Instrument/ Technique	Principle of Analysis	Analytes
Gas Chromatograph (GC)	Column travel time and area under peak indicates identity and quantity of analyte.	Organic compounds
Atomic Absorption (AA)	Intensity of absorbance at specific wavelength indicates identity and quantity of analyte.	Metals
Inductively Coupled Plasma (ICP)	Intensity and wavelength of energy emissions indicates identity and quantity of analyte.	Metals
Fluorescence Spectrometry	Intensity and wavelength of energy emissions indicates identity and quantity of analyte.	Aromatic hydrocarbons
Mass Spectrometry (MS)	Intensity of ions formed indicates identity of analyte.	Metals, organics
Infrared Spectrometry	Intensity and pattern of energy absorbance indicates identity and quantity of analyte.	Organic compounds
Ultraviolet Spectrometry	Intensity and pattern of energy absorbance indicates identity and quantity of analyte.	Organic compounds

Table 5-3: Industrial hygiene samples are analyzed using a variety of instruments and techniques, depending on the contaminants. This table summarizes some of the more common methods used for laboratory analysis of air samples.

Checking Your Understanding

1. What properties of a contaminant determine the best method to be used for analysis to detect a specific contaminant?
2. Name three methods used for metals analysis.
3. Explain the difference between absorption and emission spectrometry analyses.

5-7 Direct-reading Methods

So far we have looked at integrated sampling methods; we will now take a look at some of the ways that samples can be taken and analyzed right at the site. As a group, these methods are referred to as direct-reading methods. They include the use of instruments like combustible gas meters and oxygen meters, photoionization detectors and flame ionization detectors, and length-of-stain or detector tubes.

Probably the most important issue surrounding the use of gas meters and other direct-reading instruments is that the user must be familiar with the instrument. Operation, including alarms, indicators, sensors, and limitations, must be understood so that the instrument can be used appropriately and effectively. Calibration of direct-reading instruments is critical and must be performed prior to use and again at intervals specified by the manufacturer or dictated by use conditions; some field instruments are calibrated several times a day. The process of calibrating a direct-reading instrument is different from calibrating a sampling pump; instead of verifying a flow rate, the calibration of a direct-reading instrument is a process to verify that the instrument is responding to the contaminant and providing an accurate reading or indication of the detected concentration. Such calibrations require the use of specialty gases that contain a known mixture or concentration and to which the instrument produces a specific response. Instrument responses and alarm level settings can usually be adjusted, following the manufacturer's instructions. In addition to calibration, many instruments require a functional check, which is a sort of "go/no-go" test to make sure the instrument is working properly.

Records of calibration and maintenance actions, such as sensor replacement, must also be maintained. If direct-reading area samples are used as an indication of employee exposure, the records should be treated as other records that are generated using standard air sampling methods, with detailed notes taken regarding who, what, when, where, why, and how. Many direct-reading instruments available today have a hygiene function; this usually includes the ability to perform such functions as computing time-weighted average concentrations and producing a record that can be transferred to a computer or printer to show actual measurements taken over the sampling interval. These records can help identify peaks in concentration that occurred over the shift, allowing more detailed scrutiny of the pattern of exposure and therefore better controls for worker protection. Often direct-reading instruments with a hygiene function are small and lightweight, which allows them to be used for obtaining personal samples.

The following sections provide a brief introduction on several direct-reading methods available to the industrial hygienist. For more detailed information, refer to the bibliography at the end of the book.

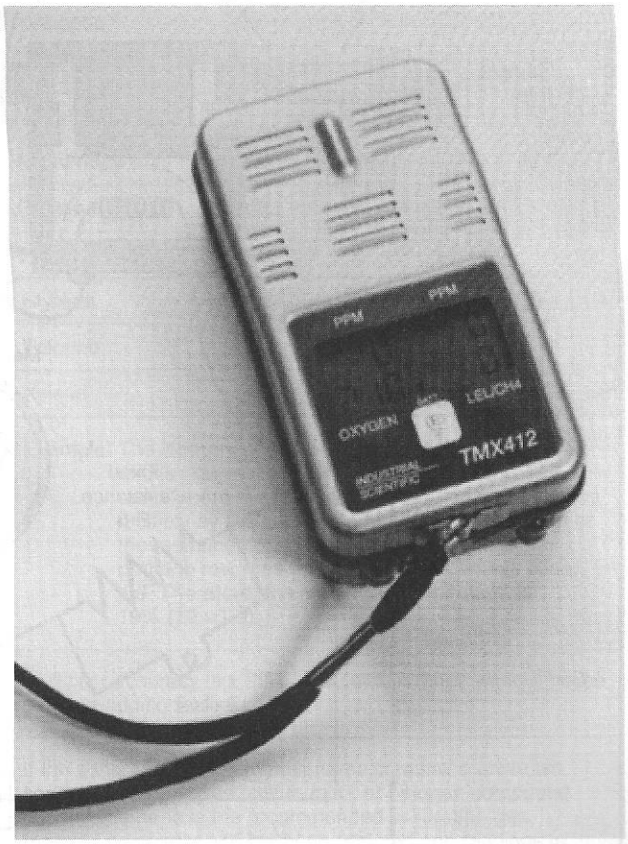

Figure 5-28: There are many direct-reading gas detection instruments available to the industrial hygiene professional today. The instrument shown here is built to withstand regular use in a variety of industrial settings. Common applications include evaluation of confined spaces and continuous monitoring of areas to detect leaks or unsafe levels of airborne contaminants.

Gas Meters

A wide variety of gas meters is available to the industrial hygiene professional for field use. These units are typically relatively small and portable, most weighing less than two pounds, and many newer models weighing in at just a few ounces. They contain a small pump that draws air into the instrument, where it passes into a sampling chamber containing the sensor unit, which is connected to a readout device. Meters can have specific applications such as oxygen detection, or they may contain several sensors, which makes them multi-gas or multifunction units. For example, many meters used for atmospheric testing of confined spaces contain a sensor for oxygen, another sensor that detects combustible gas, and a third sensor that detects the amount of toxics – usually total hydrocarbons – that are present. The "toxic" function on many of these meters is **nonspecific**, that is, it does not identify the specific contaminant that is present, but it does indicate that a hazardous substance is present. Nonspecific instruments do have useful applications in screening for contaminants, initial characterization of unknown sites, and leak detection.

