5-2 Why Sample the Air?

The presence of airborne toxins in the workplace has long been recognized. Primitive methods of respiratory protection included the use of goat bladders strung across the workers' faces; more recent examples include firefighters' use of their neckerchief or bandana. Neither of these methods are effective for removing airborne contaminants that are microscopic in size. OSHA regulations and good industrial hygiene practice rely on and/or require three basic approaches (listed in the preferred order of implementation) to protect workers from hazardous exposures: 1) an engineered control; 2) an administrative or behavior-based approach; and 3) personal protective gear – usually as a last resort. We will take a closer look at these three approaches in Chapters 11 and 12, which deal with control of airborne contaminants and selection and use of PPE.

The preferred approach to dealing with airborne hazards is to engineer them out of the process, usually through process design changes, such as containing or enclosing the material. One example of an engineered method for controlling a contaminant is capturing it with a local exhaust ventilation system that removes it from the work area. Another alternative is to substitute less hazardous materials for those that present real or potential hazards to the workers. The ideal substitute or replacement would be one that eliminates or greatly reduces the health and physical hazards to the workers; often these materials pose fewer environmental hazards as well. Regardless of the method used for worker protection, air sampling is used 1) to determine the concentration of contaminants present before design changes; 2) to monitor levels while waiting for implementation of controls; and 3) after controls have been established, to monitor their effectiveness.

In manufacturing settings, where the processes tend to be stationary and well defined, engineering out the hazard or installing controls are often feasible and can be very cost-effective when compared to the costs of worker's compensation, health care, and loss of productivity, not to mention the personal cost to employees whose health is affected as the result of inhalation of a hazardous or toxic material. There are, however, several settings where engineered controls are either not feasible or not effective in reducing or controlling levels of airborne contaminants. Examples include cleanups at hazardous waste sites, where the airborne hazards may vary daily and exist only temporarily. In these situations, air sampling is used to characterize the site, that is, to provide information about which toxic materials are present and at which levels. These data are used to plan subsequent air sampling efforts and to select the protective gear (respirators, gloves, special clothing) that will protect the workers from the materials and concentrations that have been identified.

Sampling is also performed at sites where a response to a hazardous materials release or spill has occurred. The sampling information may be used to establish safe distances, formulate evacuation plans, and select protective gear and equipment to

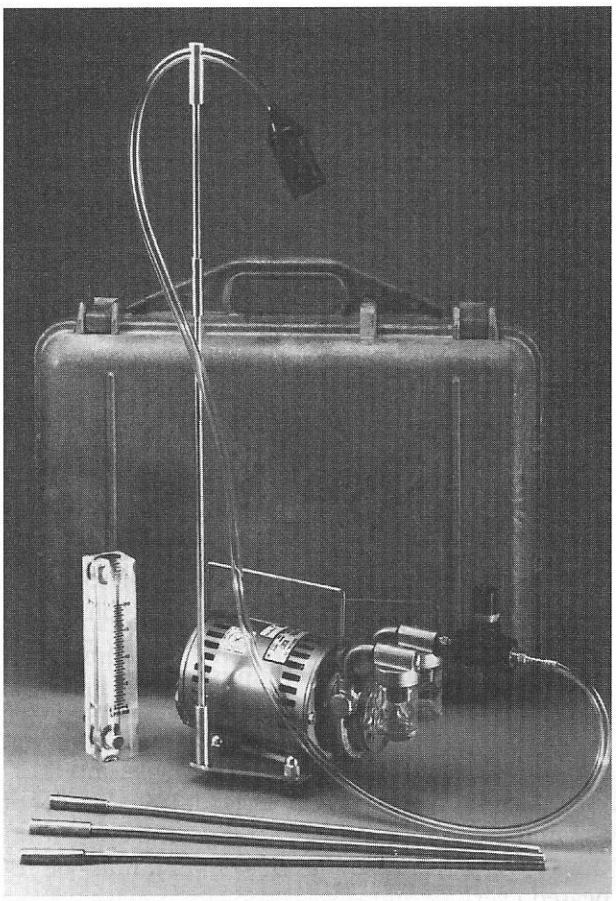

Figure 5-1: High-volume (2-15 lpm) air sampling pumps such as this are used for area sampling because they allow a relatively large volume of air to be sampled in a short time. They are also used for clearance sampling following removal of asbestos materials or lead-based paint.

be worn by responders entering the spill area. Air sampling is often done at locations where the existence of an airborne hazard is the result of the activities being performed, as in lead or asbestos abatement. In fact, sampling outside of an enclosed asbestos abatement work area is required by OSHA whenever these outside areas are occupied. These perimeter air samples provide important information about the effectiveness of the enclosure in containing the asbestos fibers. Sampling inside the work area indicates whether the work practices are effectively keeping fiber levels within limits set by regulations or job specifications.

Another reason for sampling the air is to alert personnel to a potentially dangerous atmosphere from escaping gases or other chemicals, or to warn of the uncontrolled release or leak of a material into the environment. The air may be sampled continuously or on a frequent and regular basis by an automated system connected to an alarm, which sounds at a predetermined level set by the user.

Air sampling is required by OSHA before workers enter a confined space, such as a tunnel, pit, tank, or other enclosed area, where the air may be unsafe. Specific tests must be performed to determine the amount of oxygen present, to measure the potential flammability of the air, and to find out if toxic materials are present at concentrations that pose a hazard to workers entering the space.

Finally, we arrive at what one might consider the most obvious reason for air sampling: to determine whether or not the levels of contaminants in the workplace air are within the OSHA-prescribed allowable levels, or PELs. For some contaminants, for example asbestos, OSHA regulations specify the sampling method to be used; use of a different method might yield results that are of no use in determining exposures relative to the regulatory limits. In addition to specification of a sampling and analysis method, OSHA may also specify the frequency with which sampling must occur.

For most regulated substances, the employer is required by OSHA to perform initial air sampling and may also need to implement a regular monitoring program. For example, for lead, if the results of the initial sampling reveal that airborne concentrations exceed the action level, sampling must be repeated every six months. If the samples exceed the PEL, sampling must be repeated on a quarterly basis. If periodic sampling data shows that the airborne concentrations of lead have decreased, the regulation requires that the decreased levels be demonstrated through repeated low results for samples taken at least a week apart – one low value is not enough to change the monitoring frequency. Other events that trigger additional sampling are changes in production, process, controls, or personnel that may result in actual or suspected increased exposure to lead. There are similar requirements for exposure monitoring in most OSHA substance-specific standards.

An effective industrial hygiene program will include a mechanism for identifying processes or activities for which exposure monitoring needs to be performed to 1) provide initial or baseline exposure data; 2) meet a regulatory requirement; or 3) provide historical data about exposures for company records. Monitoring programs can provide records of employee exposures over an extended time, allowing the industrial hygienist to alert management about conditions that may present unacceptable risks to employees. Monitoring is also useful for evaluating the adequacy of controls that are being used, such as ventilation or enclosed process systems. The use of respiratory protection also triggers a requirement for periodic sampling; OSHA's standard for respiratory protection, 29 CFR 1910.134, states that where respirators are used, the employer must monitor the workplace to verify that the concentrations of the contaminants of concern are within the use limitations of the respirators.

Thus, reasons for sampling the air in an occupational setting include:

- 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 and employee 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.

No matter what the reason, it is important that the person taking the samples be familiar with the purpose and intended use of the results. The use of the results will affect: the selection of the sampling

method, the type of sample(s) taken, the number of samples taken, the length of the sampling interval, the method of analysis, and the reporting of the results.

Sampling Approaches

There are two general methods for approaching the issue of air sampling. One is called **direct-reading** or real-time sampling. This type of sampling provides immediate or, at least, very fast feedback in terms of the sample results. The use of an oxygen meter to check the atmosphere inside a confined space is an example; once the sampling probe is placed in the air to be tested, the instrument will give a response within a few seconds or minutes. The second type of air sampling is **integrated sampling**. These samples are taken by drawing air through or across a collector, called the **sampling medium** (plural, media). The sampling medium is then analyzed by a laboratory to determine the amount of contaminant that is present. Sampling media commonly used for collecting integrated samples are listed in Table 5-1.

In order to collect samples for later analysis using an integrated sampling technique, the sample collector, which includes the holder or container that houses the sampling medium, is connected to the sampling pump using flexible tubing. The air enters the inlet and passes through the sampling medium, where the contaminant is absorbed or otherwise captured. The air then moves on through the pump and exits. The **sampling train** is composed of three elements: the sampling media in their holder, the tubing, and the sample pump. The components of the sampling train are dictated by the requirements of the sampling method, which will specify the sampling medium to be used for collection, as well as the total volume of air that must be sampled to yield accurate analytical results. The rate at which the air is pulled through the sampling train by the pump can be adjusted and set at the flow rate that is specified in the sampling method, and must be verified with a representative sample collector connected to the pump. We will take a closer look at air sampling pump calibration later in the chapter. Figure 5-2 is a diagrammatic representation of a sampling train.

Contaminant/Aerosol Type	Sampling Media Commonly Used
Particulates – dusts, fibers, fumes	Filters
Dusts and mists	Filters, absorbing solutions
Gases and vapors	Absorbing solutions, solid sorbent tubes, passive samplers, evacuated containers, and sample bags

Table 5-1: The type of aerosol being collected influences the choice of collection media, which is usually indicated by the sampling method. In some cases, a combination of media is needed.

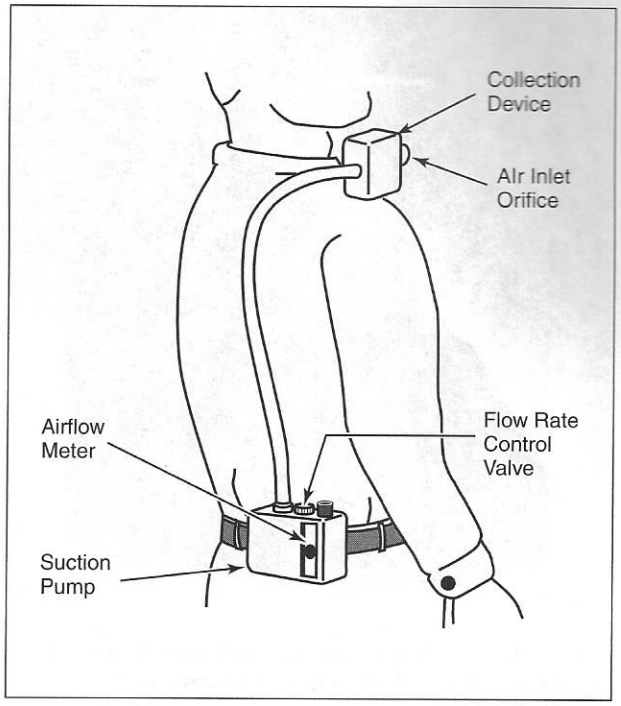

Figure 5-2: A sampling train consists of the inlet, collection device, and air sampling pump. The entire train is assembled, calibrated, and then attached to the worker as shown.

Sampling pumps come in a range of sizes with different flow capabilities. Pumps used for measuring individual exposures are generally small, weigh 1-2 pounds or less, and can pump air at rates ranging from as low as one cubic centimeter per minute (cc/min) to four liters per minute (lpm). The lower flow rates, ranging from .001 to a few hundred cc/min, are generally used for sampling gases and vapors, while flow rates of 1-4 lpm are used for many particulates. High flow pumps are capable of sampling rates of more than four lpm. These pumps are larger, heavier, and often noisier than those used for personal samples, so they are more apt to be used to take samples in a fixed location in a work area.

Figure 5-3: Personal sampling pumps such as this one are smaller and lighter than pumps commonly used for area sampling. Personal sampling pumps are used by the industrial hygienist to obtain data for evaluation against regulatory and other exposure limits.

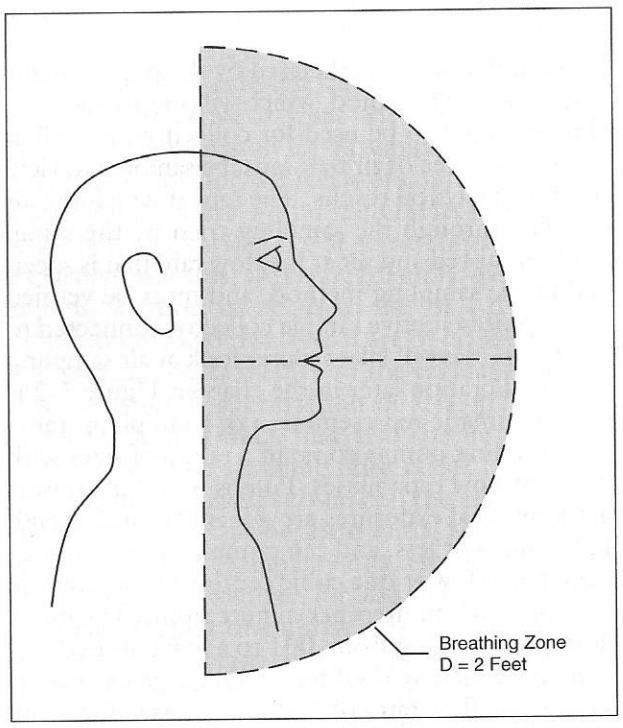

Figure 5-4: The breathing zone is defined as a two-foot diameter half-sphere around the worker's head and shoulders. This area contains the atmosphere that the worker is most likely to inhale. The inlet of the personal sample collector should be located within this region.

Personal samples are those that are obtained when a worker actually wears a sampling train during the work shift. The results of these samples are later compared against exposure limits. The sample collecting device is clipped or otherwise attached to the worker's shirt collar or lapel in order to collect (sample) the air that is representative of what the worker inhales. The region that is defined by a two-foot diameter half-sphere around the front of a worker's head and shoulders is the **breathing zone**; personal samples are therefore sometimes called breathing zone samples. In some instances, it is also appropriate to take samples of the air in a fixed location in the work area. These **area samples** provide the industrial hygienist with information about average levels of contamination and can be useful for evaluating overall air quality or the effectiveness of controls; however, they are generally not acceptable methods for evaluating worker exposure. Area sampling does have specific applications, such as monitoring the air outside of an asbestos or lead abatement (removal) area. Area samples are also used to evaluate the air following a hazardous material removal or cleanup action. These final area samples, called **clearance samples**, must show that levels of contaminant are at or below a specific concentration, which for asbestos is 0.01 fibers/cc, before the area can be released for normal occupation and work activities.

Checking Your Understanding

1. What are two reasons why OSHA might require more sampling, even if historical results show levels within regulatory limits?
2. Why is it necessary for the person doing the sampling to understand how the results will be used?
3. Explain the difference between engineering controls and exposure monitoring.
4. What is the difference between direct-reading and integrated sampling methods?
5. What type of sampling medium is used to collect particulates; dusts and mists; gases and vapors?
6. What is a personal sample? An area sample? A clearance sample?
7. Where is the breathing zone of a worker, and why is this the location for positioning a sampler when obtaining a personal sample?

