device which is now commercially available is a colorimetric air monitoring badge system. This system combines the passive dosimeter with colorimetry to quickly determine the time-weighted-average exposure of workers to SO₂, NO₂, NH₃, and HCHO (46).

The badge (Photograph 1) is exposed to the atmosphere for an appropriate length of time after which plastic blister packs containing chemical reagents are ruptured. The chemicals are mixed by palpating the plastic pack after which the concentration in parts per million hours is read from a portable colorimeter.

Another new passive dosimeter which is commercially available is an organic vapor air monitoring badge (Photograph 2) which features a backup section. The backup section serves the same purpose as the backup section in the standard charcoal tube, i.e., to determine whether or not breakthrough of contaminant from the front section has occurred. This device employs activated charcoal as a solid sorbent. Analysis is performed by gas chromatography just as with charcoal sampling tubes.

Condensation

The condensation method of sampling for gaseous agents is used to collect gaseous materials in liquid or solid form, primarily for



Photograph 1. Colorimetric Air-Monitoring Badge

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Photograph 2. Organic Vapor Air-Monitoring Badge with Back-up Section

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identification purposes (77), or to sample for gaseous contaminants (such as sulfur trioxide vapor) which are difficult to collect by other techniques (8). Samples are collected by drawing the air sample through a single or series of cold traps immersed in dry ice and acetone, liquid air, or in a liquid nitrogen refrigerant bath cooling system. The collection traps are of double-wall construction, with the sampled air passing through the space between the walls. Apparatus and procedures for condensation sampling have been previously described in detail (94).

To condense a given gas or vapor, the refrigerant should be cold enough to reduce the temperature of the substance below its boiling point and maintain the vapor pressure of the trapped material sufficiently low to prevent significant evaporation during the sampling period. Generally, the vapor pressure should be about 1 mm of mercury or lower at the cold trap temperature (42). Condensation methods have the advantage of concentrating contaminant gases or vapors and preserving them in their natural state, without a chemical reaction. This method is particularly useful when airborne concentrations of a given gaseous contaminant are low and a highly concentrated sample of the material is required for analysis. An important disadvantage of the condensation method is that the condensation unit is somewhat bulky and not considered to be a portable field instrument. Other special problems are that unwanted substances in the air sample will also condense out, often in copious quantities, such as water vapor, hydrocarbons, and other gaseous contaminants that readily condense to the liquid state at temperatures of ice water. Although a compact condensation method has been developed (51), the disadvantages inherent in this method have relegated its use to a last resort status.

DIRECT READING INSTRUMENTATION

Portable direct reading instrumentation designed to detect and measure worker exposure to airborne concentrations of *particulates* and *gases* and *vapors* has undergone significant evolution within the past decade (1970's), primarily due to the passage of the Federal Occupational Safety and Health Act of 1970, which requires each employer to provide a safe and healthy workplace. The safety and health standards promulgated under this legislation provide

an economic incentive for the commercial production of more sophisticated and accurate direct reading instrumentation, with the capability to immediately detect and measure potentially hazardous concentrations of airborne contaminants.

Direct reading instrumentations are of two general groups. The first group consists of those that produce a *color change* either in solution or detector (indicator) tubes through which the air sample has been drawn or on chemically treated papers exposed to contaminated atmospheres. The second comprises those that have *electronic circuitry* and are capable of sampling a volume of air, performing qualitative and/or quantitative analysis internally, and displaying the results immediately on a dial, illuminated digital display panel, tape printout, or strip chart recorder.

Colorimetric Direct Reading Indicators

There are essentially three types of direct reading colorimetric indicator systems used for the determination of concentrations of gaseous contaminants in air: *liquid reagents*, *chemically treated papers*, and *detector tubes* (also called indicator tubes). Detector tubes contain solid supports treated with chemical reagents. All three systems utilize the chemical properties of an atmospheric contaminant to produce a reaction with a color-productive reagent (44). Comprehensive bibliographies on this subject have been previously prepared (17)(88).

Chemical indicators primarily lend themselves to the detection and semiquantitative analysis of airborne gaseous contaminants. Their accuracy depends largely on the care with which the given type of indicator (detector) system is prepared and standardized. Among the most important considerations are the experience of the operator and his knowledge of the atmosphere being sampled. By knowing the limitations of the chemical reaction and having a general idea of the atmosphere being sampled, a relatively quick and inexpensive estimate of the agent of interest may be obtained.

Liquid Reagents

Here the reagent solution is carried into the field with an air sampling unit such as a liquid impinger or bubbler (9)(71)(89). In this inconvenient but sensitive procedure (often referred

to as "air titration" or "air colorimetry"), the reagent or scrubbing solution must trap and react with the contaminant to either produce a color change from which a semiquantitative analysis is made, or the colorless reagent is returned to the laboratory for analysis (73).