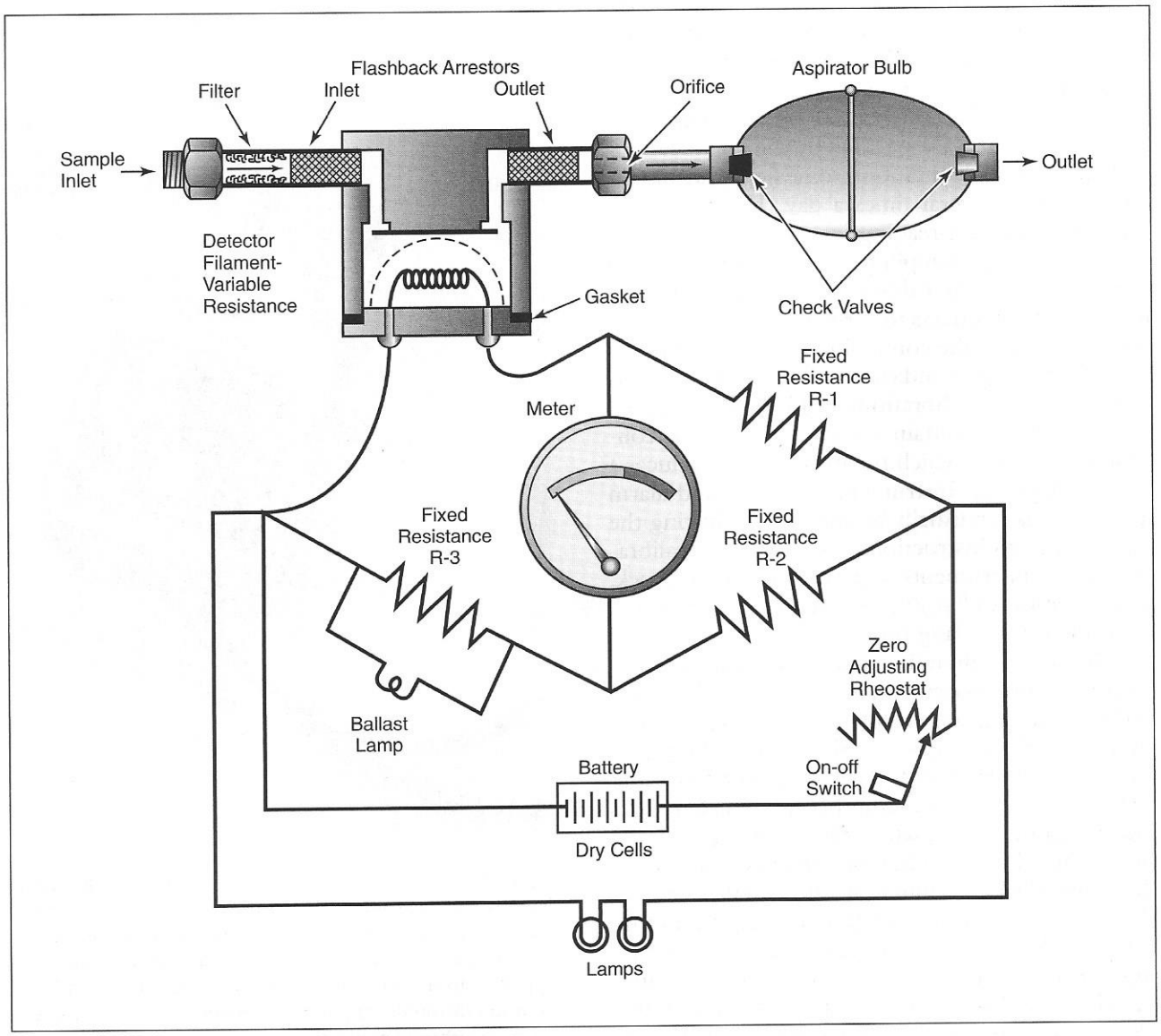

Figure 5-29: The Wheatstone bridge comprises the detection circuit in many direct-reading instruments used for evaluating the presence of combustible gases.

For many gases, the sensors consist of a gel or solid matrix in which the sampled air dissolves. The resulting reaction is detected and translated into an electronic signal, which is interpreted on a digital or analog (meter) readout. Sensors are available to detect a variety of gases, including hydrogen sulfide, chlorine, and others.

Combustible gases, such as carbon monoxide, can be detected using a fairly simple sensor device that contains an electric circuit called a **Wheatstone bridge circuit**, shown in Figure 5-29. These sensors, called catalytic combustion sensors, contain a heated filament that makes up one leg of the Wheatstone bridge circuit. The filament is coated with a catalyst that reacts with a combustible gas and generates heat. The heated filament's electrical resistance changes, causing an imbalance in the circuit. The change in conductivity of the filament produces a degree of imbalance in the circuit, which is proportional to the amount of combustible gas present. The readout device on the meter indicates the imbalance as a concentration of combustible gas, typically expressed as a percent.

Another sensor used to measure combustibility also relies on detecting a change in electrical conductivity; in this sensor, the change is produced when the combustible gas is adsorbed onto the solid surface of a **metal-oxide semiconductor (MOS)**. These sensors are named for the detector device, and are referred to as MOS sensors.

A third sensor used in combustible gas meters involves measurement of **thermal conductivity**, which is the ability of the tested air to conduct heat. Like the catalytic combustion sensor, these sensors contain a filament that is part of a Wheatstone bridge circuit. The atmosphere containing the combustible gas enters the test chamber and passes over the filament, which is heated; the filament responds to the surrounding air, which, if it contains a combustible gas, will cause a change in the temperature of the filament and thus its electrical resistance. The change in resistance is translated by the meter and shown on the indicator.