5-3 Sampling Particulates

Filters

Filters are some of the most common sampling media used by industrial hygienists. Of the nearly 2,000 sampling methods described by NIOSH and OSHA, about one-fourth requires the use of some type of filter. Air sampling filters are made using different materials and methods. The type of filter to be used will depend upon the contaminant being sampled as well as on the sampling method chosen. Because the filters are quite thin, it is necessary to place them into rigid holders, called **cassettes**, during sample collection. Filter cassettes are commonly made of polystyrene, but other materials may also be used. A support pad is usually placed beneath the filter in the cassette. In some cases, the support pad is analyzed along with the filter. Like filters, support pads are made from various materials: some are cellulose, some are porous plastic; stainless steel mesh is also used.

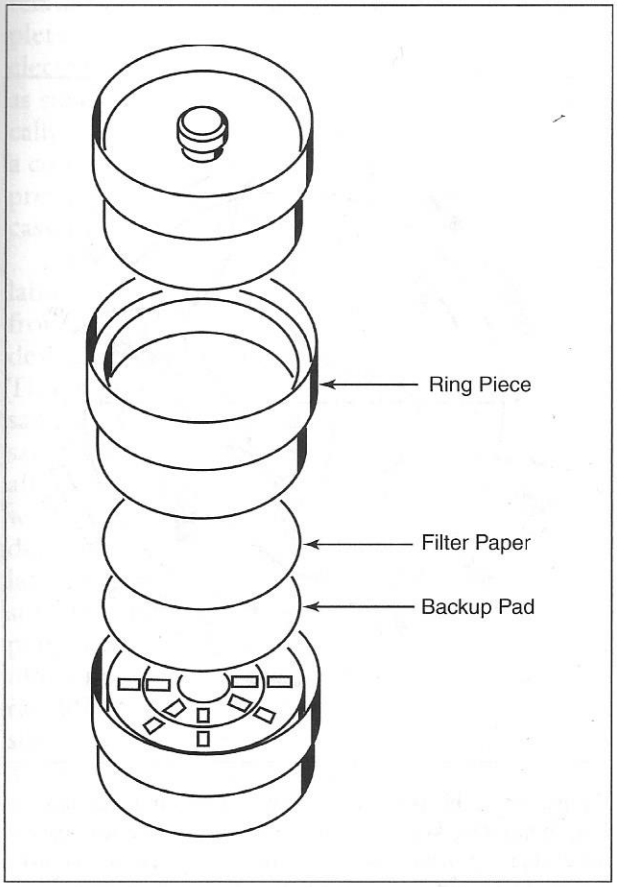

Figure 5-5: Filter and cassette assembly. Polystyrene cassettes such as this may be purchased preassembled, with the desired filter in place. Some analytical methods include the backup or support pad in the analysis.

Some methods specify the use of an **open face** cassette for sample collection. This means that the top portion of the cassette is removed during sampling. The filter and the support pad are held in place by a retaining ring that fits into the cassette base. Following sampling, the cassette is reassembled and returned to the laboratory for analysis. In a **closed face** sample, the small plug in the top of the cassette is removed and air enters the cassette through the small hole in the center; the plug is replaced following sampling, and the entire assembly is returned to the laboratory for analysis. Open face samples are used when distribution across the surface of the filter is important in the analytical result. For example, sampling for asbestos fibers requires an open face arrangement since analysis is performed on a section of the filter that is representative of the fiber loading across the entire filter. In contrast, evaluation of airborne metal fume involves analysis of the entire filter to determine the total amount of metal present. Since distribution across the surface of the filter is not a factor in metals analysis, a closed face arrangement is suitable for sampling. The sampling method will specify which arrangement is to be used.

It is logical to think that filters used for air sampling work like a screen or sieve to capture airborne contaminants. In fact, most filters used for industrial hygiene applications work much differently. Because of the way many filters are manufactured, there is no straight path through little holes in the filter. Instead, the openings or **pores** in the filter are more like a maze of many interconnected tunnels through which the air moves – turning, branching, speeding up and slowing down, as it passes through the thickness of the filter. This allows the contaminant to collide with surfaces in the filter (**impaction**), or stick to surfaces as it passes close by them (**interception**). Another possibility is that the particles might have an electric charge that causes them to be attracted to the filter material; this is called **electrostatic attraction**. The mechanism of collection will depend on the size of the particle, the electric charge of the particle and filter, the type of filter

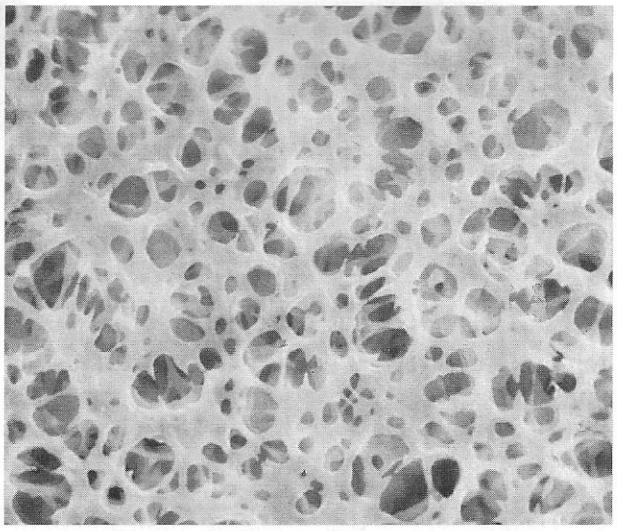

Figure 5-6: Photomicrograph of the surface of an air sampling filter. Filters used for collection of airborne particulates do not merely gather material on the surface; some particulate is actually deposited within the filter.

Mixed Cellulose Ester Filters (MCEF)

One of the most commonly used filters is the **mixed cellulose ester filter (MCEF)**. These filters are manufactured from a polymer that starts as a liquid, which is spread out in a thin layer to solidify or dry, like gelatin setting up. During the solidification process, the small openings or pores develop in the filter material. As mentioned above, the pores do not go straight through the surface of the filter (see Figure 5-7). This arrangement makes the filters very effective collectors of particles entrained in the air. The average size of the openings can be controlled in the manufacturing process, allowing the production of filters with pore sizes in a specific range suitable for collecting particulate of different sizes. MCEF filters are available with pore sizes ranging from 0.4 to 0.8 μm. Metal fume and asbestos fibers are collected on MCEF filters with pore sizes of 0.8 μm. Analysis of the filter is dependent upon the material that was collected. Filters used to sample

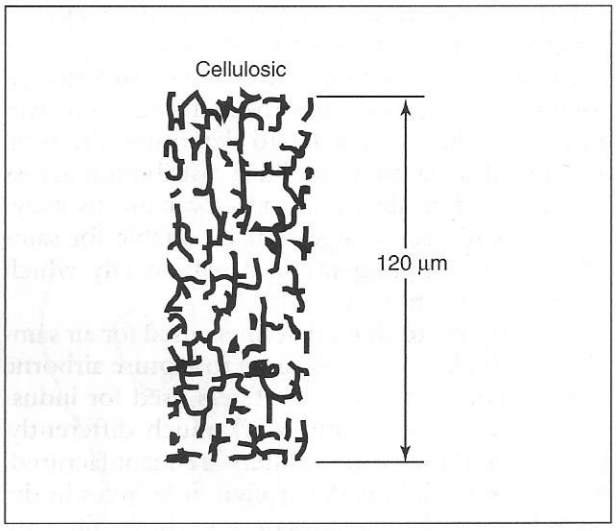

Figure 5-7: Cross-section through an MCEF filter. Filters are not sieves, but are more like mazes into which particles are pulled and become trapped.

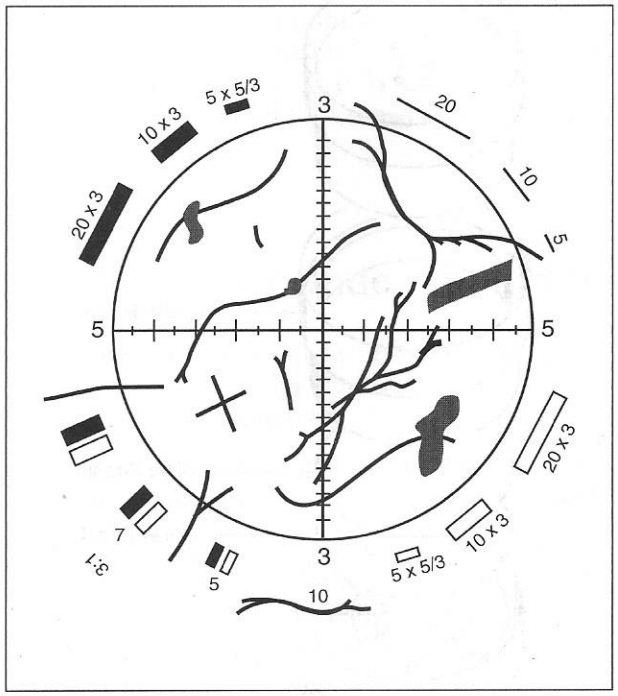

Figure 5-8: This is a diagrammatic representation of a filter being checked for airborne fibers, the method used for evaluating occupational exposure to asbestos. According to the counting requirements, all structures that are five microns or more in length and three times longer than they are wide are counted. The grid marks superimposed on the slide are from an optical insert – called a Walton-Beckett graticule – in the microscope.

being used, and the sample flow rate. It is possible that more than one mechanism will play a role in collection of a contaminant. As mentioned above, the pores make it possible to collect contaminants in the filters as well as on them. The capture efficiency of a filter is therefore not limited by the size of the pores.

for welding fumes, for example, are dissolved or digested in an acid solution, which is then analyzed for metals content. Fibers are quantified by removing a section of the filter and treating it with acetone vapor, so that it becomes clear. It is then possible to count the fibers while viewing the cleared filter through a microscope.

PVC Filters

Polyvinyl chloride (PVC) filters have good resistance to acidic and basic substances and do not absorb much water vapor from the air. Because of their **hydrophobic** properties (water resistance) and because they are lightweight, they are commonly used to collect dusts, such as silica-containing dusts. Before being used to collect dust, the filters are assigned identification numbers and placed into a sealed chamber, called a **desiccator**, which contains a water-absorbing substance like silica gel. The filters are left in the desiccator and allowed to dry completely. The filters are weighed using a sensitive electronic analytical balance, able to measure masses as small as ± 0.0001 grams. The filters are periodically weighed (e.g., every 24 hours) until they reach a constant weight within experimental error. These preweighed filters are then assembled in sampling cassettes and used for dust sampling.

After sampling, the filters are returned to the laboratory where the analyst carefully removes them from the cassettes and again places them into the desiccator. The weighing process is then repeated. This type of analysis, involving weighing of the sample, is called a **gravimetric analysis**. The presampling mass of the filter is subtracted from the after-sampling mass to determine how much dust was collected on the filter. The mass of collected dust and the sampled air volume are used to calculate the airborne concentration. These filters are sometimes further analyzed; for example if the sampling is to determine crystalline silica exposure, the filters might be examined after weighing using x-ray diffraction to identify which forms of crystalline structures are present – cristobalite, tridymite, or amorphous silica. This information can be used to determine the composition of the sand that was being used in the area where the samples were taken, which, in turn, is used to compute the PEL (see Chapter 4).

Sampling for dusts that might be inhaled requires that the industrial hygienist know what fraction of dust is of interest. As we saw in Chapter 4,

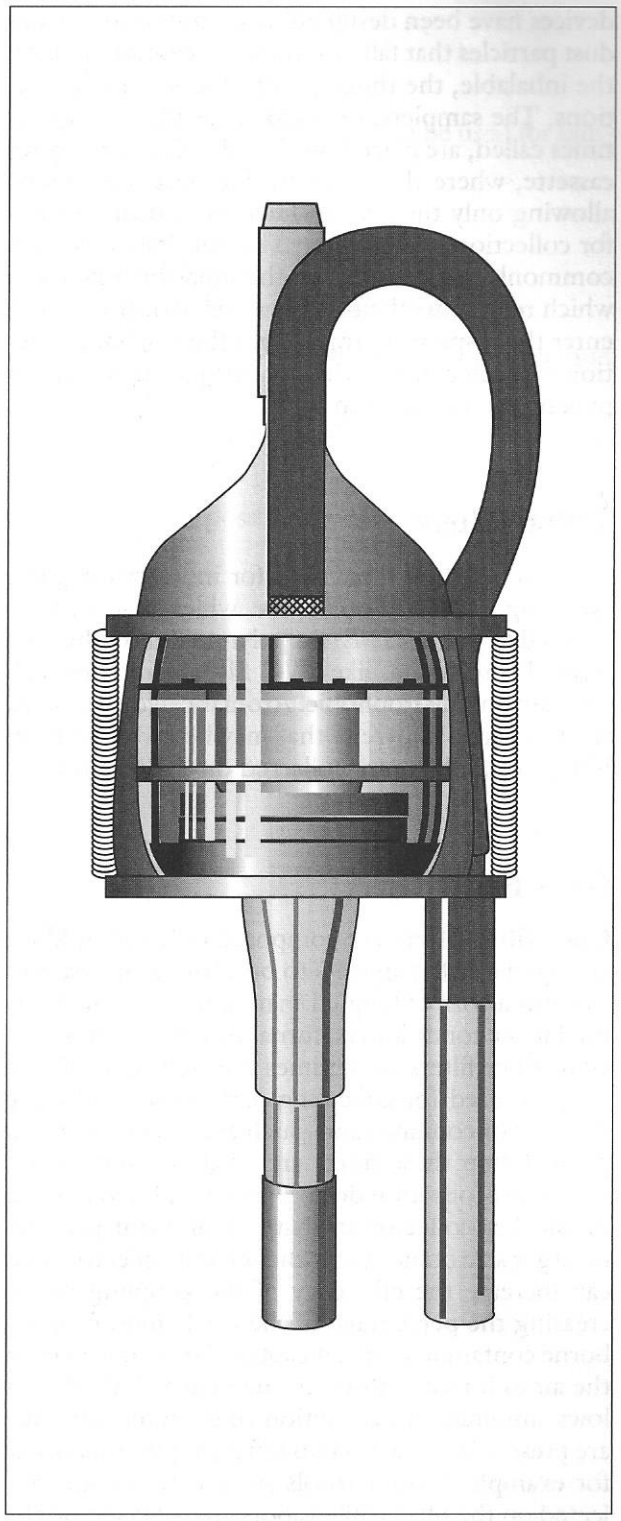

Figure 5-9: A sampling cyclone such as this is used to sample for the respirable fraction of airborne particulate. The air enters the inlet, then passes through the vortex-like separator, which removes larger particles from the air stream. The smaller particles are then collected on the filter inside the holder.

devices have been designed to separate and capture dust particles that fall into three specific size ranges: the inhalable, the thoracic, and the respirable fractions. The samplers, or **cyclones** as they are sometimes called, are placed on the inlet side of the filter cassette, where they separate the dust that enters, allowing only the desired fraction of dust to enter for collection on the filter. The two fractions most commonly sampled for are the inhalable fraction – which represents the total amount of dust that may enter the respiratory tract – and the respirable fraction – which contains the smallest particles that can penetrate into the deep lung.