Field use of liquid reagent sampling is more prevalent than the literature indicates because many laboratories have taken routine procedures and made reference solutions for direct comparison with the field sample for concentration determinations.

The use of Saltzman's reagent (80)(90) in a fritted glass bubbler to determine the ambient airborne concentrations of oxides of nitrogen has been a classic application of this method. A known titer and volume of Saltzman's reagent is placed in an all glass bubbler connected to an air pump with a length of tubing. The contaminated air is pulled through the reagent in a bubbler at a controlled rate until a perceptible color change occurs. The concentration of nitrogen dioxide in air is inversely proportional to the time required to produce a perceptible color change.

A disadvantage of liquid methods in the field is that they are inconvenient and bulky to transport. An important advantage is that the measurement of color in liquids is inherently more reproducible and accurate than the measure of color on solids.

Chemically Treated Papers

Although rarely used today because of the availability of more sophisticated, sensitive, and accurate methods, paper impregnated with chemical reagents found wide application for many years in the detection of toxic gases and vapors in work atmospheres. Examples are papers impregnated with mercuric bromide for the detection of arsine, lead acetate for the detection of hydrogen sulfide, a mixture of o-toluidine and cupric acetate for the detection of hydrogen cyanide (44), and detector tabs for carbon monoxide (58). The observed time required for a color change after exposure of a specific paper or tab to an agent is an indication of the concentration present. Other examples are chemical chalks and crayons formulated for use in sensitizing paper (40)(105) to phosgene, hydrogen cyanide, cyanogen chloride, and Lewisite (dichloro(2-chlorovinyl)arsine). Chalks, crayons, and chemically treated papers can be found in

military chemical warfare field surveillance sets today.

Detector Tubes

First developed in 1917 at Harvard University (3), the detector (or indicator) tube has been widely used in recent years as a useful, convenient, and economical tool for the detection and semiquantitative estimation of potentially toxic gaseous agents in industrial atmospheres.

Developed first for carbon monoxide, the methodology of these colorimetric indicator tubes has progressed to include a wide variety of tubes. Until World War II, the only indicator tubes in general use by industrial hygienists were for hydrogen sulfide and carbon monoxide (27). Presently, there are detector tubes for nearly 200 atmospheric gases available from four major companies and manufacturers.

A detector tube unit is composed of a pump, a colorimetric indicator tube, and possibly a conditioning tube. The preferred pump is either a bellows or a positive displacement piston type pump designed to draw a fixed volume of air with each stroke. Squeeze bulb-type pumps are no longer recommended because of reproducibility problems with the air volume drawn.

The indicator tube is a hermetically sealed glass tube containing a granular material such as silica gel, alumina, or pumice impregnated with a chemical reagent that reacts with the contaminant in the airstream as it is drawn through the tube.

To conduct a test, the two sealed ends of the indicator tube are broken off and the specified end of the tube is inserted into the rubber septum inlet of the pump after which a fixed volume of air is drawn at a controlled rate through the tube. After a short specified time has been allowed for color development, the concentration is determined. This is accomplished in one of three ways depending on the type of detector tube system used: 1) by comparing either an absolute length of stain produced in the column of indicator gel or a ratio of the stain length to the total gel length against a calibration chart to obtain an indication of the atmospheric concentration of the contaminant; 2) by comparing a progressive change in color intensity with a chart of color tints; or 3) noting the time required to produce an immediate color change in which the air volume sampled is in-

tended to be inversely proportional to the concentration of the atmospheric contaminant.

The results obtained from matching tube color change with charts of color tint is highly subjective among readers. The visual judgment, among other things, is dependent on the color vision of the readers and the quality of lighting in the immediate area. To reduce this source of reader error, the most recent types of tubes are based on the production of a variable length of stain on the indicator gel.

Another source of error is temperature. Because the chemical reaction rate is dependent on temperature, it should be recognized that many tubes will give erroneous readings at high or low temperatures.

Because of their simplicity and ease of operation, indicator tubes are widely advertised as being capable of use by unskilled personnel to rapidly assess worker exposure to potentially hazardous levels of toxic gases and vapors. While it is true that the operating procedures are simple, rapid, and convenient, it has been repeatedly demonstrated in practice that serious errors in sampler operation, in selection of sampling locations and times, and in the interpretation of results can occur unless the instrument is in the hands of a well trained operator who is supervised by a competent health professional. A manual describing recommended practice for colorimetric indicator tubes, published by the American Industrial Hygiene Association, explicates the principles of operation, applications, and limitations of these devices (3).