All three of the sensors used to detect combustible gases rely on specific properties: heat of combustion, thermal conductivity, or adsorption onto an MOS. These properties are unique to each gas; therefore the sensor's responses are also unique to each gas, and some gases will generate a stronger or weaker response from the sensor. Different gases may be used for calibration, which will produce a different response from the instrument. Often the instrument response can be adjusted by the user during the calibration process. Also, many manufacturers

GAS BEING TESTED	CALIBRATION GAS							
	ACETONE	ACETYLENE	BUTANE	HEXANE	HYDROGEN	METHANE	PENTANE	PROPANE
Acetone	1.0	1.3	1.0	0.7	1.7	1.7	0.9	1.1
Acetylene	0.8	1.0	0.7	0.6	1.3	1.3	0.7	0.8
Benzene	1.1	1.5	1.1	0.8	1.9	1.9	1.0	1.2
Butane	1.0	1.4	1.0	0.8	1.8	1.7	0.9	1.1
Ethane	0.8	1.0	0.8	0.6	1.3	1.3	0.7	0.8
Ethanol	0.9	1.1	0.8	0.6	1.5	1.5	0.8	0.9
Ethylene	0.8	1.1	0.8	0.6	1.4	1.3	0.7	0.9
Hexane	1.4	1.8	1.3	1.0	2.4	2.3	1.2	1.4
Hydrogen	0.6	0.8	0.6	0.4	1.0	1.0	0.5	0.6
Isopropanol	1.2	1.5	1.1	0.9	2.0	1.9	1.0	1.2
Methane	0.6	0.8	0.6	0.4	1.0	1.0	0.5	0.6
Methanol	0.6	0.8	0.6	0.5	1.1	1.1	0.6	0.7
Pentane	1.2	1.5	1.1	0.9	2.0	1.9	1.0	1.2
Propane	1.0	1.2	0.9	0.7	1.6	1.6	0.8	1.0
Styrene	1.3	1.7	1.3	1.0	2.2	2.2	1.1	1.4
Toluene	1.3	1.6	1.2	0.9	2.1	2.1	1.1	1.3
Xylene	1.5	2.0	1.5	1.1	2.6	2.5	1.3	1.6

Example: The instrument has been calibrated on methane and is now reading 10% LEL in a pentane atmosphere. To find actual % LEL pentane, please multiply by the number found at the intersection of the methane column (calibration gas) and the pentane row (gas being sampled)... in this case, 1.9. Therefore, the actual % LEL pentane is 19% (10 ×1.9).

Multiplier accuracy is ± 25%, subject to change without notice pending additional testing.

If the sensor is used in atmospheres containing unknown contaminants (silicone, sulfur, lead, or halogen compound vapors) methane is the recommended calibration gas. Periodic comparison of methane and pentane readings is recommended when using this chart.

Table 5-4: The response of a direct-reading instrument to a particular gas depends on what gas was used to calibrate the instrument. This chart illustrates how to correctly interpret the response of the instrument shown in Figure 5-28, based on the gas being tested and the gas used for calibration.

Combustible gases such as methane are displayed as a percent of the **lower explosive limit** (or level), **LEL**, sometimes called the **lower flammable limit**, or **LFL**. Most gas-air mixtures that support combustion will only do so within a certain range of concentrations, which has both lower and upper limits. The LEL is the lowest gas-air mixture that will support combustion. The acronym used to refer to the upper limit of combustibility is the **UEL**, for **upper explosive limit**, or sometimes, the **UFL**, for **upper flammable limit**. Most combustible gas meters come with the alarm level preset at 10 percent of the LEL. Since the LEL is itself a percent value, the alarm setting is a percent of a percent. This provides a fairly wide margin of safety. For example, the LEL of ethylene oxide is about three percent. A combustible gas meter that had been calibrated using the same gas, with an alarm set at 10 percent of the LEL, would alarm at a concentration of 0.3 percent of ethylene oxide.

provide calibration curves for different gases, which can be used to cross-reference the meter's response to other gases. For instance, a meter calibrated using methane gas will still respond to atmospheres containing pentane or butane, but the response will not be the same as to methane. Table 5-4 shows some correction or correlation factors for an instrument calibrated using methane.

Some words of caution: The presence of a combustible gas just above the UEL is potentially worse than a concentration approaching the LEL. This is because a little dilution of the mixture will push the concentration into the combustible range. Any reading above the UEL should be considered potentially very hazardous!

Another caveat in the use of a combustible gas or other direct-reading meter is that the sensors can become less sensitive over time. Depending on their design, they may have a fixed capacity for absorbing combustible materials; some have a recommended useful life, beyond which they should be replaced. Sensors can also be contaminated by interfering compounds that cause the sensor to respond incorrectly or inaccurately; silicone vapors, for example, can poison the sensor of a combustible gas meter. It is important to know the manufacturer's specifications for acceptable use conditions, including temperature, humidity, and whether the instrument may be used in a hazardous or combustible atmosphere. Since some direct-reading instruments use a sensor with a heated filament or flame, there is a risk of igniting an explosive or combustible atmosphere in the location being tested. Meters equipped with these sensors are equipped with a flashback arrestor in order to prevent the ignition of the combustible atmosphere that they are being used to test. Similar possibilities of ignition may apply to the circuitry and electronic components of any direct-reading instrument. Instruments that can be safely operated in a possibly combustible atmosphere are identified as **intrinsically safe**. Again, any questions about instrument limitations should be clarified by the manufacturer.

Photoionization and Flame Ionization Detectors

Photoionization detectors or **PIDs** (see Figure 5-30), as they are sometimes called, are an example of a nonspecific instrument that is most often used to

Figure 5-30: Photoionization detectors (PIDs) are direct-reading instruments that are used a great deal at hazardous waste sites. They are nonspecific, but useful for screening purposes during initial entries at sites where specific contaminants are unknown. The most common application is for screening to detect organic compounds.

Figure 5-31: The flame ionization detector (FID) is another type of non-specific instrument often used at hazardous waste sites during investigation and cleanup. It is generally better than a PID at detecting hydrocarbon compounds, making them useful for field screening at sites where leaking underground fuel tanks have been removed.