Teflon Filters

Another polymer filter used for industrial hygiene sampling is the **Teflon® filter**, which is sometimes referred to as the PTFE (for polytetraflouroethylene) filter. These filters, like PVC filters, are chemical-resistant and hydrophobic. Aromatic hydrocarbons, such as benzo(a)pyrene that may be given off from hot tar or asphalt, are collected on PTFE filters.

Glass Fiber Filters

Glass fiber filters are composed of layers of fibers arranged in what appears to be a haphazard pattern to form a sort of tangled mat, similar to the filters used in air conditioners, furnaces, and automobiles. Glass fiber filters, sometimes referred to as AE filters, are used for collecting particulates and some droplets of contaminants, such as mercury and acid gases. Often these filters are used as a sort of upstream precollection device; they are placed in front of another collector so that contaminant particles of larger size do not enter the second collector. This can increase the efficiency of the sampling by increasing the percentage of the total amount of airborne contaminant that is captured or removed from the air as it moves through the media. This also allows simultaneous collection of contaminants that are present in the air in two different physical forms; for example, solid aerosols such as fumes are collected on the filter while vapors are collected on the sorbent.

Coated/Treated Filters

Some sampling methods require the use of filters that have been coated with a specific chemical: these are the **coated/treated filters**. These coatings vary, depending on the contaminant to be collected. The coatings enhance collection by chemically reacting with the contaminant as the air is drawn through the filter. An example is NIOSH Method 6004 for sampling sulfur dioxide. This method requires the use of a 37 mm diameter MCEF followed by a cellulose filter coated with potassium hydroxide. There are several OSHA methods for sampling organic amines that use two 37 mm glass fiber filters coated with sulfuric acid. Like other sampling media, these can be ordered from suppliers and arrive preloaded into cassette holders, ready for use.

Potential Problems Associated with Filter Collection

Collection on filter media does pose some potential problems to the occupational health professional. Among these problems are:

— Overloading – It is possible to overload filters. If the analysis requires examination of the filter, as in fiber sampling, the presence of too much particulate can make it difficult or impossible to accurately quantify the fibers collected on the filter. In the case of contaminants that are analyzed gravimetrically, including such contaminants as silica-containing dust or respirable dusts, too much particulate on the filter can make loss of material a source of error during handling and weighing of the filter.

— Static electricity – Static electricity can also be a problem for filters subject to gravimetric analysis. The filters pick up a charge and are then either repelled or attracted by the balance tray, causing errors in mass determination.

— Moisture or physical damage (tearing, bursting) – It is also possible for filters to become wet; they can tear or burst due to changes in flow or to failure of the IH to remove the inlet plug.

— Contamination with interfering substances – Filters can become contaminated with materials that interfere with the analysis and result in over- or under-estimates of the amount of contaminant that is present.

It is important that the professional who is performing the sampling be aware of the limitations and potential problems associated with the particular sample method so that the best sampling data possible may be obtained during the sampling event.

Checking Your Understanding

1. Explain the physical structure of the following filters used for air sampling: MCEF; glass fiber filters; coated filters.
2. Define/explain the following mechanisms for capture of contaminants by filters:
   a. Impaction;
   b. Interception;
   c. Electrostatic attraction.
3. Name the type of filter likely to be used for sampling the following:
   a. Silica-containing dust;
   b. Welding fume;
   c. Asbestos fibers;
   d. Aromatic hydrocarbons.
4. Explain the difference between open-face and closed-face sampling.
5. What is the purpose of adding chemical coatings to a filter?
6. What are the possible consequences of overloading a filter?

5-4 Sampling Gases and Vapors

Sorbent Tubes

Sorbent tubes are small glass tubes that contain sampling media. To use the tubes, the IH snaps off each end and inserts one end of the tube into a holder that is connected to the sampling pump. Most sorbent tubes have arrows on them to indicate the direction of airflow. If there is no directional arrow on the tube, the end nearer the small backup section should be placed into the sampling tube or holder. The tube holder has a clip for attachment to the worker's shirt, and most holders also cover the sharp inlet end of the tube to prevent the worker from possible cuts. The media or **sorbent** that is in the tube can be one of a number of materials, such as charcoal, silica granules (called silica gel), or one of several other granular polymers. As with filters, the sampling method will specify the type of sorbent tube that must be used for sample collection; the sorbent is also sometimes coated with a chemical compound to enhance collection efficiency for a specific contaminant. Collected compounds are removed, or **desorbed**, from the sorbent using a solvent, most often carbon disulfide. Some methods utilize heat to separate the contaminant from the sorbent.

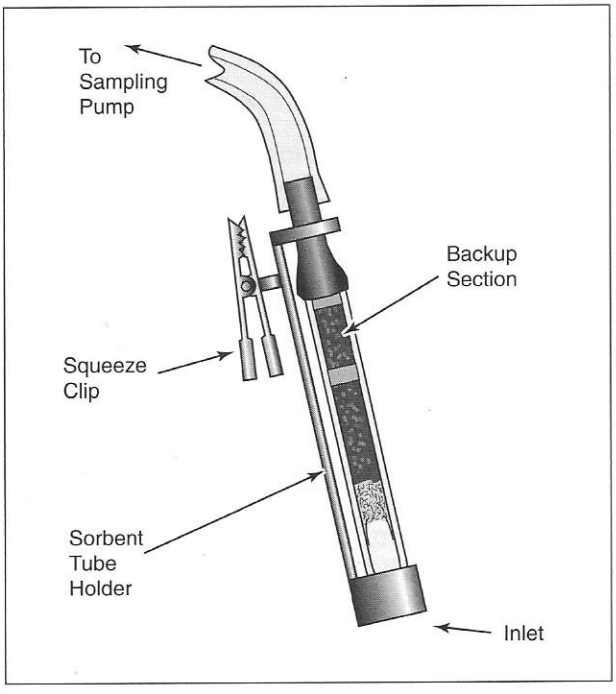

Figure 5-10: Sorbent tubes are made of glass; the ends must be broken off by the IH prior to sampling. Sorbent tube holders are constructed to cover the broken ends of the tube, thus protecting the worker from cuts. The tube must be oriented with the backup (smaller) section of sorbent closest to the sampling pump. The sample holder should be attached to the worker's lapel so that the sorbent tube is held in a vertical position.

Sorbent tubes collect contaminants through mechanisms that somewhat resemble those of filters. The most common types of sorbent used for occupational exposure sampling include charcoal and silica gel. Activated charcoal contains microscopic openings where molecules are trapped. Silica gel provides a surface on which contaminants may condense or to which they might simply adhere. Other sorbents have specific applications and are selected because of the affinity of the sorbent for certain kinds of compounds, or because of chemical coatings that have been added to the sorbent. Manufacturers have trademark names for some of these: Tenax, XAD2, Chromosorb, and others. We will not address these other sorbents; for more information, see the references at the end of the book.

Charcoal, or more accurately, **activated charcoal**, is used for a wide range of occupational exposure sampling applications. The charcoal, much of which comes from coconut shells, is activated through heating with 800-900°C steam. This causes the air spaces in the charcoal to expand, so that a cross-section looks more like a sponge or a layer cake; it is in these air spaces that the contaminant is trapped. Charcoal tubes are used to collect a variety of polar and non-polar molecules. Molecules that have a partial positive charge at one end and a partial negative charge at the other end are called **polar compounds**. Charcoal tubes are used in collection of organic solvents and vapors including many alcohols, ketones, and a variety of aromatic compounds. Another commonly used sorbent is silica gel, produced from the action of sulfuric acid on sodium silicate. Silica gel tubes are most often used to collect polar compounds; examples of such materials are amines and halogenated compounds such as hydrogen chloride, hydrogen bromide, and hydrogen fluoride. There are other sorbent tubes, some containing charcoal or silica gel with a coating of a chemical that increases the sorbent's ability to capture a specific contaminant. Again, the sampling method will specify the sorbent to be used.

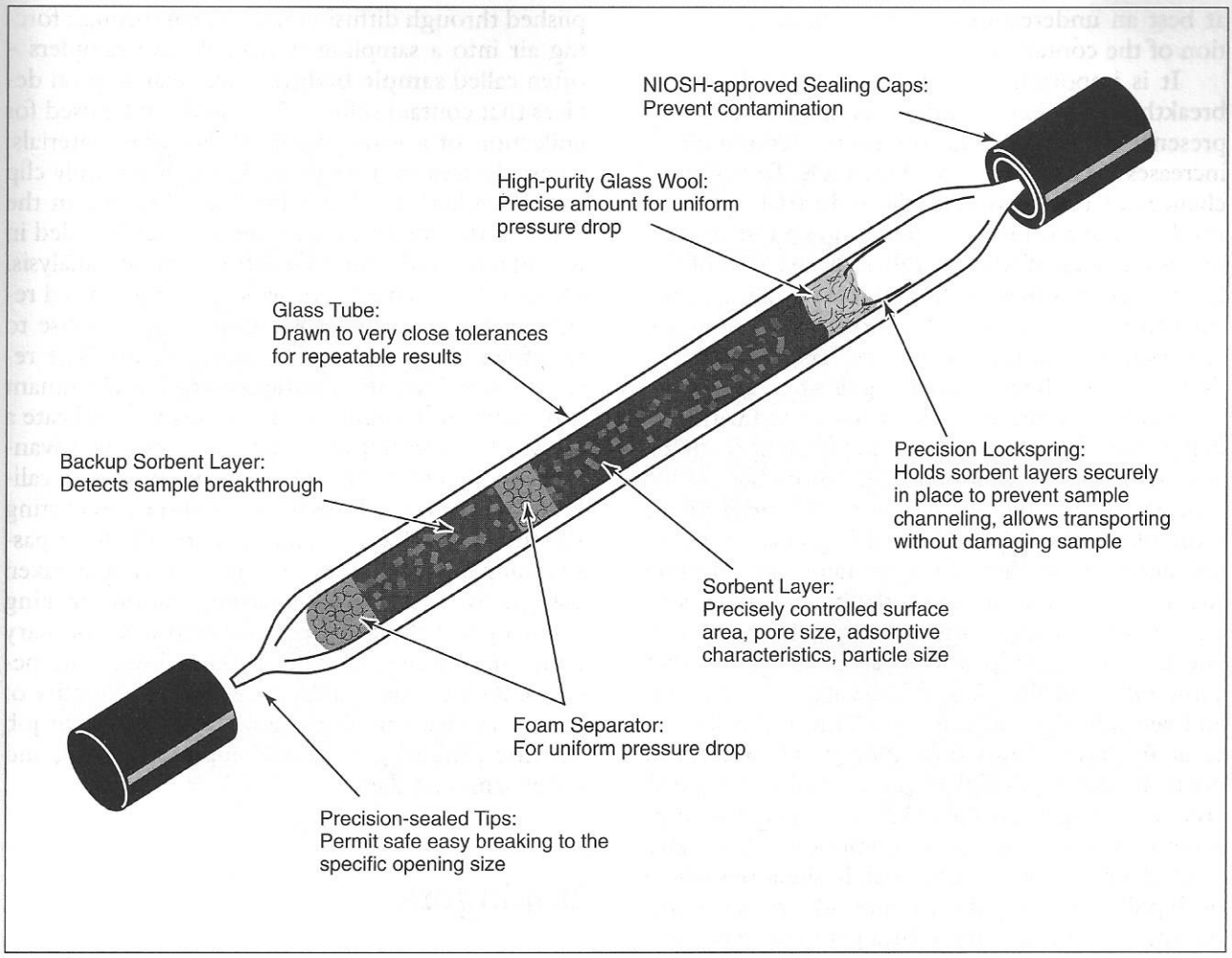

Figure 5-11: The internal assembly of sorbent tubes is based on an original specification from NIOSH. Larger tubes have proportionately more sorbent material in the sorbent and backup layers.

Many sorbent tubes in use today are assembled according to an original NIOSH specification that applied to charcoal tubes. The specification called for a 7 cm-long glass tube with an outside diameter of 6 mm and an inside diameters of 4 mm. The charcoal was to be small enough to fit through a 20/40 mesh screen. The main or front section was to hold 100 grams of media; a smaller section, called the back or backup section, was to contain 50 grams of media. Each section was separated by a plug of glass fibers, with additional glass fiber plugs at each end to hold the sorbent in place. Today, foam plugs are used instead of the glass fibers, since the foam presents less air resistance. Larger tubes are also available; they are larger in terms of overall dimensions and use proportionately greater volumes of sorbent. The larger tubes, with their increased volume of sorbent, allow for longer sampling intervals and larger volumes of air to be sampled using a single tube. Figure 5-11 shows the construction of a typical sorbent tube.

The backup section of sorbent has an important role, which is capturing any contaminant that passes through the front or main section. The indicating arrow on the sorbent tube is to ensure that the tube is properly oriented, so that air enters the front section of sorbent first. If the laboratory analysis of the backup section shows that it contains an amount of contaminant equal to 20-25 percent of the amount of contaminant captured in the front section, it is an indication that the front section of sorbent was possibly completely saturated during the sample collection. This condition is called **breakthrough**. When this occurs, the sample results are

at best an underestimate of the actual concentration of the contaminant.

It is important to consider the possibility of breakthrough when planning a sampling event. The presence of a high concentration of contaminant increases the chances of breakthrough. To minimize chances of breakthrough, the industrial hygienist needs to use a shorter sampling interval, make frequent changes of sorbent tubes, or use one of the larger sorbent tubes. Although it is not always possible to do so, failure to plan for this contingency can result in inaccurate sample results, which are of limited use to the industrial hygienist.

Another common problem associated with sorbent sampling is the use of the incorrect sorbent, or at least, the use of a sorbent that is not effective for capturing the contaminant of interest. This happens most often when the industrial hygienist is uncertain about the nature of the contaminant. In these situations, a charcoal tube is the most popular sorbent used; typically, a large volume of air is sampled, and the tube is sent for analysis in the hopes that something will show up. While charcoal is a useful and versatile sorbent, it is not a universal collector. Charcoal has its limits: it can be a good collector of polar molecules, like alcohols, as well as nonpolar compounds, like benzene. However, nonpolar compounds may displace polar compounds that have been adsorbed onto the charcoal. In situations where both polar and nonpolar compounds are being collected, it is common for a silica gel tube to be used in series or separately to collect the polar compound.

The temperature and relative humidity in the area during sampling can affect any solid sorbent's ability to capture and hold contaminants, usually adversely. Also, the presence of other compounds for which the sorbent might have a stronger attraction or capture ability can result in the interfering compound displacing contaminant that has already been collected. This will result in data that indicate a lower-than-actual concentration of the contaminant.