Perhaps the most difficult problem associated with the use of indicator tubes is that of interfering gases. The problem primarily lies in the use of indicating reagents which lack specificity. For example, the use of a hexavalent chromium compound as a tube reagent to oxidize a number of organic substances (which produce a given chromatic color reaction) is non-specific (44). All readily oxidizable substances may affect the indication. Also, aromatic hydrocarbons, halides, hydrides, and chlorinated hydrocarbons are chemicals widely used in industry and often found as mixtures in air. These are examples of class compounds for which single reagent formulations in detector tubes have been used. A single reagent formulation limits the usefulness of these tubes in mixed exposure areas, since several gases are present and the tube can give only one reading. Additionally, two or more gases can interfere with each other

during the color-producing reaction. However, the single reagent formulations can still be useful in estimating maximum worker exposure because almost all interferers increase the stain length.

Historically, there have been and still are serious problems with tube quality due to a lack of quality control among manufacturers. Rigid quality control of reagent(s) purity, grain size of supporting material, method of packing tubes, moisture content, uniformity of tube diameter, and proper storage precautions are required for optimal and consistent performance of any detector tube. The most critical problem is that there are few standardized methods for generating known concentrations of calibration gases for these tubes. The use of detector tubes that are produced with poor quality control and that have questionable performance requirements could result in an occupationally hazardous situation remaining unrecognized or uncorrected.

A move was made in 1973 to rectify this problem by the issuance of regulations for certification of gas detector tube units. These regulations appeared in the Federal Register on May 8, 1973, (38FR 11458) and were incorporated in the Code of Federal Regulations as Title 42 CFR Part 84 under authority of the Occupational Safety and Health Act of 1970. However, in 1978, HEW withdrew these regulations since they were no longer federally mandated, but certification continued under the National Institute for Occupational Safety and Health's (NIOSH) Guidelines.

Performance requirements for gas detector units were also developed by NIOSH, with the cooperation and assistance of members of the Joint Direct Reading Gas Detecting Systems Committee of the American Industrial Hygiene Association and American Conference of Governmental Industrial Hygienists.

NIOSH certifies a manufacturer to produce a gas detector tube unit to meet the minimum requirements set forth in the NIOSH Guidelines (basically $\pm 35\%$ accuracy at $\frac{1}{2}$ the exposure limit and $\pm 25\%$ at 1 to 5 times the exposure limit). The quality of future production lots is evidenced by a quality assurance plan which NIOSH approves as part of the certification. Adherence to the quality assurance plan is verified by periodic plant inspections and by testing samples purchased on the open market.

As of July 1980, NIOSH had issued certifications for 63 gas detector tube units from 5