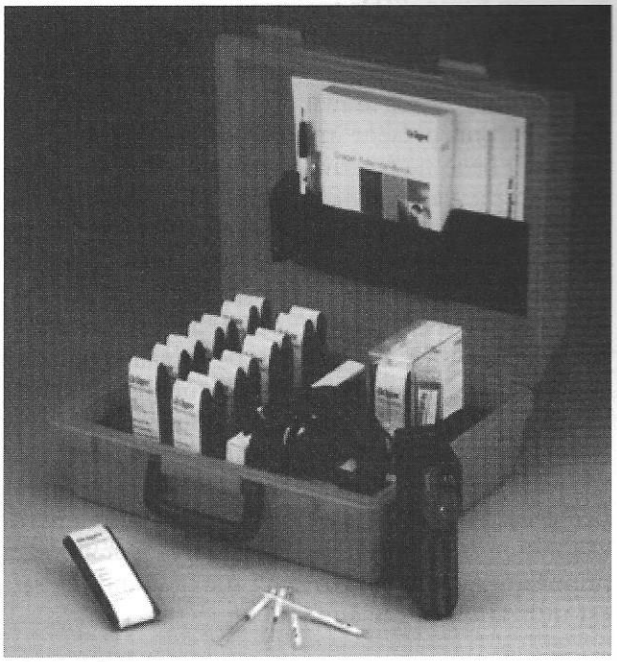

Figure 5-32: Detector or length-of-stain tubes are among the most portable and versatile direct-reading methods for chemical detection. Tubes are available for detecting a wide variety of materials within a wide range of concentrations.

detect organic vapors, such as alcohols, ketones, ethers, and others. The mechanism of operation utilizes the light energy from a tiny ultraviolet lamp. The air pump in the instrument draws air into the test chamber, where the light energy given off by the lamp is absorbed by the contaminant molecules. These become charged particles or ions, which are collected by an electrode; this produces a current that is proportional to the concentration of the contaminant ions (molecules) in the test chamber. The signal that results is translated by the meter into a readout. One limitation of these instruments is that they are nonspecific; on the other hand, this makes them most useful for screening an atmosphere for a set of suspected, or known, contaminants.

Another limitation is that its functioning is based on the molecules being ionized by the lamp in the test chamber. Some molecules require more energy to become ionized; the amount of energy required to ionize a molecule is a physical property called the **ionization potential**, or **IP**, which is expressed in electron volts using the symbol eV. (The ionization potential of ethyl benzene, for instance, is 8.76 eV.) The energy output levels of lamps used in PIDs are given in eV also. In order to detect a contaminant using a PID, the ionization potential of the contaminant molecules must be equal to or lower than the energy output of the lamp in the instrument. Because ionization potentials of common airborne vapors vary widely, most PIDs can be fitted with lamps that have different energy outputs. This allows the use of a lamp in the energy range that is needed to detect the presence of the contaminants of concern. Using a high-energy lamp may seem to provide the widest range of applications; however, high-energy lamps do not last as long, and they may not generate the same response as a lower-energy lamp for a specific compound. The use of the higher energy lamp does nothing to increase the specificity of the instrument, which is limited by the physics inherent in the sensor.

Flame ionization detectors, or **FIDs** (see Figure 5-31), operate on a principle similar to that of PIDs in that the contaminant molecules are ionized through absorption of energy. In the case of the FID, this energy comes from a heat source specifically, a

hydrogen flame. FIDs are commonly used to detect hydrocarbons, to which they are most sensitive, but they also can detect most organic compounds. During sampling, air is drawn into the instrument, and carbon atoms present in the molecules of the contaminant become positively charged when they pass through the flame. The resulting ions are collected on a platinum loop, creating an electric current that is proportionate to the rate at which the ions are collected. This current is translated into a readout value on the instrument. Because it is nonspecific, the FID is subject to limitations similar to that of the PID. However, both are useful for screening and initial characterization of unknown atmospheres as well as for monitoring known contaminants that are within the detection abilities of the instrument being used. As with any direct-reading instrument, calibration and familiarization with the operation are important factors in providing the best and the safest utilization of the equipment.

Detector or Length-of-Stain Tubes

Detector tubes are sometimes referred to as **length-of-stain tubes**, which is a reference to the way they are used to indicate the presence of a contaminant. These tubes – which resemble an oversized sorbent tube – are sealed at each end and contain a solid sorbent coated with a reagent that reacts with a contaminant and causes a color change. The tubes are marked with graduations along their length; generally, the length of the colored area or stain is indicative of the concentration. Once the ends are snapped off and the tube is in place, air is drawn into the tube by a hand pump or an electric pump. These pumps, like other samplers, must be calibrated so that the volume of air drawn through the tubes is known. Higher volumes of air, useful for detecting low levels of contamination, are sampled by drawing additional pump strokes of air through the tube. These tubes are versatile, portable, and useful for field activities such as screening, leak detection, initial site characterizations, and other applications. They are available for a wide variety of contaminants; the results are typically accurate within 25 percent. Because of this, they are a good choice when the contaminants of concern are known, when simple "go/no go" kinds of results are adequate, and when the situation calls for a simple but reliable sampling method.

Checking Your Understanding

1. What is meant by the term nonspecific when talking about a direct-reading instrument?
2. Name three applications for nonspecific instruments.
3. What is the importance of intrinsic safety as it applies to direct-reading instruments?
4. What is a length-of-stain tube?

5-8 Air Sampling Strategies

Performing the actual air sampling event can be compared to completing a series of steps. Each step must be completed before continuing the process. The steps are:

1. Determine the agents to be sampled. This may be based on a regulatory requirement, baseline or initial sampling, employee complaints, or a review of MSDSs for materials being used in the area.

2. Select the sampling method based on the expected concentration of contaminant, interfering compounds, laboratory recommendations, or other factors.

3. Obtain and review a copy of the sampling method, which will contain information about sample media, flow rates, analysis, etc.