Passive Samplers

The term **passive sampling** is used to describe sampling that is done without an air sampling pump. The use of the term passive is a little misleading, since the contaminant does move toward the collection surface; however, its collection is accomplished through diffusion rather than through forcing air into a sampling device. Passive samplers – often called **sample badges** – are small clip-on devices that contain solid sorbent and can be used for collection of a wide variety of airborne materials. These devices are very easy to use: they simply clip to the worker's lapel and are worn throughout the shift. At the end of the day, the sampler is sealed in a container and sent to a laboratory for analysis. Other passive samplers provide user-interpreted results in the form of a color change in response to the presence of a particular contaminant. The response may indicate whether or not a contaminant is present, or it might vary in intensity to indicate a range of concentrations. There are obvious advantages to the use of such samplers: no pumps to calibrate, no battery failures to worry about, no putting the tube in backwards! Analytical results from passive sampling techniques are as good as samples taken using active methods for most applications, making them a good choice where ease of use is a primary concern. As is the case with any sampling event, specific data must be recorded, such as the identity of the person wearing the sampler, notes on their job activities, the length of the sampling interval, and other sampling data.

Impingers

Air contaminants that are nonreactive and highly soluble in a specific solution may be collected using a measured volume of that particular solution in an **impinger**, which is a glass container, also known as a bubbler or a gas-wash bottle. Impingers, which come in a range of sizes to fit a variety of applications, resemble a graduated cylinder with a long inlet tube fitted into a stopper. The inlet tube extends nearly to the bottom of the vial, which holds the solution. The sampling pump is connected so that a partial vacuum is created inside the impinger, drawing air through the inlet tube, where it exits into the solution. The air bubbles up through the solution, and this contact between air and liquid allows the contaminant to dissolve in the liquid. Some impingers have modified inlet tubes, designed to circulate air or otherwise increase contact between the air and the absorbing solutions. Some commonly used impingers have fritted inlets; the **frit** resembles a porous stone, similar to the ones used for aeration

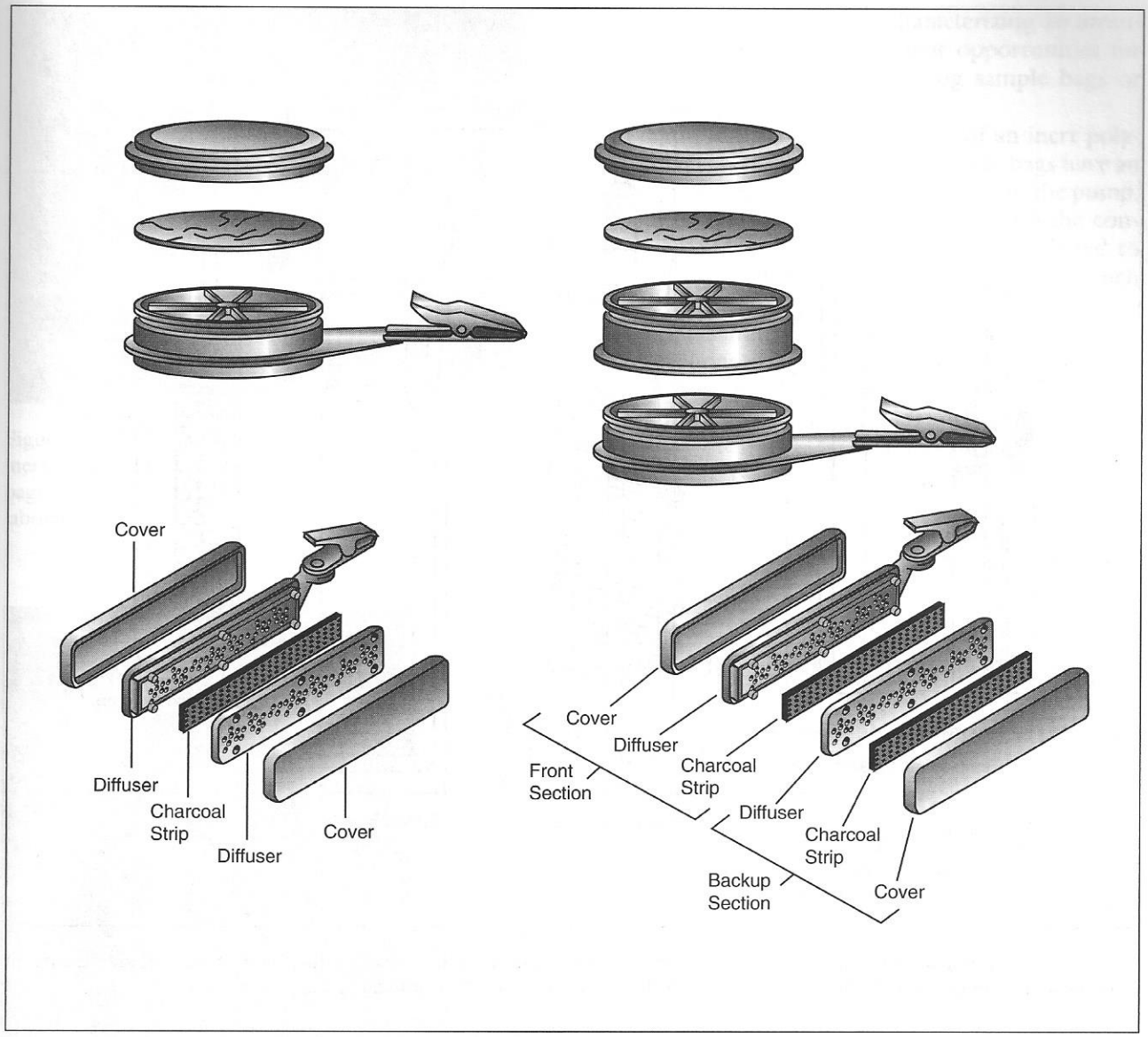

Figure 5-12: Some typical passive samplers. These devices are easy to use, since they require no calibration and no sampling pumps. Following sampling, a cover is snapped over the top of the sampler, and the entire assembly is sent to the laboratory for analysis.

of an aquarium. Frits may be coarse, medium, or fine depending on the number and size of the openings; selection of a particular grade of frit will usually be specified in the method. The frit breaks the airstream into small bubbles; this maximizes the surface area of air that contacts the solution, increasing the amount of contaminant that is dissolved or absorbed in the solution. The use of a fritted bubbler can increase the collection efficiency of hard-to-collect vapors and gases, but it also introduces some flow losses due to pressure drops, which can be high for a fine frit.

Solutions used in impingers vary depending on the contaminant of interest. The solution may be a specific compound mixed at a certain concentration, for instance a sodium hydroxide solution used for ammonia sampling. At the other extreme, distilled water is a common absorbing solution for many materials that are water-soluble. After sampling, the solution may be sealed in the impinger cylinder, or

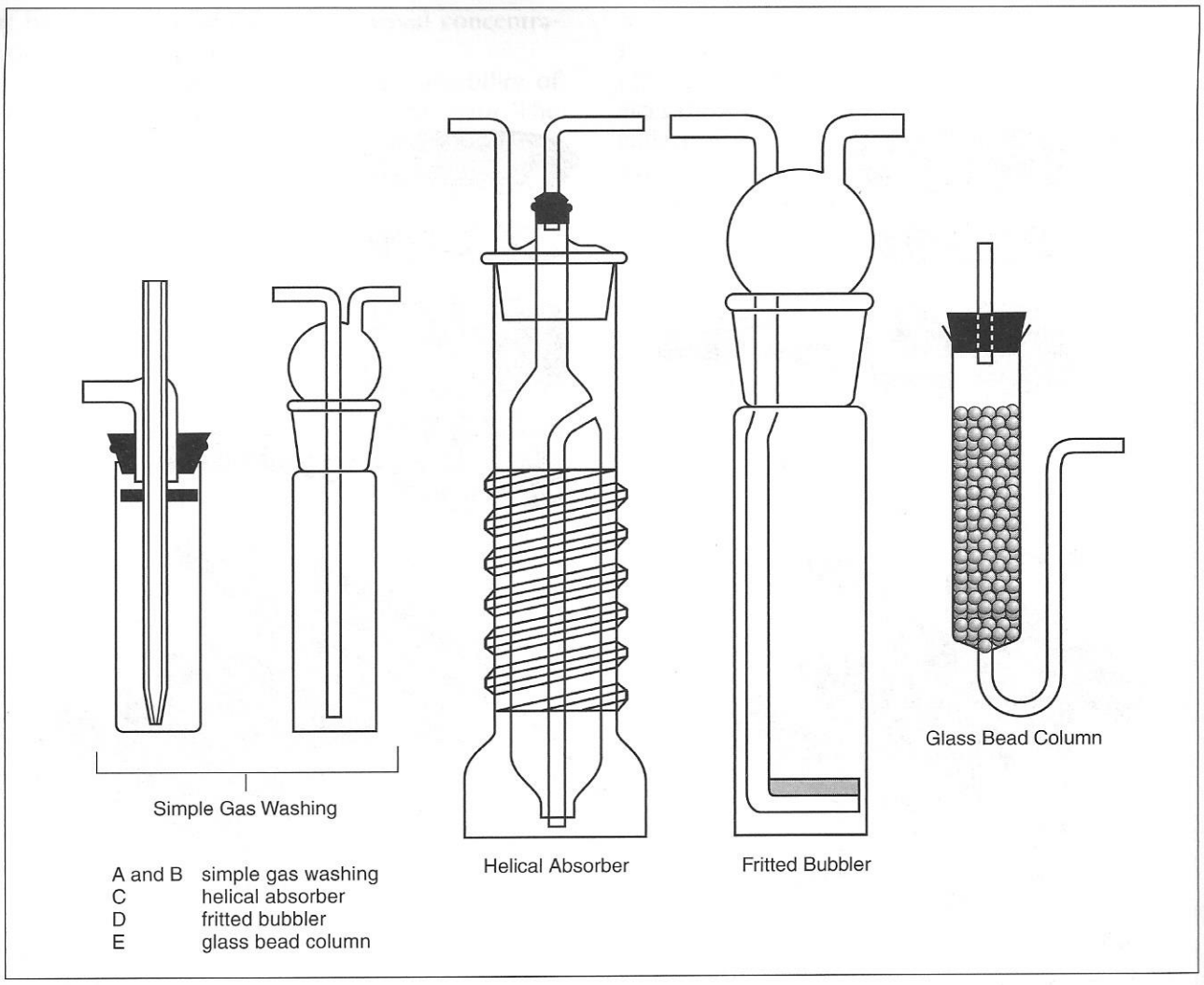

Figure 5-13: Impingers, also called gas-wash bottles or bubblers, are used to collect soluble, non-reactive contaminants in a solution. The solution is often transferred to a bottle or vial for transport to the laboratory for analysis.

placed into a different container, and sent to the laboratory for analysis. Again, the sampling method will specify the analytical steps for determining the amount of contaminant that has been collected in the solution.

Possible problems that can arise during use of impingers include loss of solution through spills or leaks; breakage of the cylinder; or evaporation during sampling. Also, some of the solutions used in impinger sampling are corrosive, which makes their use for personal sampling less desirable than a method that uses a sorbent tube or another collection medium.

Grab Samples – Sample Bags and Evacuated Cylinders

A **grab sample** is an integrated sample, but one that represents a very brief sampling period. Grab samples are like snapshots. The sample captures a moment in time, but is not necessarily an indication of constant or average conditions. Grab samples may be useful for evaluating compliance with a ceiling or peak limit. In many situations, the industrial hygiene professional may wish to obtain a grab sample for screening and identification of possible contami-

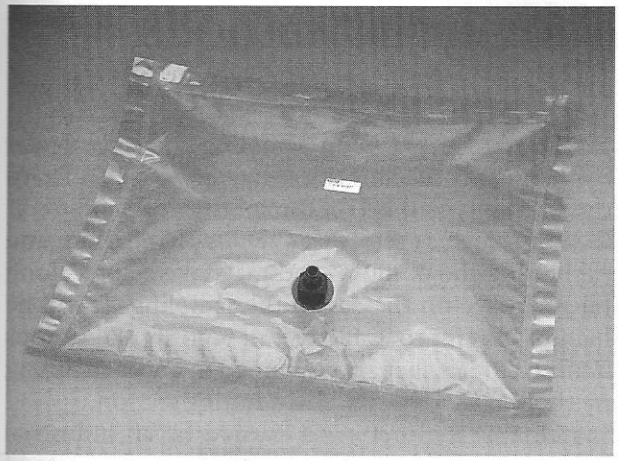

Figure 5-14: Sample bags made out of Teflon or another inert polymer are useful for obtaining grab samples. The bags are light and easy to use, and are returned to the laboratory for analysis.

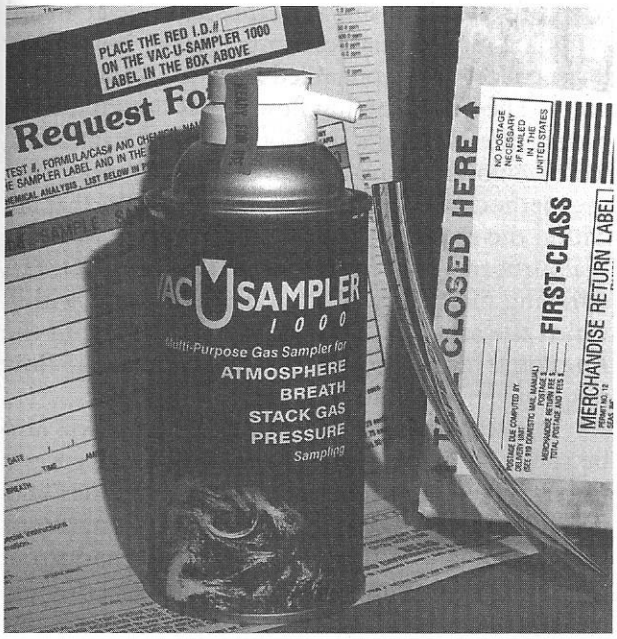

Figure 5-15: Evacuated containers – usually made of glass or metal – are used for grab samples. Air is drawn inside when they are opened; they are then sealed and returned to the laboratory for analysis.

nants, or as a first step in characterizing an atmosphere. These instances present opportunities for sampling gases and vapors using sample bags or evacuated containers.

Sample bags are often made of an inert polymer, such as Teflon® or Tedlar®. These bags have an attached fitting that allows connection to the pump, which pumps air into the bag along with the contaminants. The bag is then sealed and shipped to the laboratory for analysis. Figure 5-14 shows such a bag.

An **evacuated container**, also called an evacuated cylinder, is just what the name implies: a container from which air has been removed and the container has then been sealed. To sample using one of these, the seal is broken and the contaminated atmosphere is drawn into the evacuated container. The opening is then sealed, and the container is shipped to the laboratory for analysis of the contents. Figure 5-15 shows an evacuated container.