Table I-37
NIOSH CERTIFIED GAS DETECTOR TUBE UNITS

| Calibrated for | Certification | Manufacturer | Model Tube/Pump(s) |
|-----------------------|----------------------|---------------------|---------------------------|
| Acetone | *TC-84-054 | MSA | 460423/83499 or 463998 |
| Ammonia | *TC-84-023 | Gastec | 3M/400 |
| Ammonia | *TC-84-031 | Drager | CH20501/31 |
| Ammonia | *TC-84-032 | Kitagawa | 105Sc/400 |
| Ammonia | *TC-84-033 | Kitagawa | 105c/400 |
| Ammonia | *TC-84-034 | MSA | 460103/83499 or 463998 |
| Benzene (A) | *TC-84-043 | Gastec | 121/400 |
| Benzene (A) | *TC-84-044 | Drager | 67-28071/31 |
| Carbon Dioxide | TC-84-021 | Gastec | 2L/400 |
| Carbon Dioxide | TC-84-025 | MSA | 85976/83499 or 463998 |
| Carbon Dioxide | TC-84-026 | Kitagawa | 126Sa/400 |
| Carbon Dioxide | TC-84-027 | Kitagawa | 126a/400 |
| Carbon Dioxide | TC-84-029 | Drager | CH23501/31 |
| Carbon Disulfide | *TC-84-066 | Drager | 67-28071/31 |
| Carbon Monoxide (A) | TC-84-012 | Drager | CH25601/31 |
| Carbon Monoxide (A) | TC-84-013 | Drager | CH20601/31 |
| Carbon Monoxide (A) | TC-84-014 | Gastec | 1La/400 |
| Carbon Monoxide (A) | TC-84-015 | MSA | 91229/83499 or 463998 |
| Carbon Monoxide (A) | TC-84-019 | Kitagawa | 106S/400 |
| Carbon Monoxide (A) | TC-84-045 | Kitagawa | 100/400 |
| Carbon Monoxide (A) | TC-84-067 | MSA | 465519/83499 or 463998 |
| Carbon Monoxide (B) | TC-84-013 | Drager | CH20601/31 |
| Carbon Monoxide (B) | TC-84-067 | MSA | 465519/83499 or 463998 |
| Carbon Tetrachloride | TC-84-036 | Gastec | 134/400 |
| Chlorine | *TC-84-041 | Gastec | 8La/400 |
| Chlorine | *TC-84-042 | MSA | 460225/83499 |
| Chlorine | *TC-84-070 | Drager | 67-28411/31 |
| Ethyl Benzene | *TC-84-064 | Drager | 67-28381/31 |
| Ethylene Dichloride | *TC-84-058 | MSA | 461863/83499 or 463998 |
| Hexane (normal) | *TC-84-063 | Drager | 67-28391/31 |
| Hydrogen Chloride | TC-84-071 | Drager | CH29501/31 |
| Hydrogen Cyanide | TC-84-051 | Drager | CH25701/31 |
| Hydrogen Cyanide | *TC-84-052 | Kitagawa | 112Sb/400 |
| Hydrogen Cyanide | *TC-84-068 | Gastec | 12L/400 |
| Hydrogen Sulfide (A) | TC-84-020 | Gastec | 4LL/400 |
| Hydrogen Sulfide (A) | TC-84-022 | MSA | 460058/83499 or 463998 |
| Hydrogen Sulfide (A) | TC-84-024 | Drager | 67-19001/31 |
| Hydrogen Sulfide (A) | TC-84-037 | Kitagawa | 120b/400 |
| Hydrogen Sulfide (B) | TC-84-062 | Drager | CH29801/31 |
| Hydrogen Sulfide (B) | TC-84-072 | MSA | 463875/83499 or 463998 |
| Methyl Bromide | *TC-84-056 | Drager | 67-28211/31 |
| Methylene Chloride | *TC-84-061 | Drager | 67-28331/31 |
| Nitric Oxide | *TC-84-048 | Drager | CH31001/31 |
| Nitric Oxide | *TC-84-049 | Gastec | 10/400 |
| Nitric Oxide | *TC-84-059 | MSA | 460424/83499 or 463998 |
| Nitrogen Dioxide | *TC-84-016 | Drager | CH30001/31 |
| Nitrogen Dioxide | *TC-84-018 | Gastec | 9L/400 |
| Nitrogen Dioxide | *TC-84-040 | MSA | 83900/83499 or 463998 |

Table I-37
NIOSH CERTIFIED GAS DETECTOR TUBE UNITS (Continued)

| Calibrated for | Certification | Manufacturer | Model Tube/Pump(s) |
|-------------------|---------------|--------------|------------------------|
| Nitrogen Dioxide | *TC-84-048 | Drager | CH31001/31 |
| Perchloroethylene | *TC-84-065 | MSA | 460467/83499 or 463998 |
| Sulfur Dioxide | *TC-84-017 | Gastec | 5La/400 |
| Sulfur Dioxide | TC-84-028 | Kitagawa | 103Sd/400 |
| Sulfur Dioxide | TC-84-030 | Drager | CH31701/31 |
| Sulfur Dioxide | TC-84-035 | Kitagawa | 103d/400 |
| Sulfur Dioxide | TC-84-046 | MSA | 92623/83499 or 463998 |
| Sulfur Dioxide | TC-84-069 | Drager | 67-28491/31 |
| Toluene | TC-84-050 | Drager | CH23001/31 |
| Toluene | TC-84-053 | Gastec | 122/400 |
| Toluene | TC-84-057 | MSA | 461371/83499 or 463998 |
| Trichloroethylene | TC-84-038 | Gastec | 132H/400 |
| Trichloroethylene | TC-84-039 | Drager | CH24401/31 |
| Trichloroethylene | TC-84-055 | MSA | 460328/83499 or 463998 |
| Vinyl Chloride | TC-84-060 | Gastec | 131L/400 |

*The unit indicates a general class of compounds (amines, hydrocarbons, strong oxidents, etc.) to differing degrees. The calibration is certified only for the compound listed.

The above includes all the gas detector tube units certified by NIOSH through July 1, 1980. The units are sorted by the gas for which they are certified. Some gases contain more than one testing range and are listed more than once with "Range A" or "Range B" immediately following the gas name.

manufacturers (68)(2) (see Table I-37). While the certified units represent the bulk volume sold in the United States, they are certified to measure only 23 gases.

Long-Term Detector Tubes

The successful development and use of the detector tube as an instrument for rapid detection and semi-quantitative determination of worker exposure to gaseous contaminants has led to the development of long-term detector tubes which can sample work atmospheres over an extended period of time (up to 8-hours) to measure the worker's integrated or time-weighted-average exposure.