4. Obtain adequate sampling media and equipment, based on type and number of samples, including blanks.

5. Calibrate sampling pumps or instruments to be used for sampling.

6. Perform sampling.

7. Ship samples to laboratory for analysis.

8. Interpret analytical results.

9. Prepare a report to employees and management.

The entire process should be methodical and documented, usually on a standardized form, to assure that all the required information is recorded. Some steps, such as calibration of a direct-reading instrument or sampling pump, may generate a separate record.

The number of samples that are to be obtained is usually determined according to one of two approaches. One approach is to attempt to identify the workers who are most likely to be exposed to the highest levels of contaminants – these are the **maximum risk employees**. Another approach is to identify populations or groups that have similar exposures. Such a group, called a **homogenous exposure group** or **HEG**, can often be defined by job title or the function of the workers – material handlers, hopper fillers, appliers of spray coatings, and so on. Once the HEGs have been defined, the industrial hygienist can employ a random sampling scheme to select persons for sampling out of the group. These approaches are described in more detail in the NIOSH publication, *An Occupational Exposure Sampling Strategy Manual* and in the AIHA publication *A Strategy for Occupational Exposure Assessment.* The importance of selecting who is to wear the sampler cannot be stressed too much, since these few measurements may be used to represent the exposure of the entire group.

Blanks

If the number of workers is small, it may be possible to obtain sampling data for all. More often, due to limited resources, the industrial hygienist must choose who will wear the sampling train or where the area sample will be placed. As a general guideline, at least three samples should be obtained. **Field blanks** should also be prepared and submitted with the samples for analysis. A field blank consists of sample media that are exposed to the same conditions as the media used for the actual sampling, but are not connected to a sampling pump. For example, during a solvent sampling activity involving five samples, two charcoal tubes are opened and immediately capped, sealed, and labeled. These are the field blanks. The accepted number of field blanks is 10 percent of the total number of samples, or at least two regardless of the total number of samples. The field blanks are subject to the same **chain of custody** and other sample handling procedures as the rest of the samples. This is a quality control step intended for detection of any potential contamination that could be introduced into the process through sample handling. Field blanks that analysis reveals to contain measurable levels of contaminant could indicate problems with sampling or handling of the media, or also a previously unsuspected source of interference or contamination.

Laboratory blanks are sample media that are not sampled on, but are prepared and analyzed by the laboratory. This is another quality control step

that is taken to detect problems with preparation and analysis of the samples. Blank values are sometimes deducted from sample values – this produces data that are said to be **blank-corrected**. If both field blanks prepared in the example above had contamination at a level of two micrograms, it would be assumed that all the samples contained this extra amount. The analytical data for the samples would then be blank-corrected by subtracting two micrograms from the total amount of contaminant found on each of the tubes.

Sources of Error in Air Sampling

The results of air sampling events can be affected by many things, some of which cannot be controlled. Uncontrollable sources of error are usually assumed to be self-correcting or self-limiting through randomness. It is also possible to introduce error into any sampling process through actions or through the failure to take certain actions. These sources of error are not random and – to a certain extent at least – they are controllable. Standard sampling and analytical methods are developed to include steps that, if followed, will assure sampling accuracy, such as the calibration of sampling pumps. Direct-reading methods are also subject to operator-introduced error. Some examples of sampling error or of **bias** that can be introduced (and therefore controlled) by the industrial hygiene professional performing the sampling are:

— Using inappropriate sample collection media;

— Using a direct-reading instrument outside of its limitations and applications;

— Use of incorrect flow rates, resulting in a sample volume that is too large or too small to allow accurate quantitation of the contaminant;

— Failing to perform calibrations or functional checks on direct-reading instruments;

— Overloading the sample collector;

— Errors in calculations – flow rates, sample volumes, resulting concentrations;

— Sampling in the presence of interfering compounds;

— Failure to follow special handling procedures such as protecting samples from light or heat;

— Placement of sample collectors by the industrial hygienist in hopes of detecting higher or lower measurements;

— Neglecting to keep complete and accurate records.

Once samples have been received at the laboratory, they are again subject to possible mishandling or other events that can affect the results. Some events that can happen at the laboratory include:

— Improper storage/handling of samples while awaiting analysis;

— Delays in analysis that exceed time limits for stability of samples (holding times);

— Use of incorrect analytical techniques, including use of instruments that are not set up according to the parameters specified in the analytical method;

— Failure to properly prepare the samples for analysis;

— Contamination of samples with other samples or laboratory chemicals;

— Errors in calculations;

— Mix-ups such as incorrect labeling of samples and transposing numbers;

— Loss of samples due to breakage, spillage, or other events.

Most analytical methods include a numerical factor that accounts for the uncontrollable portion of **sampling and analytical errors**, or **SAE**s. This numerical value is used to evaluate whether the sample results indicate exposures within acceptable limits such as an OSHA PEL, for example. We will look at the application of the SAE near the end of the chapter.

Laboratory Accreditation

The American Industrial Hygiene Association administers a laboratory accreditation program; facilities that meet the criteria of the program are said to be AIHA Accredited. Laboratories selected to perform analysis of industrial hygiene samples should be AIHA-Accredited. This provides the industrial hygienist with assurance that quality control procedures are in place, and that the laboratory consis-

tently reports accurate results. The process for obtaining accreditation includes completion of a written application that describes the laboratory's operational procedures, followed by a site visit to verify that conditions at the laboratory are as described in the application. The application and review process comprehensively evaluates the laboratory, addressing areas such as internal quality assurance, sampling materials and procedures, qualifications of laboratory personnel, chain-of-custody and sample handling, calibration and maintenance of analytical instruments, and health and safety programs.

Laboratories seeking accreditation must also demonstrate analytical proficiency by participating in the AIHA's Proficiency Analytical Testing, or PAT, program. This program consists of periodic analysis of unknown samples, the results of which are reported to the AIHA by the laboratory. Areas of accreditation for industrial hygiene laboratories include metals, solvents, asbestos, and lead; laboratories may be accredited one, or all, areas. The AIHA also administers an accreditation program that meets EPA's requirements for environmental lead analysis - that is, analysis of samples of soil, paint chips and similar items. This program is known as the Environmental Lead Laboratory Accreditation Program, or ELLAP. A listing of accredited laboratories may be obtained by contacting the AIHA.