Checking Your Understanding

1. Name the two sorbents commonly used for industrial hygiene air sampling.
2. What is meant by activated charcoal?
3. What is meant by the term breakthrough, and how does this affect the results of an air sample?
4. Name two positive traits or aspects of passive samplers.
5. What is a fritted bubbler, and what does it do for sampling efficiency?
6. What is an evacuated cylinder and how is it used?

5-5 Standard Sampling and Analysis Methods

Sampling and analysis methods (also called "sampling methods" or simply "method" throughout the chapter) have been developed and validated for many airborne contaminants. Both OSHA and NIOSH have published sets of standard methods for sampling and analysis, the majority of which are for air samples. Our discussion will focus on those methods that are used for the sampling and analysis of air.

The OSHA sampling methods are collectively called the *OSHA Reference Methods*; NIOSH methods can be found in the *NIOSH Manual of Analytical Methods*, currently in its fourth edition. Sampling methods provide detailed instructions about collecting the sample and analyzing it for the contaminant, which is referred to as the **analyte**. Methods contain – among other things – the following information:

—The sampling media to be used;

—The sampling flow rate;

—The volume of air that is to be sampled;

—Instructions for sample preservation and handling;

—Detailed procedures to be followed for the analysis.

Methods also provide information about the statistical reliability of the sampling method, including an indication of the accuracy of the method. Before it is acceptable for use, a NIOSH method must be shown to be able to provide a result that is within 25 percent of the actual concentration, 95 times out of 100 tries. This means that we can be 95 percent sure that the method, when followed, will yield results that are within 25 percent of the actual concentration. The techniques used for sampling must allow for capture of the contaminant on the sample medium, where it will remain in a stable form. All or most of the contaminant must also be able to be removed from the medium on which it was collected, for analysis in the laboratory. To meet these stringent performance requirements, much planning and testing is involved in developing a sampling method. A detailed description of the criteria used in evaluating methods can be found in the introductory section of the *NIOSH Manual of Analytical Methods.*

Prior to performing sampling for a particular contaminant, the industrial hygienist will refer to the sampling method for the specifics of sample collection – such as selecting the sample medium and calibrating the pumps – and may take a copy along for reference on the day of the sampling. It will be helpful to refer to Table 5-2 to identify the various items or topics that are contained in an air sampling method as we describe them in this section.

One of the first skills learned by an industrial hygienist is the process for verifying the flow rate of air through an air sampling device. This process, called **calibration**, is done to make sure that the air passes through the collection or sampling medium slowly enough so that any contaminant present in the air is absorbed, dissolved, or otherwise collected, depending on the sample medium and the mechanism of collection. The flow must also be at an appropriate rate so that contaminant that has already been collected is not pulled off the sampling medium. The best sampling flow rate is determined as part of the method's development and validation, which involves many tests and trials to make sure the method will consistently provide results that are within the required 25 percent accuracy for the actual airborne concentration. NIOSH and OSHA sampling methods will often specify a range within which the sampling flow rate should be set; in the Ammonia by IC procedure, for example, the flow rate is given as 0.1 to 0.5 lpm.

The total volume of air to be sampled will also be specified in the method and may be given as a range as well; a number of different volumes may be specified for evaluating different concentrations of contaminant. In the latter case, the industrial hygienist performing the sampling must decide the appropriate volume, based on the expected concentration of the contaminant. For example, if very low concentrations are expected in the work area, a greater volume of air will need to be sampled. High concentrations of contaminant may require smaller volumes to avoid overloading the sample collector, which can invalidate the results. The method for ammonia sampling is quite flexible in this regard; the working range is given as 24 to 98 ppm for a 30-liter sample.

The sensitivity of the sampling and analytical method also plays a role in the volume of air that must be sampled. Laboratory techniques used to

AMMONIA by IC **6016**

NH_3 **MW: 17.03** **CAS: 7664-41-7** **RTECS: BO0875000**

METHOD: 6016, Issue 1 **EVALUATION: FULL** **ISSUE 1: 15 May 1996**

OSHA: 50 ppm
NIOSH: 25 ppm; STEL 35 ppm; Group III Pesticide
ACGIH: 25 PPM; STEL 35 PPM
(1ppm = 0.697 mg/m³ @ NTP)

PROPERTIES: gas: MP-77.7°C; BP -33.4°C; VP 888 kPa (8.76 atm) @ 21.1°C; vapor density 0.6 (air = 1); explosive range 16 to 25% v/v in air

SYNONYMS: none

SAMPLING

SAMPLER: SOLID SORBENT TUBE (sulfuric acid-treated silica gel) a 0.8 µm MCE prefilter may be used to remove particulate interferences.

FLOW RATE: 0.1 to 0.5 L/min

VOL-MIN: 0.1 L @ 50 ppm
-MAX: 96 L @ 50 ppm [1]

SHIPMENT: routine

SAMPLE STABILITY: at least 35 days @ 5°C [2]

BLANKS: 2 to 10 field blanks per set

SAMPLING

RANGE STUDIED: 17 to 68 mg/m³ [1] (30-L samples)

BIAS: –2.4% [1]

OVERALL PRECISION ($\hat{S}_{rT}$): 0.071 [1]

ACCURACY: ± 14.5%

MEASUREMENT

TECHNIQUE: ION CHROMATOGRAPHY, CONDUCTIVITY DETECTION

ANALYTE: ammonium ion (NH_4^+)

EXTRACTION: 10 mL deionized water

INJECTION VOLUME: 50 µL

ELUENT: 48 mM HCl/4mM DAP-HCl/4 mM L-histidine-HCl; 1 mL/min
alternate: 12 mM HCl/0.25 mM DAP-HCl/ 0.25 mM L-histidine-HCl; 1mL/min

COLUMNS: HPIC-CS3 cation separator; HPIC-CG3 cation guard; CMMS-1 cation micromembrane suppressor

CONDUCTIVITY SETTING: 30 µS full scale

CALIBRATION: standard solutions of NH_4^+ in deionized water

RANGE: 4 to 100 µg per sample [3]

ESTIMATED LOD: 2 µg per sample [3]

PRECISION ($\bar{S}_r$): 0.038 [2]

APPLICABILITY: The working range is 24 to 98 ppm (17 to 68 mg/m³) for a 30-L sample. This method is applicable to STEL measurements when sampled at ≥ 0.2 L/min.

INTERFERENCES: Ethanolamines (monoethanolamine, isopropanolamine, and propanolamine) have retention times similar to NH_4^+.
The use of the alternate (weak) eluent will aid in separating these peaks.

OTHER METHODS: This method combines the sampling procedure of methods S347 [4] and 6015 with an ion chromatographic analytical procedure similar to Method 6701 [5] and OSHA Method ID-188 [3].

NIOSH Manual of Analytical Methods (NMAM), Fourth Edition, 5/15/96

Table 5-2: NIOSH methods are the standard in the United States for sampling and analysis of airborne contaminants, although OSHA methods are also used. Analytical methods contain instruction in taking the sample, including sampling media and flow rate; they also provide instruction on how to conduct analysis of the samples in the laboratory.

analyze samples have boundaries or limits, beyond which the results are not reliable. These limits, which may be expressed as the **limit of detection (LOD)**, or the **limit of quantitation (LOQ)**, represent the smallest amount of contaminant that can be reliably detected and quantified, respectively, using the sampling and analytical techniques in the sampling method. These limits are usually listed on the first page of the NIOSH method; in the ammonia example, the estimated LOD is 2 µg per sample.

Some contaminants require special handling, such as refrigeration, or protection from light. If special handling is required, the method will provide this guidance; the ammonia method indicates routine shipment, which means there are no special handling requirements. Sample stability can be crucial if the collected contaminant is unstable or loses stability quickly following sampling; this can be the result of a chemical reaction or a weak chemical bond that holds the contaminant on the sample medium. Ammonia samples collected according to our example method are stable for at least 35 days if refrigerated.

The sampling method also contains detailed instructions to be followed in preparing the sample for analysis as well as setting up the equipment or instrument in the laboratory. We will examine some of the more common analytical techniques in the next section.

Calibration and Determination of Sample Volume

The process of determining the rate at which the sampling pump draws air through the sample collector is called calibration. In order to determine the flow rate, it is necessary to establish the time it takes for the pump to move a known volume of air. This is done by measuring the flow of air through the sampling train and comparing the measured flow to a reference or calibration standard. Most air sampling pumps used for industrial hygiene purposes have some method for adjusting the sampling flow rate – a valve, set screw, or an electronic controller. Many adjustment controls allow the user to approximate the desired flow rate, but most do not provide a precise setting and even if they do, it is wise to verify the flow rate. In order to obtain an accurate measure of the flow rate, the sampling train is assembled just as it would be used during the sampling event, using the pump that will be used for the sampling and the same type of collector – sorbent tube, filter, or impinger. The inlet side of the sampling train is then connected to a calibration standard.

The simplest example of a calibration standard used by industrial hygienists is an **inverted buret**, which resembles an upside-down graduated cylin-

Box 5-1 ■ Determining a Flow Rate

An example calculation for determining a flow rate follows. Imagine the sampling train in Figure 5-16 has been connected to an inverted buret for calibration. The industrial hygienist timed the movement of a soap bubble from 500 to 0 ml, with the following results:

Volume timed: 500 ml
Time #1: 13.42 seconds
Time #2: 13.50 seconds
Time #3: 13.49 seconds

The average time to move 500 ml of air is 13.47 seconds calculated by adding time intervals #1, 2, and 3, and dividing the sum by 3. To determine the flow rate, we must convert ml/seconds to liters/minute, or lpm. To do this, conversion factors, or equivalencies, are used as follows:

$$\frac{500 \text{ ml}}{13.47 \text{ sec}} \times \frac{1 \text{ liter}}{1{,}000 \text{ ml}} \times \frac{60 \text{ seconds}}{1 \text{ minute}} = 2.22 \text{ lpm}$$

The calculated flow rate for the sampling train is 2.22 lpm.

der. Burets used for calibrating sampling pumps are typically marked with lines indicating various volumes – say, for a 1,000 milliliter (ml) or 1 liter buret, a line at zero, and then perhaps a line every 50 ml. The top of a buret used for calibration has a small glass fitting to which the inlet end of the sampling train is connected. To time the movement of the air, a soap bubble is generated inside the buret by momentarily submerging the bottom end of the buret in a weak soap solution. As the bubble moves up into the buret, its movement from one volume mark to another is timed with a stopwatch. This process is repeated using the same volume marks as reference points until at least three consecutive measurements are within a second or two of each other; the times are then averaged. The volume of air that was moved is equal to the volume represented by the distance between the lines that were used in timing. For example, say the watch was started at the 500 ml mark and stopped at the 0 ml mark; the volume is 500 ml. Once the time interval for this is measured, a flow rate – commonly expressed as liters per minute (lpm) – can be calculated. A volume of 500 or 1,000 ml is commonly used since the marks are far enough apart for the industrial hygienist to accurately time the bubble; also, the numbers are relatively convenient to work with. Figure 5-16 shows an inverted buret used to calibrate an air sampling pump.

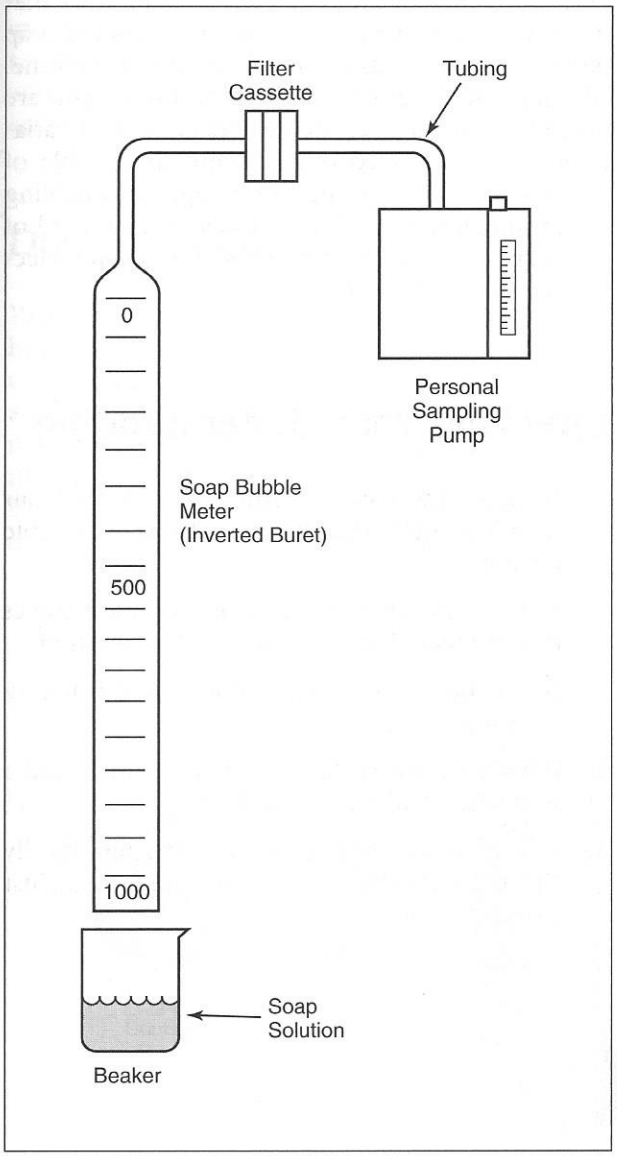

Figure 5-16: Calibration of the sampling train must be performed prior to the sampling event. The sampling train is assembled in the same configuration that will be used for sampling, with the inlet connected to the calibration device. This diagram illustrates a sampling train that is ready for calibration using a bubble meter, a primary calibration standard.

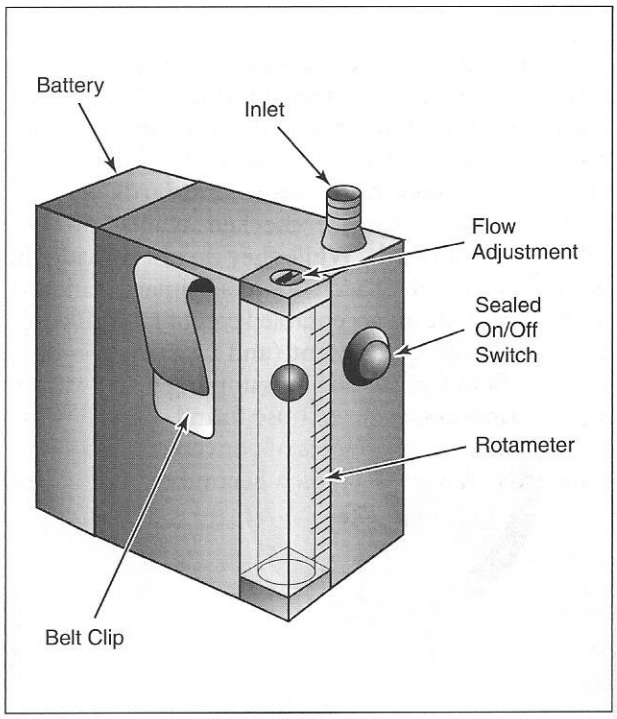

Figure 5-17: Some personal sampling pumps are equipped with a built-in rotameter. Rotameters – which are also available as free-standing devices – are secondary calibration standards. Once the rotameter has been calibrated against a primary standard, it can provide a convenient and accurate method for calibrations in the field.