Long-term detector tubes (LTT) are similar to short-term detector tubes in both physical appearance, method of detection, and display of a contaminant's concentration. Long-term detector tube samples are acquired by drawing the air through the tube at a controlled low flow rate with a battery powered pump.

A color change occurs in the LTT when the air sample contains the gas or vapor to which the tube is sensitive. The tube has been calibrated and marked by the manufacturer, allowing the amount of contaminant to be determined by

reading the length of stain and making a simple calculation.

Most long-term tubes can sample continuously for periods up to 8 hours; short-term tubes typically sample only ½ to 5 minutes. The flow rate through an LTT is usually a low constant—5 to 20 ml/minute. A short-term tube has a flow rate that varies with the elapsed time, measured from the time the hand pump is released. Short-term tubes are very sensitive to flow rate and must be used with the specific pump recommended by the manufacturer. LTT's seem to be usable with any low flow pump, as long as the flow rate is constant and within the range recommended by the manufacturer (43).

The LTT and pump can be worn by the worker as he goes about his regular routine. At the end of the sampling period the tube can be read and the worker's exposure for that day recorded as part of his occupational work history.

With the LTT, only the worker's time-weighted-average exposure is reflected. To acquire an indication of the concentration of a gas over a short interval of time, the short-term detector tube is used. To measure peak concentrations, as required in determining compliance or non-compliance with short-term exposure limits and

ceiling values, electronic direct-reading instruments equipped with a strip chart recorder are used.

There are currently three manufacturers of long-term detector tubes; National/Drager, Mine Safety Appliances, and Kitagawa. The tubes are new to the industrial hygiene community and have not yet been critically evaluated.

Detector tubes have a valuable place in the arsenal of air sampling instrumentation used to detect worker exposure to potentially harmful gases and vapors. Their usefulness will ultimately depend on the quality with which they are produced and the knowledge and good judgment with which they are used. Some mechanism must be derived to provide occupational safety and health professionals with quality detector tubes for rapidly detecting a wider spectrum of toxic gases and vapors to which workers may be exposed in occupational environments. Following a recent study of the NIOSH Certification Program conducted by a team of highly qualified consultants from several professional disciplines, formal recommendations were presented in an interim report regarding the future role NIOSH should play in the testing and certification of hazard measuring instruments (70).

Electronic Direct Reading Instrumentation

The rapid development of portable and sensitive electronic direct reading instrumentation for evaluating workroom atmospheres has largely been due to the borrowing of air sampling and analysis technology already developed in the disciplines of radiation protection and air pollution control.

This class of direct reading instruments incorporates electronic sensors utilizing infrared and ultraviolet radiation, flame and photoionization, and chemiluminescence capable of detecting and measuring airborne concentrations of gases and vapors in a matter of seconds. Most of these instruments can be equipped with automatic continuous recording devices which generate real time data (representing peak exposure concentrations at any point in time) as well as time weighted data (averaging concentrations over time from a few seconds or minutes to full 8-hour work periods or longer), depending on the kind of exposure information required.

Among the most innovative improvements in electronic direct reading equipment has been

the recent mating of electronic direct instrumentation with microcomputers. Advances in microprocessor technology allow computerized instrument versions to retain the size and technical features of the previous versions in addition to having the control and mathematical capabilities of a microcomputer based system. Among the important functions the computerized version can accomplish are: immediate treatment and reduction of a mass of exposure data to a readily usable form upon termination of sampling, correction of interferences, and depending upon the capability of the basic instrument, automatic analysis for multi-component mixtures.

The operating principles of direct reading instrumentation are based upon the physical and/or chemical properties of the gaseous agents they detect and quantify. As a group, these principles are based on two phenomena:

The first is the *physical* principle in which the electronic detector or sensor element that generates the electrical signal with its information content is immediate to the air sampling process. A classic example is the mercury vapor meter where the principle involved is the absorption of ultraviolet (UV) light by mercury vapor which has a strong absorption line in the 253.7 millimicron region of the UV spectrum. The instrument consists of an absorption chamber, with a UV light source located on one end of the chamber and a photosensitive detector/sensor element located on the other. A sample of the immediate atmosphere being monitored is drawn through the instrument's absorption chamber where the UV light is absorbed by mercury vapor present in the airstream. The presence of the mercury vapor reduces the UV radiation reaching the photosensitive detector element in proportion to the concentration present. The change in intensity of UV radiation reaching the photosensitive detector element, which is connected to one arm of a Wheatstone bridge, creates an unbalanced condition that is detected and displayed on a meter as mercury vapor concentration in terms of milligrams of mercury per cubic meter of air (mg/m^3).