Limits of Air Sampling

Air sampling does have its limitations. Some understanding of these is necessary so that the industrial hygienist can appropriately interpret sampling results, and make decisions and/or recommendations to management regarding the use of methods for controlling or eliminating the hazardous exposure. This section will discuss the issues associated with reliance on air samples as an indication of the absorbed dose of the exposed worker and some related topics.

As already mentioned, air sampling data are often accepted as an indication of the actual level of exposure of the workers and are assumed to be an indication of the absorbed dose. This is a faulty assumption. Airborne concentrations probably are best thought of as a representation of a potential level of exposure. There are many variables that can affect the actual amount of the contaminant that is absorbed by the exposed worker population. These include:

- —Age and gender;
- —Health status/level of fitness;
- —Nature of work (sedentary or strenuous);
- —Breathing rate;
- —Pre-existing health conditions, medications, allergies;
- —Concurrent exposures, including hobbies and nonoccupational sources.

Besides the variety of influencing factors, each factor will vary from person to person. This makes the estimation of absorbed dose an educated guess at best. This is where the "art" part of industrial hygiene comes into play. The industrial hygienist must consider the entire set of variables, not just the numbers, and make a recommendation that will protect the health of the worker accordingly.

The problems associated with reliance on the air concentration as an indicator of absorbed dose have been addressed to some degree through the use of the biological exposure indices, or BEIs presented in Chapter 3. The BEIs are levels of contaminants, or of metabolic by-products associated with their absorption, that can be measured in blood, urine, exhaled breath and sometimes other tissues. Like air samples, concentrations of contaminants or indicators in body tissues are not a definitive and final answer; and like TLVs, BEIs do not represent black-and-white lines between what is safe and what is not safe. However, they do contribute to the overall exposure picture and can be quite useful when considered along with other factors such as air sampling measurements, work practices, engineering controls being used, and other observations made by the industrial hygienist. Some regulatory standards require the use of biological samples, in addition to air sampling. For example, lead levels are measured in the blood of lead-exposed workers. These levels are monitored and used to determine how long a worker must be away from lead exposure to allow the body to eliminate some of the accumulated lead. Table 5-6 shows an excerpt from the ACGIH TLV booklet, which contains a list of BEIs as well.

Another issue associated with air sampling data is one of **representativeness**, that is, whether or not the data are truly representative of the air concentrations in the work location(s) where the sampling took place. Most sampling data are obtained over a one-day or two-day time period, often following a

ADOPTED BIOLOGICAL EXPOSURE DETERMINANTS			
Chemical [CAS #] Determinant	**Sampling Time**	**BEI**	**Notation**
ACETONE [67-43-1] (1994)			
Acetone in urine	End of shift	100 mg/L	B, Ns
ANILINE [62-53-3] (1991)			
Total p-aminophenol in urine	End of shift	50 mg/g creatinine	Ns
Methemoglobin in blood	During or end of shift	1.5% of hemoglobin	B, Ns, Sq
ARSENIC AND SOLUBLE COMPOUNDS INCLUDING ARSINE [7784-42-1] (1993)			
Inorganic arsenic metabolites in urine	End of workweek	50 µg/g creatinine	B
BENZENE [71-43-2] (1987) [See Note Below]			
Total phenol in urine	End of shift	50 mg/g creatinine	B, Ns
Benzene in exhaled air: mixed-exhaled end-exhaled	Prior to next shift	 0.08 ppm 0.12 ppm	 Sq Sq
CADMIUM AND INORGANIC COMPOUNDS (1993)			
Cadmium in urine	Not critical	5 µg/g creatinine	B
Cadmium in blood	Not critical	5 µg/L	B

Note: The Chemical Substances TLV Committee has proposed a revision of the TLV for benzene. See Chemical Substances Notice of Intended Changes and TLV Documentation.

Notations provide the following information:

"Sc" Notation	This notation indicates that an identifiable population group might have an increased susceptibility to the effect of the chemical, thus leaving it unprotected by the recommended BEI. The specific BEI documentation should be consulted for information.
"B" Notation	This notation indicates that the determinant is usually present in a significant amount in biological specimens collected from subjects who have not been occupationally exposed. Such background levels are included in the BEI value. For information on background levels, consult the specific documentation.
† "Nq" Notation	Biological monitoring should be considered for this compound based on the Committee' s review of the literature; however, a specific BEI could not be determined due to insufficient data.
"Ns" Notation	This notation indicates that the determinant is nonspecific, since it is observed after exposure to some other chemicals. These nonspecific tests are preferred because they are easy to use and usually offer a better correlation with exposure than specific tests. In such instances, a BEI for a specific, less quantitative biological determinant is recommended as a confirmatory test. The documentation should be consulted for information on factors affecting interpretation of these BEIs.
"Sq" Notation	This notation indicates that the biological determinant is an indicator of exposure to the chemical, but the quantitative interpretation of the measurement is ambiguous (semiquantitative). These biological determinants should be used as a screening test if a quantitative test is not practical or as a confirmatory test if the quantitative test is not specific and the origin of the determinant is in question.

In some instances, BEIs for confirmatory and screening tests are not listed, but the pertinent documentation provides information for estimation of the reference value. Examples are measurements of inhaled chemicals (which are extensively metabolized) in exhaled air. BEIs for some screening tests are derived as an upper (or lower) limit of the levels observed in unexposed populations. Examples are measurements of cholinesterase or methemoglobin.

Table 5-6: This excerpt from the ACGIH TLV booklet shows biological exposure indices for some common industrial materials. While not a substitute for TLVs or PELs, the BEIs are useful as complementary data points in evaluating a worker's absorption of a hazardous material.

triggering event such as a spill, a leak, a system failure or breakdown of engineering controls, or an employee complaint. As such, the sample may represent a worst-case situation or at least something that is not "normal" for the operation. One of the most common remarks to the industrial hygienist performing exposure sampling is: "You should have been here yesterday (or last week, or last month), it was really (bad/strong/thick/heavy) then!" Repeated sampling over a long period will provide statistically more accurate data regarding the actual concentrations.