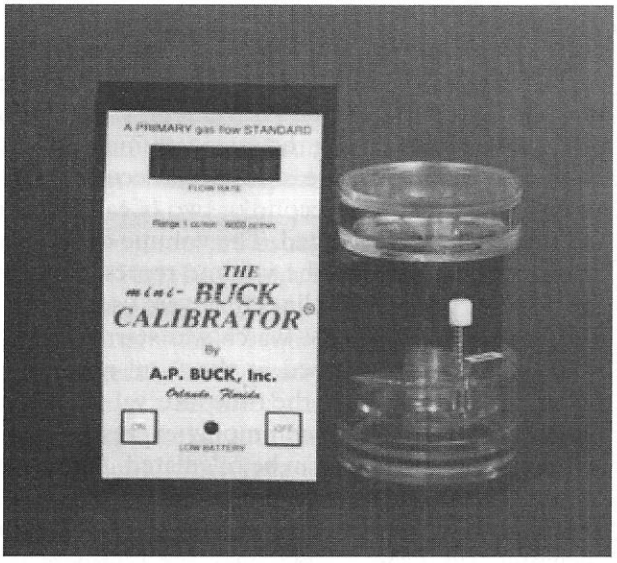

Figure 5-18: Electronic calibrators such as this one operate using the same principle as the bubble meter. They offer the advantage of being faster; also, most can be purchased with options such as computer software, printers, and capabilities for calibrating a wide range of flow rates.

Although the inverted buret is a simple device, it is a **primary calibration standard**. Primary calibration standards are based on direct measures of a reference value, such as the known volume of the buret. **Secondary calibration standards** are calibration devices that are checked against primary calibration standards. While they do not provide the same high degree of accuracy as a primary standard, they do provide an acceptable level of precision and are often more convenient (and practical) to carry into the field for use during sampling. Flow meters and **rotameters**, such as those found on some sampling pumps, are examples of convenient secondary standards. A rotameter is a secondary calibration standard that consists of a clear tube with a metal or plastic float; the position of the float on a graduated scale along the length of the rotameter indicates the flow rate. Secondary calibration standards must be periodically checked against a primary standard; OSHA's technical manual recommends an interval of six months. If the secondary standard is damaged, it should be recalibrated before it is used again.

While the inverted buret is simple to use, other more convenient and more portable devices have been developed, such as automatic calibrators that use electronic eyes to detect the passing of the soap bubble within a glass cylinder of known volume. Although the volumes used in these instruments are much less than a liter, the devices are in fact variations on the inverted buret. Some are capable of being connected to printers or computers, enabling the production of a printed or electronic record of the calibration test. Figure 5-18 shows some electronic calibration devices.

Checking Your Understanding

1. What are the statistical criteria that NIOSH air sampling methods must meet to be acceptable for use?
2. List at least seven items or information topics that are included in an air sampling method.
3. Name three reasons why calibration of sampling pumps is necessary.
4. What is the difference between a primary and a secondary calibration standard?
5. Why do you think it is important to periodically check a secondary calibration standard against a primary one?

5-6 Laboratory Analytical Techniques

The analysis of the air sample in the laboratory is described in detail in the sampling method. Instruction is provided for preparation, setup, and calibration of laboratory instruments. The particular method of measurement will depend on the contaminant, or analyte, that is to be measured. As is the case with sampling methods, the analytical method that is used depends in part on the characteristics of the contaminant. This section will briefly address some of the methods used in the analysis of airborne contaminants.

Dusts and Fibers

Particulate contaminants such as dusts and fibers may be analyzed using gravimetric methods, as described earlier. The evaluation of dusts is the most common application of gravimetric analysis. Airborne dusts may also be evaluated in terms of particle size, while fibrous contaminants, such as asbestos, are counted. Both particle sizing and fiber counting techniques involve the use of a microscope fitted with an optical insert, called a **graticule** or **reticle** (see Figure 5-8). The graticule may contain grid lines, circles, rectangles, or other patterns, which are of a known size and are precisely spaced at known distances, thus serving as reference. Because the graticule is part of the optics, it is superimposed over the field of view of the observed slide. This allows the analyst, called a **microscopist**, to use the grid marks to estimate particle sizes, or count the particles or fibers that fall within a specific area of the superimposed image of the grid. Analysts performing these types of evaluations receive specialized training, and take part in quality control programs to provide a periodic check on their application of technique, since a certain level of proficiency is necessary to ensure consistent, accurate results.

Gas and Vapor Analysis

Gases and vapors may be collected on sorbent tubes, filters, or in solutions. The method used for analysis of such samples depends in part on the collection

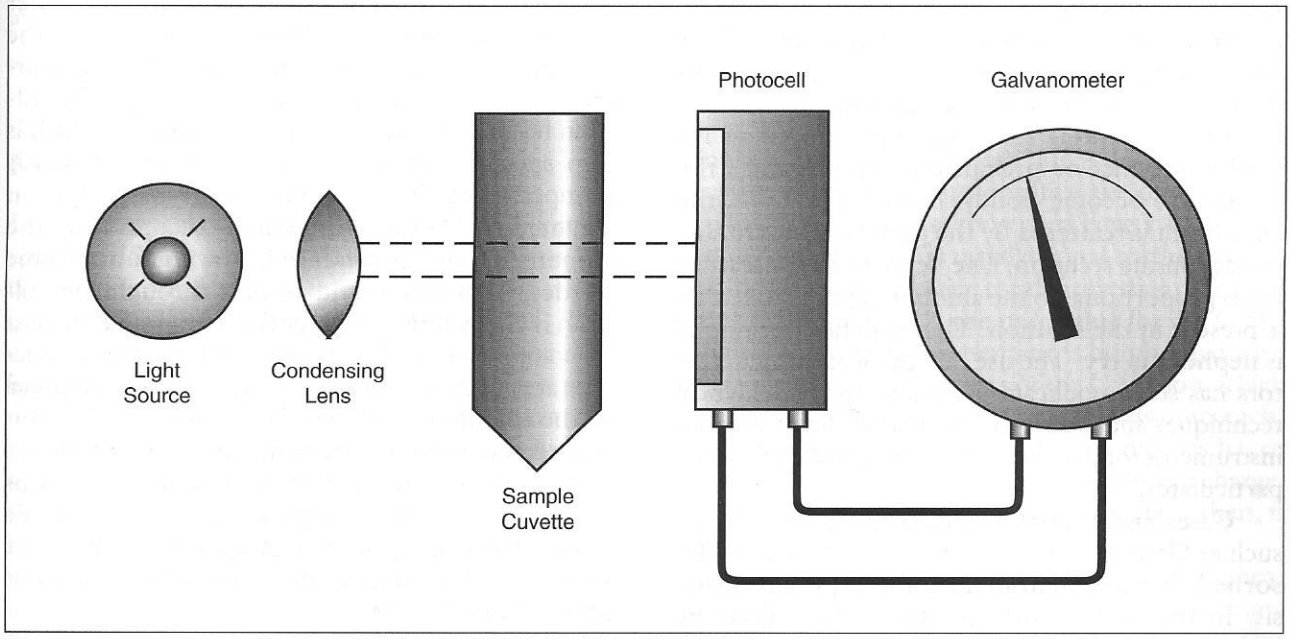

Figure 5-19: Spectrophotometers are used in analysis of some industrial hygiene samples. This method measures the amount of light transmitted through a solution, which is proportional to the degree to which a chemical reaction has taken place between the contaminant and the solution reagent.

medium as well as on the chemical properties of the contaminant.

Gases and vapors that are collected by dissolution or absorption in a solution may be analyzed by a **titration** method involving the use of chemical reagents that are added to the absorbing solution. The reagent is added gradually, in measured amounts, until the endpoint of a reaction is reached. The endpoint may be indicated by a change in the color of the solution; for instance, the solution may remain colorless as more reagent is added, and then change to a bright pink color. The intensity of the color, which is proportional to the concentration, is then measured in an instrument called a **spectrophotometer**. Spectrophotometers contain a light source on one side, and a light detector on the opposite side. The solution to be tested is placed into a small test tube called a **cuvette**, which is placed into the test cell in the spectrophotometer, between the light source and the detector. The amount of light that is absorbed by the solution is proportional to the concentration of the compound created by the reaction between the contaminant and the reagent present in the solution. The instrument is first set at zero, using unreacted absorbing solution; this provides a reference value for the amount of light that would pass through a solution containing no contaminant. The solution resulting from the titration is then tested. The reading is expressed in terms of **absorbance**, which is the amount of light absorbed in the solution, or, conversely, as the **percent transmittance**, which is the amount of light that passes through the solution, as compared to the solution used to zero the instrument.

Some reactions result in formation of an insoluble product or **precipitate**, which causes the solution to become cloudy. In such situations, the light beam is scattered by the particles that are suspended in the solution. The degree of light scattering is proportional to the amount of precipitate that is present in the solution. This analytical technique is **nephelometry**. The use of light-scattering detectors has some applications in laboratory analytical techniques and is also widely used in direct-reading instruments for detection of dusts and other airborne particulates.

Gases and vapors collected on solid sorbents such as filters and silica gel or charcoal must be **desorbed**, or removed from the sorbent, prior to analysis. In the case of sorbent tubes, this is done by passing a solvent through the tube to "wash" the contaminant off the solid. Carbon disulfide is one of the most common desorbing solvents; heated air is also sometimes used as a desorbing mechanism. Filters used as sorbents may be treated with a desorbing solvent, or the entire filter (and support pad) may be dissolved, or **digested**, in an acid solution, as is the case in analysis of some metals. The entire solution is then analyzed.

The instruments used to analyze industrial hygiene samples collected on solid sorbents employ a variety of principles. Instruments and detectors used to identify specific compounds utilize the chemical properties of the contaminant. Some of the analytical instruments used in the laboratory are described briefly in the next section.

Gas Chromatography

A **gas chromatograph**, or **GC**, operates something like a still. The contaminant is desorbed and then injected into the GC, where it passes through a long tube or column containing a solid sorbent. The column acts like a distillation tower, allowing some molecules to pass through more quickly than others, separating the compounds in the sample. Sorbents used in the column of a GC vary, depending on the analytes, and include materials such as silica gel. The particular sorbent used in the column is specified in the analytical method, along with other variables such as the length of the column and the temperature at which the column is maintained during analysis. The sample is moved through the column by an inert **carrier gas**, the identity of which is also specified in the method. The carrier gas is pumped through the column at the rate specified in the method. As each compound emerges from the column, a graph is produced. The amount of time needed for a compound to pass through the column is characteristic of a specific compound or class of compounds and is used to identify the analyte. The area under the peak of the graph is proportional to the amount of material. The identity of the compound is determined by comparing the sample results to those produced by known concentrations of specific compounds. Figure 5-20 shows the basic components of a gas chromatograph. Figure 5-21 shows a sample output from a GC analysis used to identify an unknown.

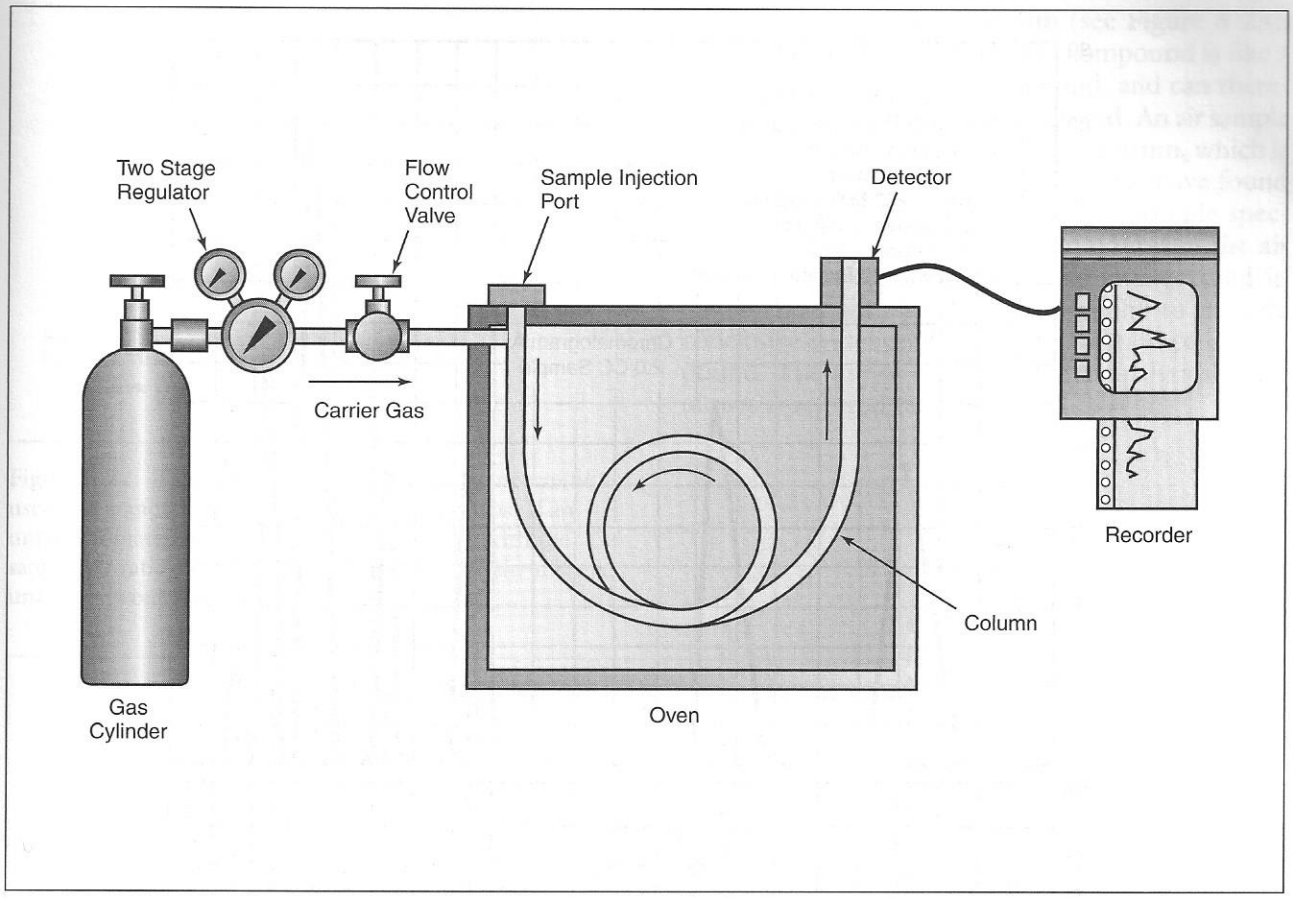

Figure 5-20: Gas chromatography is used for analysis of many gas and vapor contaminants. This analytical technique separates the molecular components of the sample in the same way as a still: each component moves through the column at a different rate. The time necessary for passage through the column is indicative of the compounds present in the sample.