The second is the *chemicophysical principle*, in which the gas or vapor undergoes a chemical reaction, and a physical method is used to detect the changes caused by this reaction. Either the consumption of one of the reactants or the production of a product is measured. In either case, a physical property of a reactant or of a product

is measured. Oxidation-reduction reactions are typical examples of chemico-physical detection methods. The chemical part of the method is the oxidation or reduction of the contaminant; the physical part is a measurement of the number of electrons required to regenerate one of the reactants.

The Mast ozone meter employs a chemico-physical method of detection. Ozone (O₃) is used to oxidize potassium iodine to molecular iodine and potassium hydroxide. The free iodine produced reacts with a thin hydrogen layer that covers a wire electrode. This reaction consumes both hydrogen and iodine to yield hydrogen iodide. The removal of the thin layer of hydrogen allows a polarization current to flow through the wire, regenerating the thin hydrogen layer. For each ozone molecule in the sample, two electrons flow in the circuit. The microcoulomb sensor counts these electrons and displays the concentration of ozone in parts per million (ppm).

The scope and intent of this section does not lend itself to a comprehensive survey of existing electronic direct reading instrumentation. Rather, it delineates how chemical and physical properties of gaseous materials, together with detection methods and various performance parameters can be used to select a specific instrument to measure a given gas. Table I-38 lists methods of detection for agents causing occupational respiratory disease (ORD). Table I-39 lists the methods of detection, the chemical species to which the detector is sensitive, and a brief description of the principle of detection. Table I-40 lists the performance criteria upon which the various instruments can be evaluated and a description of the criteria.

For an excellent work describing most of the direct reading as well as nondirect reading air sampling instrumentation, the reader is referred to a publication by the American Conference of Government Industrial Hygienists (1).

Table I-38

MAJOR METHODS OF DETECTION FOR COMMON AGENTS CAUSING ORD.

X indicates the existence of a commercially available instrument employing the listed method of detection.

| Detector | Agents | | | | | | | | | |
|-------------------|-----------------|-----------------|-----------------|-----------------|----------------|-------------------|----|------------------|----|-----|
| | NH ₃ | Cl ₂ | NO _x | SO _x | O ₃ | COCl ₂ | Hg | H ₂ S | C* | S** |
| Flame Photometric | | | | X | | | | | | |
| Chemiluminescence | | | X | | X | | | | | |
| Colorimetry | X | | X | X | | | | | | |
| Coulometry | | | | X | X | | | | | |
| Electrical | | | | | | | | | | |
| Conductivity | X | | | X | | | X | | | |
| Flame Ionization | | | | | | | | | X | |
| IR Photometry | | | X | | | | | | | |
| Photoionization | | | | | | | | | X | X |
| Derivative | | | | | | | | | | |
| Spectrometry | X | | X | X | | | | | X | X |
| Thermal | | | | | | | | | | |
| Conductivity | | X | X | X | | X | | X | | |
| Voltammetric | | | | | | | | X | | |
| Electro | | | | | | | | | | |
| Chemical | | X | X | X | X | X | | | | |
| Microcoulomb | | | | | | | | | | |
| Redox | | | X | | | | | | | |

Table I-38

MAJOR METHODS OF DETECTION FOR COMMON AGENTS CAUSING ORD. (Continued)

X indicates the existence of a commercially available instrument employing the listed method of detection.

| Detector | NH ₃ | Cl ₂ | NO _x | SO _x | Agents | | Hg | H ₂ S | C* | S** |
|------------------------------|-----------------|-----------------|-----------------|-----------------|----------------|-------------------|----|------------------|----|-----|
| | | | | | O ₃ | COCl ₂ | | | | |
| Mass Spectrometry | | | | | X | | | | | |
| Electron Impact Spectrometry | | | X | X | | | | | | |
| Electron Capture | | | X | | | | | | | |
| UV Photometry | | X | X | | X | X | | X | X | X |

*Carbon containing ORD agents.

**Sulfur containing ORD agents.

**Table I-39
DETECTORS***

| Method of Detection | Gas or Vapor Detected | Description of Detector |
|---------------------|--|--|
| Flame photometric | Sulfur compounds | When a sulfur compound is burned in a hydrogen flame, energy at a wavelength of 394 nanometers is emitted. This energy is detected by a (UV) photometer and related to the concentration of the sulfur compound through a calibration curve. This curve plots contamination concentration along the X-axis and light intensity along the Y-axis. |
| Chemiluminescence | O ₃ NO/NO _x | When a molecule is excited to an unstable state (higher energy) and allowed to decay to a more stable (lower energy) state, a photon of energy is emitted within a specific wavelength range. The intensity of the emitted energy is related to the concentration of the excited molecule. |
| Colorimetry | SO ₂ NO ₂ NO _x NH ₃ Cl ₂ HCN | Certain gases can react with liquid color producing reagents that quantitatively convert the gas or the reagent to a colored liquid. The intensity of the color is related to the concentration of the contaminant gas. The intensity is measured using a visible light photometer set at the appropriate wavelength. |
| Coulometry | O ₃ SO ₂ NO ₂ NO CO H ₂ S | The consumption of electrons by a chemical reaction is measured using a microcoulomb sensor. One microcoulomb equivalent is the number of electrons required to reduce a mass of water on the order of nanograms. A microcoulomb is defined as a current of one micro-ampere flowing for one second. |