One of the larger issues associated with air sampling is that the results are inevitably compared to a predetermined exposure limit. We looked at exposure limits in a previous chapter. Whether the limit is a statutory (regulatory) limit or a recommended limit from NIOSH or the ACGIH, or an internal company standard, there are some questions to consider in comparing measured air concentrations to such a limit. These include:

—What health effect is the limit intended to protect or prevent against? Acute effects, such as irritation or a nuisance, or a chronic effect such as cancer?

—What types of toxicological studies have been done? Have some areas been neglected, such as reproductive effects?

—Are the toxicological data applicable to the exposed population? (Most of the current data for human exposures are based on studies that involved white males.)

—Does the limit account for exposure to a combination of toxic materials? What about cumulative and synergistic effects?

—Does the limit adequately protect hypersensitive workers, cigarette smokers, and others who might be more susceptible to the negative effects associated with exposure? Examination of the ACGIH *Documentation of TLVs* will reveal that some TLVs have been established at levels known to cause some individuals to experience an adverse effect. (Recall the disclaimer by the ACGIH that TLVs are to protect most, not all, workers.)

There are no easy answers to the above questions, but they should be considered by the industrial hygienist who is interpreting the air sampling results and applying exposure limits.

Calculating and Interpreting Results

Once data are obtained from the laboratory, it may be necessary to calculate the airborne concentrations that correspond to each sampling interval. Many laboratories calculate the concentration as a service to the industrial hygienist; however, their calculations assume that the IH has provided all the correct information.

The concentration of particulates and fumes is typically reported in terms that express a mass per unit volume, as in micrograms (μg), or milligrams (mg), per cubic meter (m^3), as: $\mu g/m^3$ or mg/m^3. The convention is to report concentrations of most gases and vapors as parts per million, or ppm, which is a volume-to-volume ratio. It may be necessary to convert concentrations from one ratio to the other. The conversion is easy to make, but it is necessary to have certain information about the contaminant, such as its molecular weight and the concentration of the contaminant in either a mass per unit volume or a volume-to-volume ratio. The equations for making these conversions are:

$$\text{ppm} = \frac{C\ (\text{mg/m}^3) \times 24.45}{\text{MW of contaminant}}$$

$$\text{mg/m}^3 = \frac{C\ (\text{ppm}) \times \text{MW of contaminant}}{24.45}$$

Where

C = the concentration of the contaminant;

MW = molecular weight; and

24.45 = a constant that represents the volume, in liters, of one mole of a gas at standard temperature (25°C) and pressure (1 atmosphere).

The conversion factors above may also be used to convert an exposure limit from one unit to another. Here are a couple of examples of conversions:

From ppm to mg/m^3:

50 ppm n-butyl acetate, which has a molecular weight of 116.2; converted to mg/m^3:

$$mg/m^3 = \frac{50 \text{ ppm} \times 116.2}{24.45}$$

$$= \frac{5810}{24.45}$$

$$= 237.6 \text{ mg/m}^3$$

From mg/m^3 to ppm:

14 mg/m^3 of diphenyl, which has a molecular weight of 169; converted to ppm:

$$\text{ppm} = \frac{14 \text{ mg/m}^3 \times 24.45}{169.2}$$

$$= \frac{342.3}{169.2}$$

$$= 2.02 \text{ ppm}$$

Laboratories generally assume the concentration will be compared against an 8-hour time weighted average limit, but this is not always the case. We saw in an earlier chapter how to calculate time-weighted averages; we will use another example here to illustrate how air sampling data are compared to exposure limits.

Consider a case where sample data obtained over three sampling intervals indicated an 8-hour TWA exposure to 2-heptanone was 105 ppm. The OSHA PEL is 100 ppm. The compliance officer must determine whether this measurement indicates an exposure within regulatory limits.

Remember that the NIOSH sampling methods have been validated to provide reliable results 95 times out of 100. The analytical results are evaluated statistically to determine whether the results are at this 95 percent confidence level. The analysis looks at the results from two positions: one of underestimation of exposure, where the result is corrected for error using the SAE and compared to an upper limit; and one where the results are compared to a lower limit. The statistical terms for these limits are the 95 percent **upper confidence limits (UCL)** and **lower confidence limits (LCL)**, or 95 percent UCL and 95 percent LCL. These limits are calculated and used by the OSHA compliance officer as follows:

1. First, a standardized concentration, represented by Y, is calculated. This is done by dividing the full-shift sampling result by the PEL value. In our example, it would be the 105 ppm 8-hour TWA sample result, divided by the PEL of 100 ppm; the result is 1.05, a unitless number since the ppms canceled out:

   Y = full-shift sampling result/PEL

   Y = 105 ppm/ 100 ppm = 1.05

2. Second, the 95 percent upper confidence limit or UCL is calculated. This limit is equal to the standard concentration Y, plus a factor that accounts for the sampling and analytical error associated with the method. For our example, the SAE value listed in the method is 0.10. To determine the 95 percent UCL, then:

   95 percent UCL = Y + SAE
   95 percent UCL = 1.05 + 0.10 = 1.15

3. The lower confidence limit is calculated similarly to the UCL, only the SAE factor is subtracted from, rather than added to, the standard concentration Y:

   95 percent LCL = Y − SAE
   95 percent LCL = 1.05 − 0.10 = 0.95

4. OSHA interprets the results of the above calculations as follows:

   — If the 95 percent UCL is less than or equal to 1, a violation of the allowed exposure limit does not exist.
   — If the 95 percent LCL is greater than 1, a violation of the allowed exposure does exist.
   — If the 95 percent LCL is less than or equal to 1, and the 95 percent UCL is greater than one, there is a possible overexposure. This is the case in our example.