Mass Spectrometry

In a **mass spectrometer**, also referred to as a **mass spec** or **MS**, the sample is desorbed from the collection medium and injected into the instrument, where it is bombarded with a beam of electrons. This causes the molecules in the sample to become **ionized**. Each charged particle, or **ion**, that is produced, has a specific mass. The relationship between the mass of an ion and its charge is unique and is expressed as a ratio of mass (m) to charge (e), or **m/e**. When the sample is bombarded with electrons, a number of ions may be produced, each with its own m/e value. The intensity of each m/e value is proportionate to the amount of the ion that is produced. The m/e value that has the highest intensity is called the base peak, and is assigned a value of 100; all the other m/e values are compared to the base peak. Because most ions have a +1 charge, the m/e ratio value is usually equal to the mass of the ion, making it easier to identify them. For example, in Figure 5-22, the m/e value for the $C_2H_5^+$ ion produced when neopentane is bombarded with electrons is equal to the mass of the $C_2H_5^+$ ion, which is equal to 24 (2 carbon atoms at 12 mass units each) plus 5 (5 hydrogen atoms at 1 mass unit each), or 24 + 5 = 29. The mass value is divided by the charge, 1, or 29/1 = 29. The m/e value for $C_2H_5^+$, then, is 29.

The MS is equipped with a detector that measures the intensity of each m/e value, producing a plot that shows the relative intensities of each. This

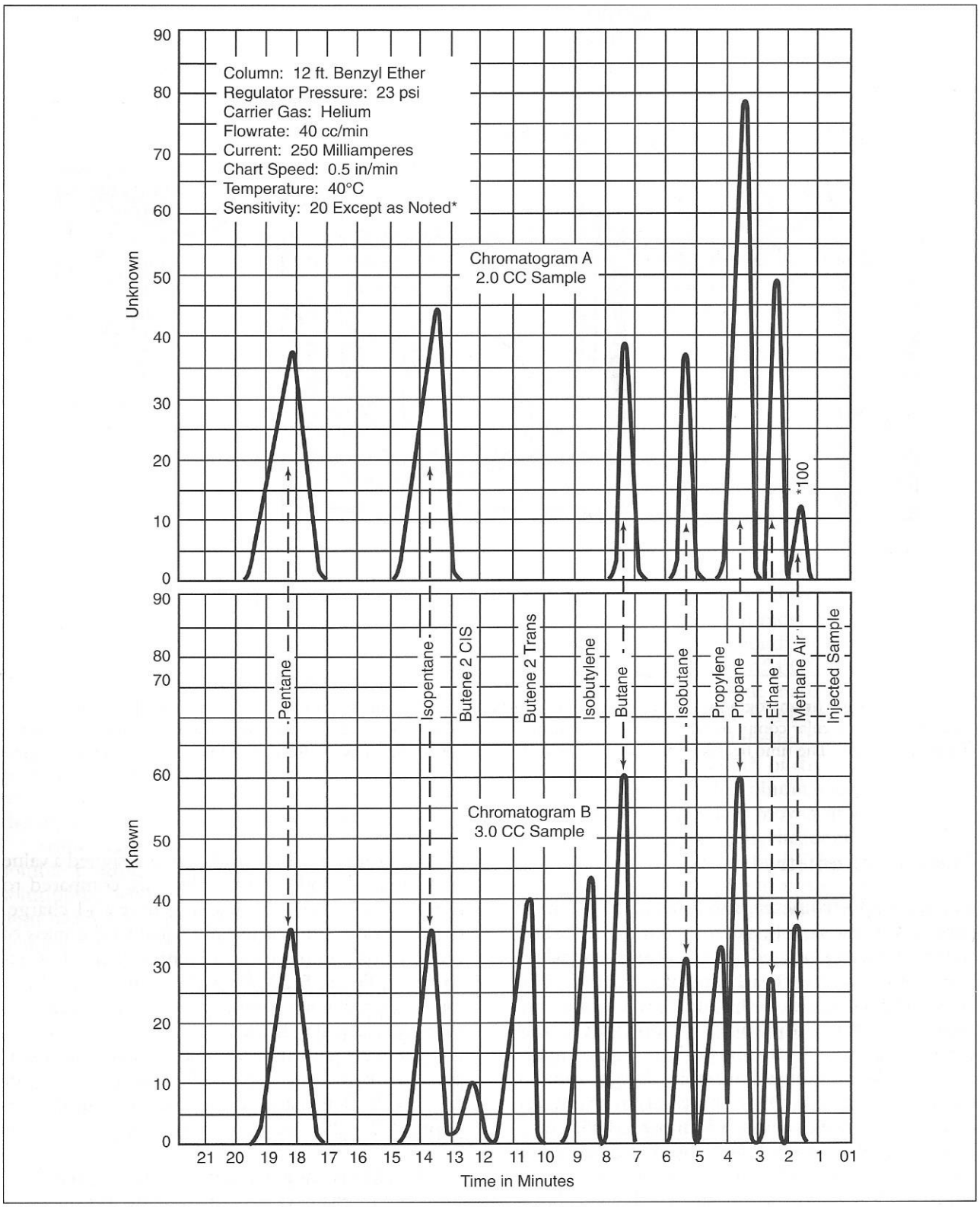

Figure 5-21: The output of a gas chromatograph shows how long it took the compound to move through the column; the area under the peak in the graph is proportional to the amount present. The output produced by analysis of an unknown can be compared to the output produced by analysis of a sample of known composition. In this example, the unknown compound contains pentane, isopentane, butane, isobutane, propane, ethane, and methane.

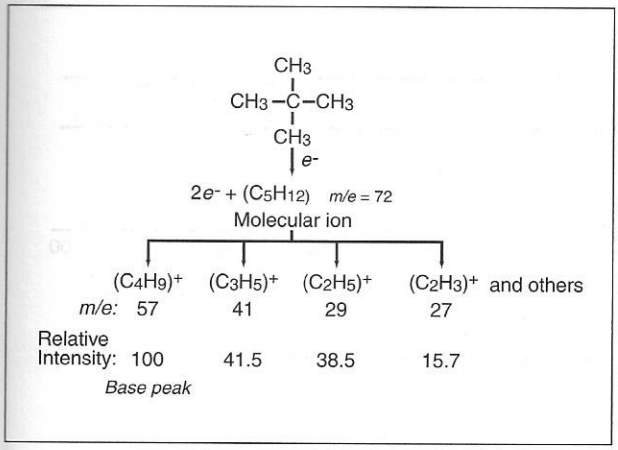

Figure 5-22: This mass spectrum for neopentane can be used as a standard to compare against unknowns. If an unknown material produced a mass spectrum with the same m/e ratios, it would be considered a match, and the unknown would be identified as neopentane.

plot is called a **mass spectrum** (see Figure 5-23). The mass spectrum of a specific compound is like a fingerprint, unique to a compound, and can therefore be used to identify the compound. An air sample analyzed by MS produces a mass spectrum, which is compared to a reference set. When we have found the spectrum that is a match for the sample spectrum, we have identified the compound in the air sample. Mass spectrometry is sometimes used in conjunction with gas chromatography to provide conclusive evidence of the identity of a sampled compound. The use of these combined analytical techniques is referred to as **GC/MS**.

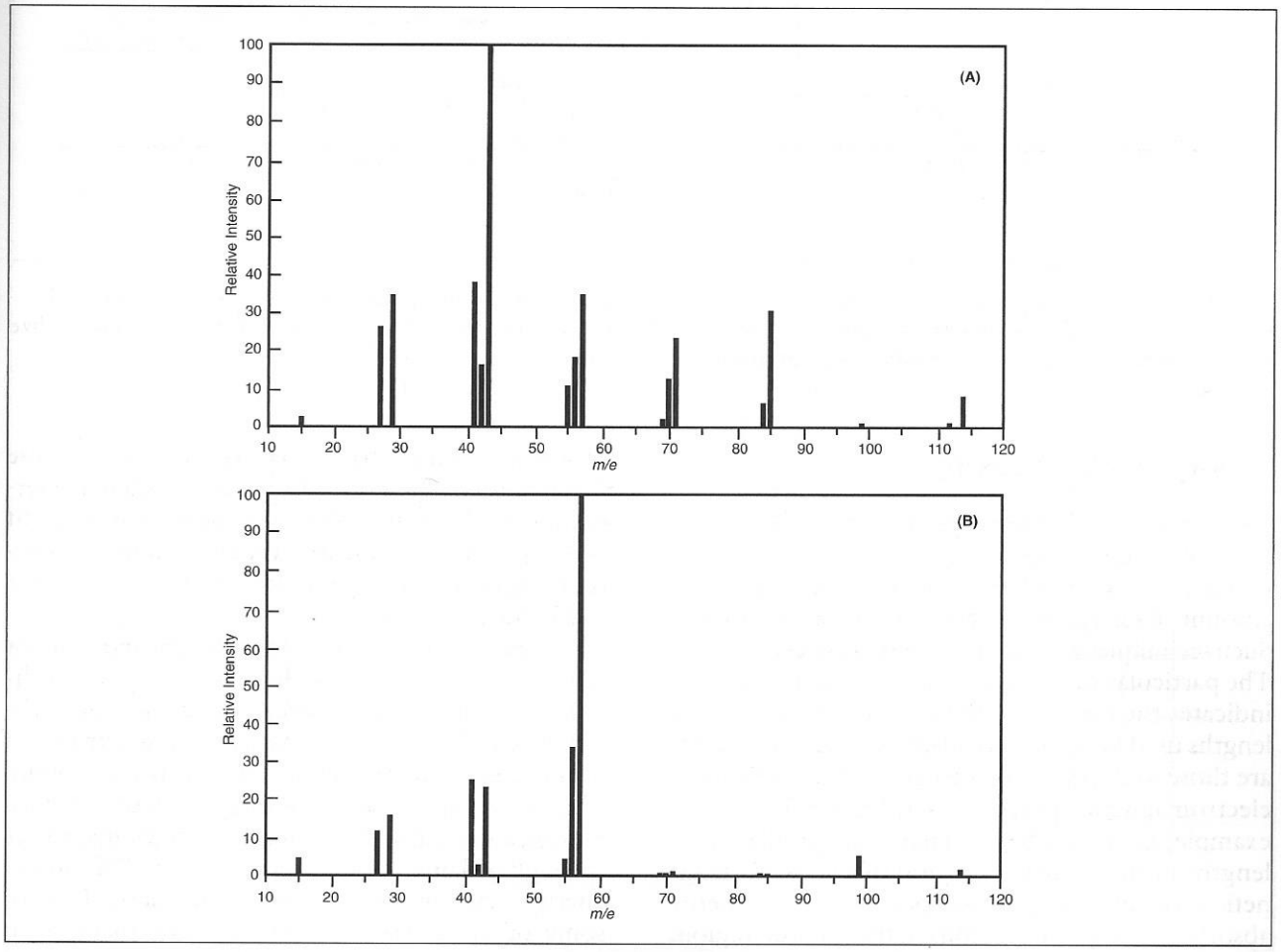

Figure 5-23: Similar to analysis by gas chromatography, the output produced by the mass spectrometer must be compared against a known or reference output to determine the compound that is present. These mass spectra are for n-octane (A) and 2,2,4-trimethylpentane (B).

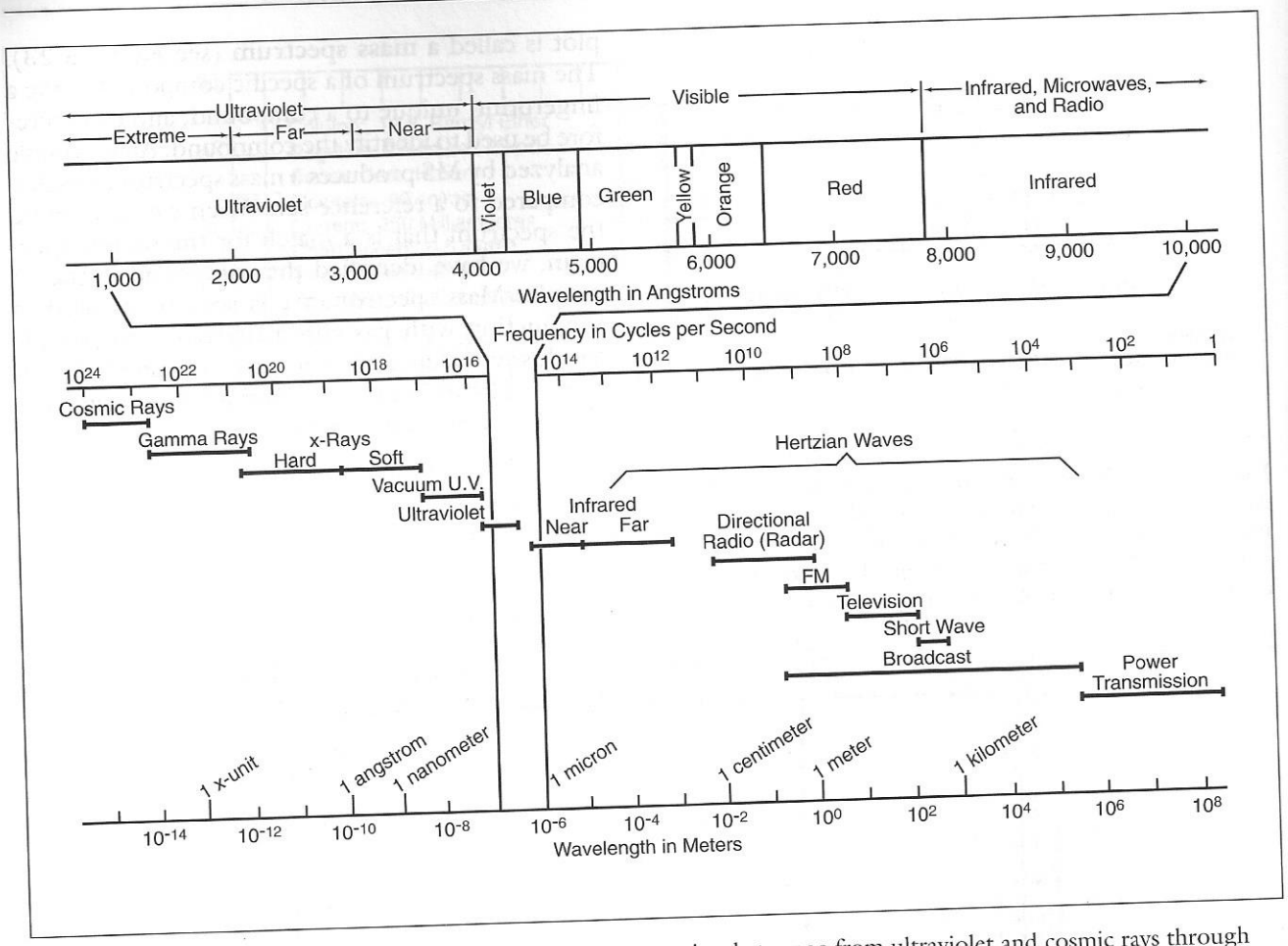

Figure 5-24: The electromagnetic spectrum includes wave energies that range from ultraviolet and cosmic rays through visible light, infrared, microwaves, and power transmission. Analytical techniques for identifying organic compounds utilize the absorbance of specific wavelengths in the ultraviolet and infrared regions.