Table I-39
DETECTORS* (Continued)

| Method of Detection | Gas or Vapor Detected | Description of Detector |
|----------------------------|---|--|
| Electrical conductivity | NH ₃ H ₂ S SO ₂ | Gases that ionize in aqueous solution change the resistance of the solution to the flow of electrons. The more ions present in the solution, the greater the electron flow at a constant potential difference. This method of detection is nonspecific, i.e., the electrical conductance depends only on the number of ions present and not on the type of ions. |
| Flame ionization | Any volatile hydrocarbon | A gas is burned in a hydrogen flame, producing a large number of ionic fragments. These ions flow to a collection electrode where they are counted electronically. The method is nonspecific, responding to any hydrocarbon. |
| Photometry, IR | Hetroatomic gases CO N ₂ O NO NO ₂ CH ₄ SO ₂ C ₂ H ₄ Ammonia 2-Butonone CS ₂ CO ₂ CO CCl ₄ Chloroform Dimethyl formamide Ethylene oxide Methylene chloride Styrene Toluene Trichloroethylene | Infrared radiation produced by two hot filament sources passes through two parallel tubes—one a reference cell containing only pure air; the other a sample cell containing the contaminated air. The contaminant absorbs (at its absorbing wavelength) some of the IR radiation. The difference in the percent transmittance between the two cells is related to the concentration of the contaminant. This method is somewhat specific, depending on the wavelength selected and the other constituents of the sample. |
| Photoionization | Xylene Benzene Toluene Diethyl sulfide Diethyl amine Styrene Trichloroethylene CS ₂ Acetone Tetrahydroforan Methyl ethyl ketone | The ionization potential of a molecule is measured in electron volts (ev). If light energy greater than the ionization potential of a given gas is passed through the gas, a certain percentage of the molecules will ionize by absorbing the energy. The ions produced are collected, counted, and related to the concentration of the contaminated gas. |

Table I-39
DETECTORS* (Continued)

| Method of Detection | Gas or Vapor Detected | Description of Detector |
|-------------------------|---|--|
| | Aromatics (naphtha) Vinyl chloride Methyl mercaptan | |
| Derivative spectrometry | NO ₂ NO SO ₂ NH Cl ₂ O ₃ Naphthalene Pyrrodiline Others... | This method relates the rate of change in a gas' energy absorption to the wavelength at which the absorption is being measured. The first to n th derivative of the absorption equation is plotted along the Y-axis, and the concentration in PPM's along the X-axis. The rate of change in absorption as the wavelength changes is more sensitive to small changes in the concentration of the absorbing gas than the absorption equations up to a factor of 10. |
| Thermal conductivity | H ₂ He O ₂ N ₂ CO CO ₂ CH ₄ Ethane C ₁ to C ₂ hydrocarbons Alcohols Aromatics NH ₃ Cl ₂ H ₂ S N ₂ O CO ₂ | A wire is heated by passing a current through it. The current is such that the rate of heat transferred from the wire to a carrier gas stream passing over the wire is just equal to the amount of heat produced by the constant current through the wire. This leaves the temperature of the wire constant, and at a constant temperature, the resistance to electron flow is constant. Different gases have specific heats of conductance. If a gaseous contaminant is injected into the carrier gas stream, the amount of heat transferred from the wire will change. This results in a change in the wire temperature and resistance to electron flow through the wire. The change in resistance is measured and related to contaminant concentration. |
| Voltammetric | CO 10,50,100,600 SO ₂ H ₂ S | A potential difference is maintained between a sensing and a reference electrode. The gas molecules are the current carrying elements, linking the two electrodes together. As the ionic or partially charged molecules migrate to the sensing electrode, a small current flows through the system. This current is related to the concentration of the contaminant gas. |
| Electrochemical | SO ₂ H ₂ S Mercaptans Thiophene Organic sulfides | Gas molecules are absorbed on an electrode, where they are oxidized or reduced (depending on the gas) at a given potential difference between the electrode and a measuring electrode. The number of electrons required to complete |