Employers can use these same tests to determine whether or not they are violating an exposure limit; however, in the case of the possible overexposure, as in our theoretical example above, it is better for the employer to assume that an overexposure does exist. This is especially critical when dealing with agents for which there are specific control measures, training, medical surveillance, and ongoing air sampling requirements that apply to exposures at or above a PEL or action level.

Checking Your Understanding

1. Explain how air sampling results that are below the PEL can indicate a possible overexposure situation.
2. What are BEIs and how are they used by an industrial hygienist?
3. Name five factors that can affect a worker's absorbed dose of a hazardous material.
4. Name and discuss three issues or problems related to use of air concentrations as safe levels of worker exposure.

Summary

Sampling the air may be done for many reasons:

- —Identification of contaminants in an emergency situation (such as a hazardous material spill) or in an unknown atmosphere (as in a confined space);
- —Identification of potential overexposure situations or high-exposure activities;
- —Providing a historical record of employee exposures for company records;
- —Evaluating effectiveness of engineering controls;
- —Verifying adequacy of respiratory protection;
- —Initial determination of exposures;
- —Periodic sampling to meet regulatory or company policy requirements;
- —Evaluation of exposure status relative to an exposure limit.

The purpose of the sampling may affect the method chosen for sample collection and analysis. There are publications available from NIOSH and the AIHA to assist the industrial hygienist in designing a sampling scheme to ensure that the samples provide representative data that are statistically defensible.

There are two basic approaches to air sampling for industrial hygiene applications: 1) direct-reading, which produces immediate feedback about contaminants that are being measured, and 2) integrated sampling, where the sample is sent to a laboratory for analysis. The type of approach that is used will depend on the purpose of the sampling, the regulatory requirements, and the availability of methods and equipment. Each approach has its advantages; direct-reading methods provide fast feedback and involve simple and straightforward methods. Integrated sampling requires more preparation and must be performed by a trained professional following established and validated methods. Because the analysis is done in the laboratory, there is a delay between the sampling event and receipt of results. In both approaches, results may be affected by errors or bias introduced during the sampling event or – for integrated sampling – during sample handling or analysis.

Direct-reading methods involve the use of portable instruments such as gas meters and detector tubes. The instruments may be specific or nonspecific, depending on which sensor or detector is used. Many sensors are specifically designed to detect a particular substance – such as oxygen or hydrogen sulfide – or they may respond to a certain type or class of compounds – such as combustible gas mixtures. It is important to understand the capabilities and limitations of detection devices to allow for appropriate interpretation of the readings they provide. Other direct-reading methods involve colorimetric or length-of-stain tubes, which undergo a color change if the contaminant tested for is present. The length of the stain is read against a scale on the tube and is an indication of the concentration. Other methods involving a color change come in the form of badges or clip-on devices that resemble a credit card. These change color in response to the presence of a particular contaminant and may provide a response that varies in intensity through a range of concentrations. Other direct-reading instruments include the photoionization and flame ionization detectors, which are used for detecting organic vapors.

Integrated sampling methods require a medium for collecting the contaminants present in the air. The air may be drawn through the sample medium by a pump; the contaminant may also be collected through diffusion onto the surface of the medium, as in passive sampling. Integrated methods for collecting air contaminants utilize the physical and chemical properties of the contaminants themselves: impaction, interception, filtration, and dissolution are among the mechanisms used to remove contaminants from the air and collect them on the sample medium. Sorbent tubes and impinger solutions are commonly used for collecting gases and vapors, while filters are generally used for collecting particulates. Passive samplers in common use for gas and vapor sampling contain activated charcoal or another solid sorbent for collecting the contaminant.

Sampling methods for integrated sampling undergo a rigorous testing process to validate the steps used for sample collection and analysis. Validated methods are available from NIOSH and OSHA. The methods contain specific instructions about collecting the samples, including sampling equipment, sample collection media, flow rates and sample volumes, shipping, and analysis. The methods also contain information about the sensitivity of the analytical technique for measuring the contaminant. Following the method will minimize the amount of error that is introduced into the system by the industrial hygienist and the laboratory.

Several laboratory techniques and instruments are used to analyze the media used for collection of air samples. The method of analysis depends on the medium with which the sample has been collected as well as on the physical properties of the contaminant; it may also utilize the chemical properties of the contaminant, or certain characteristics that are inherent in the compound due to the arrangement of the molecules and the type of chemical bonds that are present. Analytical techniques vary in sophistication from gravimetric and counting techniques to more sophisticated methods such as gas chromatography, atomic absorption, and others.

Interpretation of sampling results requires an understanding of the accuracy of the sampling method. To determine compliance with OSHA limits, data are compared to upper and lower confidence limits to test the possibility that an overexposure condition exists. It is possible that data may be shown to be inconclusive at proving whether or not an overexposure exists. In this situation, the employer should assume the worst and proceed as if there were an overexposure or over the PEL condition.

The industrial hygiene professional must be aware that there are many issues associated with the use of airborne concentrations as representing the absorbed dose of the exposed worker. Age, gender, fitness level, pre-existing medical conditions, exposure to a combination of materials, and the physical demands of the work are all factors that can influence the body's absorption of a hazardous material. The industrial hygienist must also consider the representativeness of the data that was obtained during sampling. The use of air concentrations as defining safe levels of exposure also raises questions about the appropriateness of the limit as it applies to the conditions of exposure: what is the condition and susceptibility/sensitivity of the exposed population, what effect(s) does the limit protect against, and how complete are the toxicological data? These are some of the issues that comprise the "art" part of the art and science of industrial hygiene.

Critical Thinking Questions

1. Convert the following concentrations from ppm to mg/m^3:

   a. 1,200 ppm toluene (MW: 92)
   b. 2,500 ppm ethanol (MW: 46)

2. Convert the following concentrations from mg/m^3 to ppm:

   a. 0.050 mg/m^3 lead (MW: 207)
   b. 2,000 mg/m^3 cyclopentane (MW: 70.2)

3. Explain what the 95 percent confidence limits are and how they are used to compare sampling data to an exposure limit value.

4. What are the BEIs and what sort of information do they provide? Are they better than PELs or TLVs? Explain your answer.