Absorption Spectroscopy

Ultraviolet and Infrared Spectrometry – These two analytical techniques, as well as atomic absorption (described below), involve the measurement of the amount of energy that is absorbed by a compound. Such techniques are called **absorption spectroscopy**. The particular wavelength where energy is absorbed indicates the identity of the compound. The wavelengths used for analysis of many organic compounds are those in the ultraviolet to infrared regions of the electromagnetic spectrum (see Figure 5-24). For example, benzene absorbs energy at specific wavelengths in the ultraviolet region of the electromagnetic spectrum. Organic compounds exhibit energy absorbance at specific regions of the infrared region, depending on the types of chemical bonds that are present in the molecules. Ultraviolet (UV) and infrared (IR) spectrometry techniques produce a plot or spectrum similar to the mass spectrometer. These spectra are then compared against spectra in a reference set to determine which compounds are present in the air sample. Some ultraviolet and infrared spectra for various compounds are illustrated in Figures 5-25 and 5-26.

Atomic Absorption – **Atomic absorption**, or **AA**, is similar to some of the other analytical techniques we have already discussed in that the technique relies on a specific pattern, or spectrum, of energy absorption to identify the analyte compound. The AA is used most commonly to detect metals. During atomic absorption analysis, the sample passes through a flame or other heat source. This added energy results in an increase of the energy level of some of the electrons, while others remain in an unexcited, stable energy condition called **ground state**. Because most of the electrons remain in a ground state, it is better from an analytical stand-

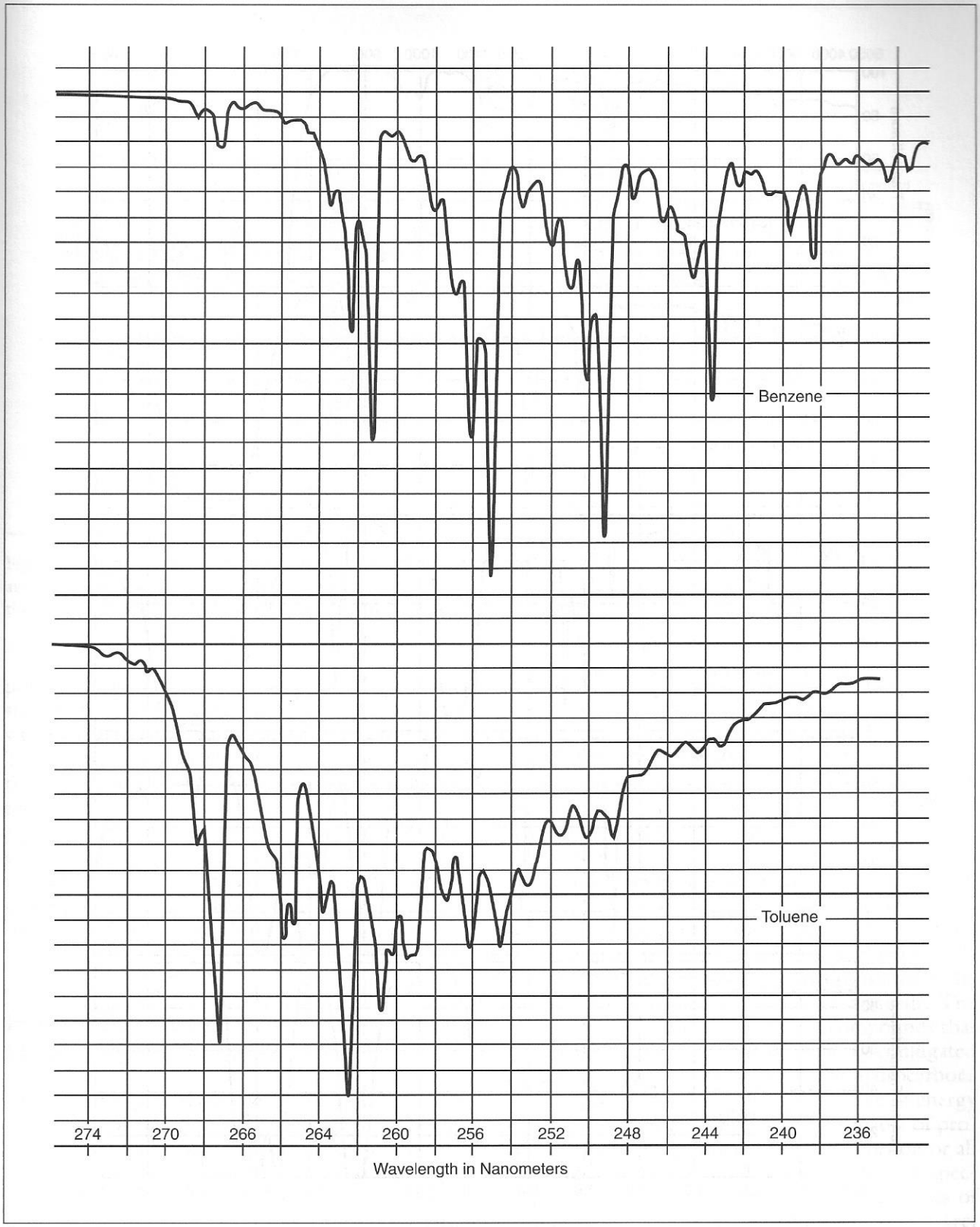

Figure 5-25: The absorbance of energy at specific wavelengths is a characteristic of organic compounds. These patterns of absorbance are like fingerprints, in the sense that they allow the specific compound to be identified. Shown here are the absorbance spectra of wavelengths in the ultraviolet region for benzene and toluene.

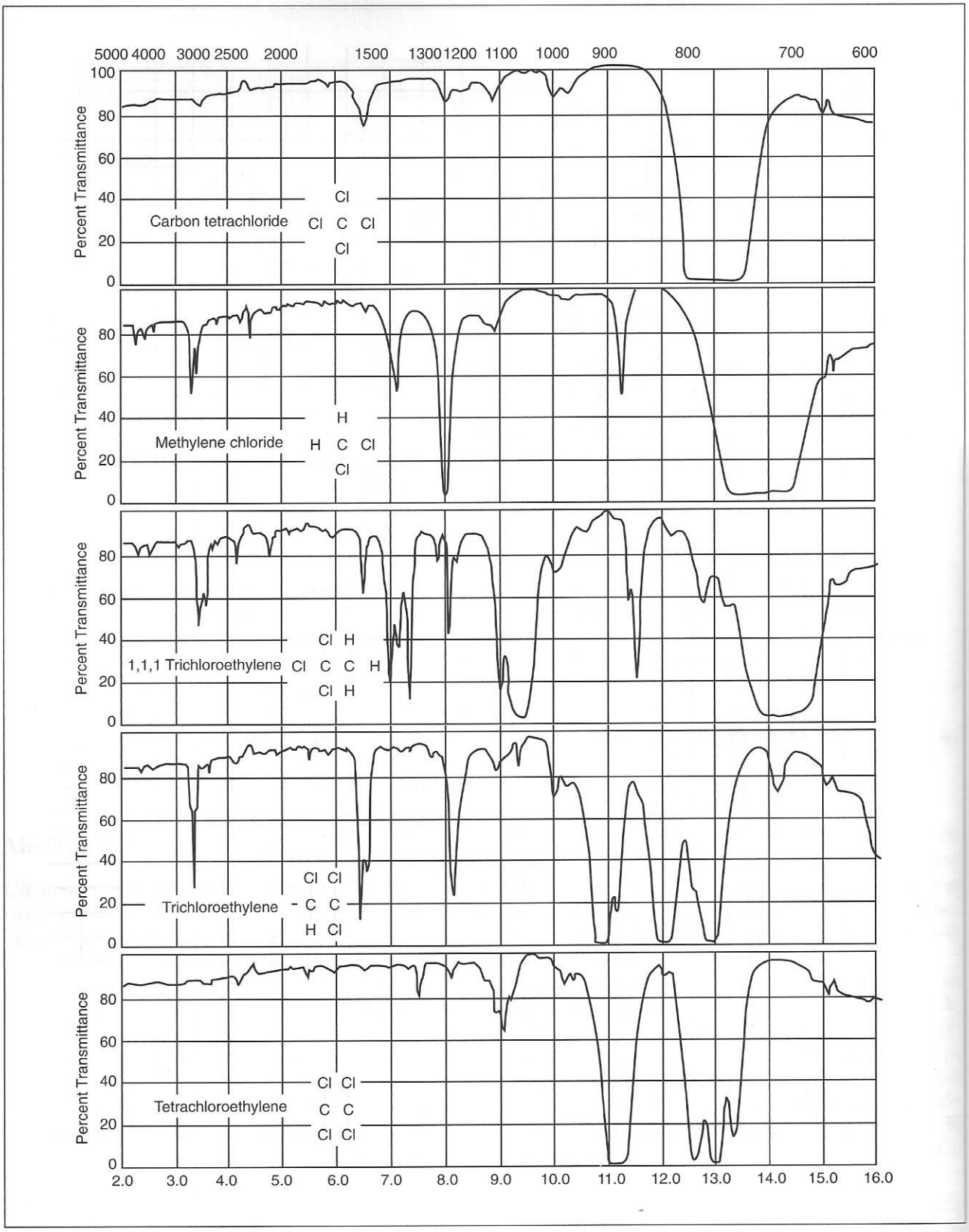

Figure 5-26: Chlorinated hydrocarbons tend to absorb energy in the infrared region. Shown here are IR spectra for five common industrial solvents (wavelength in micrometers).

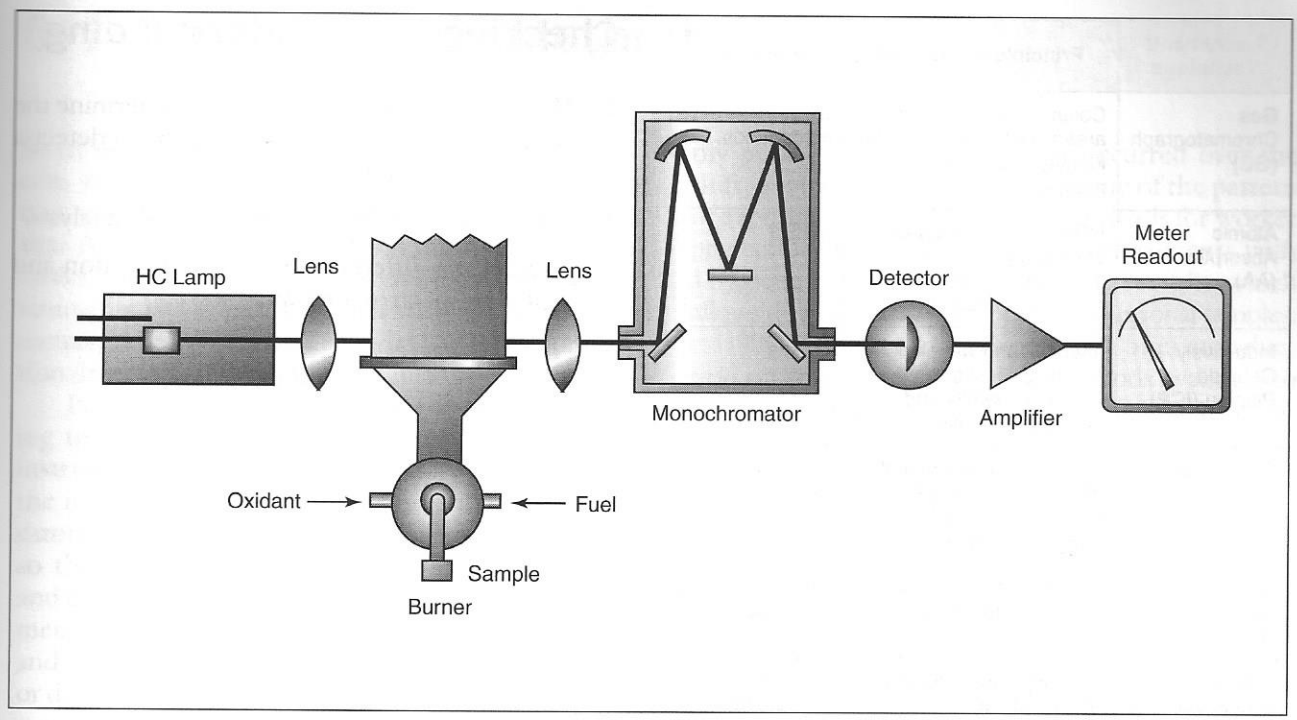

Figure 5-27: In atomic absorption analysis (AA) electrons in the sample absorb energy when passing through a cloud of atomic vapor. The wavelength of the energy absorbed by these electrons indicates the particular element that is present in the sample. This type of analysis is commonly used for metals.

point to take measurements on these. In an AA instrument, these unexcited electrons absorb energy when they pass through a cloud of atomic vapor. The AA detector indicates the wavelengths at which the strongest absorption of energy is occurring by the ground-state electrons. The absorption of energy at a particular wavelength indicates the presence of a specific element. The degree of absorption is proportional to the amount of the element that is present in the sample. Figure 5-27 shows the basic structure of the atomic absorption spectrometer.

Inductively Coupled Plasma and Fluorescence Spectrometry

An **inductively coupled plasma** or **ICP** analysis is an example of **emission spectroscopy**. Like absorption spectroscopy, emission spectroscopy utilizes the ability of electrons to absorb energy. In contrast to absorption spectroscopy, however, emission spectroscopy measures the energy loss of the excited electrons as they return to the ground state. As in the case with other methods of analysis, the spectrum of emissions is specific to the analyte, and the intensity of the emissions is proportional to the amount that is present. This analytical technique is useful for metal scans, where a number of elements can be analyzed from the same sample; for example, an air sample taken during welding might be analyzed to determine which of a number of metals are present in the fume.

Fluorescence spectrometry is similar to ICP analysis in that the intensity and wavelength of the energy that is emitted from excited electrons is used to indicate the presence of certain compounds. Unlike ICP, fluorescence spectroscopy is used in the analysis of organic compounds, not metals. The method is most useful for organic compounds that contain aromatic rings, as in benzene, or conjugated double bonds, such as the aromatic hydrocarbons present in coal tar emissions. The source of energy used to excite the sample is a lamp capable of producing light energy through either a portion or all of the ultraviolet region of the electromagnetic spectrum. Lamp selection depends on the analytes of interest; common lamps include the xenon-arc, tungsten, and mercury lamps, each of which produces light in a specific range of the spectrum.