Table I-39
DETECTORS* (Continued)

| Method of Detection | Gas or Vapor Detected | Description of Detector |
|------------------------------|---|---|
| | Disulfides Vinyl chloride CO Combustible Gases Cl ₂ NO NO _x | the redox reaction is related to the concentration of the contaminant gas. |
| Microcoulomb redox | O ₃ NO ₂ | Similar to the voltammetric and the electrochemical methods. |
| Mass spectrometry | CO CO ₂ NO NO ₂ N ₂ O SO ₂ O ₃ Hydrocarbons | When a molecule is fragmented, a variety of ions are formed. If these ions are entrapped in a flow of carrier gas and subjected to a magnetic field perpendicular to the flow, the ions will be deflected from their normal flight path. The degree of deflection will depend on the charge to mass ratio of the ionic fragments. Mass spectrometry requires a very small sample size, usually a few microliters of the gas. The method is highly specific and can be combined with gas chromatography for even greater specificity. |
| Electron impact spectrometry | SO ₂ NO CO CH ₄ | An electron beam causes the molecules to emit energy in specific wavelength ranges. This energy is collected and measured by the detector. |
| Electron capture | SF ₆ CCl ₄ Freon | A radioactive source ionizes some molecules in the carrier gas stream producing a constant current. When the sample gas passes through the sample cell, it absorbs some of the electrons, causing the signal to change. |
| Gas chromatography | | |
| Electron capture | See Table I-37 | |
| Flame ionization | See Table I-37 | |
| Flame photometric | See Table I-37 | |
| Thermal conductivity | See Table I-37 | A method of separating a mixture of two or more gases based on the solubility coefficient of the gas in various mediums. |
| Photometry, UV | Mercury vapor Halides O ₃ SO ₂ NO ₂ | |

*Specific instruments employing a given method can be found in *Air Sampling Instruments for Evaluation of Atmospheric Contaminants* (1).

Table I-40
CRITERIA FOR INSTRUMENT EVALUATION

| Criteria | Description |
|---------------------|---|
| Accuracy | Accuracy refers to how close to the true atmosphere gas or vapor concentration the instrument reads. The true value can be determined by use of an accepted primary standard or a reference measurement. Accuracy can be stated as a percentage deviation from the true value. |
| Calibration | Calibration refers to the establishment of a direct correspondence between the instrument reading and the sample concentration. Once calibrated, an instrument must be periodically checked to verify that it is still within an acceptable calibration range. Unstable instruments (subject to poor reproducibility, temperature, and zero drift) require frequent calibration. |
| Interference | <p>Interference refers to instrument response to anything other than the gas or vapor being measured. The instrument may give either a higher or lower reading than would be produced by the true pollutant concentration acting on the sensor alone.</p> <p>The industrial hygienist must be aware of all possible sources of interference to the instrument employed. Appropriate precautions and corrections must be made for interferences.</p> |
| Noise | Noise refers to spontaneous, spurious changes in the instrument output signal that are unrelated to the concentration of the gas or vapor being studied. Noise originates in the electronic components of the system. |
| Precision | Precision refers to the repeatability of instrument response to the same gas or vapor concentration over a period of time. Repeated measurements are taken, and a mean and a standard deviation are calculated. A large standard deviation relative to the size of the mean indicates the instrument is imprecise. |
| Range | Range refers to the span of concentrations the instrument can detect. The lower limit of the range is the minimum detectable concentration, a value that is not necessarily near zero. The upper limit of the range is a concentration value that does not exceed the instrument's upper calibration. |
| Reliability | Reliability is operation of the instrument without mechanical or electrical failure. An instrument requiring frequent repair will require frequent calibration checks and cannot be trusted. Reliability will be decreased with frequent repair. |
| Stability | Stability refers to the ability of an instrument to respond in the same way over a long period of time. Two performance parameters of stability are calibration and zero drift. |
| Response | Response time refers to the time lag between the point at which the sample enters the system and the point at which the instrument displays 90% of the sample concentration. Fast response time is required when the gas or vapor concentration fluctuates wildly, and/or when the concentration is governed by a ceiling limit concentration that should not be exceeded, even momentarily. |

Table I-40
CRITERIA FOR INSTRUMENT EVALUATION (Continued)

| Criteria | Description |
|--------------------|--|
| Sensitivity | Sensitivity refers to the minimum amount of the gas or vapor being studied that will provide a repeatable signal which is distinguishable from the background noise. One specification of sensitivity is the "lower detectable limit," which is the minimum pollutant level that will provide a signal at twice the noise level. |
| Specificity | Specificity is the lack of instrument response to gases or vapors other than the one under study. |
| Zero drift | Zero drift refers to deviation from zero reading over time. The drift can be due to instability in sample flow rate, to temperature sensitivity of the instrument, and to degradation of the sensor (20). |

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