CHAPTER 4

Vapor Generation Techniques

CWAs are manufactured and stored by government facilities for basically two reasons. Stored CWAs serve as an effective deterrent to “first use” of CWAs by others. Secondly, manufacture of these agents permits necessary research of agent characteristics, and provides a means for research of detection techniques and antidote developments. Early detection and warning of even minute amounts of CWAs and/or TICs in the air are essential to minimize casualties.

To develop effective detection devices, methods to evaluate their effectiveness are prerequisites. Open-air dissemination of toxic compounds for testing purposes has been banned in the United States for decades. Researchers resort to diverse methodologies and techniques to create test atmospheres/environments. Much effort has been focused on simulating real-world scenarios in the laboratory.

As mentioned in Chapter 3, sampling is one of the most difficult steps in testing the capabilities of chemical and biological agent detectors. Methods to produce and deliver a controlled stream of air with a precisely controlled concentration of the target compound are crucial for evaluating detector performance. Problems arise in ensuring that the sample presented to the detector during the evaluation represents a realistic scenario. Also, physical property measurement studies, such as vapor pressure, adsorption equilibrium, and toxicity are required to assess contamination spread to derive physical hazard assessments. All of these studies rely on precisely generated streams of air in which the concentration of target chemicals is stable. In this chapter, we discuss common airstream generation techniques used by researchers.

Safety precautions are the utmost importance when working with highly toxic chemicals. Mishandling can cause harm not only to laboratory workers but also others in the vicinity. Chemical behavior and all safe-handling procedures must be understood before attempting to generate these toxic vapors. The material safety data sheet (MSDS) (see Appendix A for example) must be understood, and a specific standing operation procedure (SOP) should be developed and followed to minimize the risk of accidental exposure to the toxic components. The SOP should detail all necessary precautions and operational instructions. Potential hazards are spelled out. The SOP is especially critical when the application involves the use of lethal chemical agents or other highly toxic materials. A single mistake could cause catastrophic fallout, including injury or death to operators and others.

The SOP is generally prepared by the principal investigator who lists all conceivable precautions throughout the process from beginning to the end. The organization safety office must review and assess the risks. A dry run (operation minus the toxic material) through the steps is performed before approval is granted. During the dry run, the procedures are observed by a panel of knowledgeable individuals who provide comments and critiques.

Before an operation begins, operators must read and sign the SOP indicating that all steps have been understood. Pre- and postoperation checklists ensure that the apparatus, protective equipment, engineering controls, and other items involved are in proper order. The checklists will also serve as a reminder to the operator of precautions.

Operations involving the use of CWAs are considered as surety operations. All surety operations require a buddy system, that is, two people who are knowledgeable and qualified for working with surety materials must be present before and during the operation. These individuals must undergo an extensive clearance process called the Chemical Personnel Reliability Program (CPRP) to guarantee their integrity and proper training for working with controlled materials. In the event of mishap, a buddy would presumably be available to rescue the other person or secure help.

An abbreviated SOP sample appears in Appendix B. It shows the necessary contents of a typical SOP. Safe handling of toxic materials cannot be overemphasized.

4.1 GAS LAW AND GAS CONCENTRATION

To fully understand the reasons behind vapor generation methods, reference to a few basic laws of physics is necessary. Physical, chemical, and gas laws dictate the behavior of a gas under different conditions. For purposes of simplicity, under normal circumstances, a gas generated in the laboratory is assumed to behave similarly to the ideal gas. We briefly review the Ideal Gas Law for its applicability to various generation techniques, and provide a method for vapor concentration calculation.

4.1.1 Mole, Molar Weight, Molar Volume, and Mole Number

Three important concepts used in the following discussion are mole, molar weight, and mole number. A “mole” of a given substance contains 6.02×10^{23} molecules, commonly known as Avogadro’s number. For example, 1 mole of nitrogen gas contains 6.02×10^{23} nitrogen molecules. Similarly, a mole of water contains 6.02×10^{23} water (H_2O) molecules.

Molar weight is the weight of 1 mole of a substance that is equivalent to the atomic weight, molecular weight, or formula weight in grams. For example, the molecular weight of ammonia is 17 atomic mass units (amu). Therefore, its molar weight is 17 g, which contains 6.02×10^{23} molecules. According to the Ideal Gas Law, 1 mole of a gas, at 0°C and standard sea-level atmospheric pressure of 760 mm of mercury (Hg), occupies 22.4 liters of space.

The mole number is the number of moles that a specific amount of a substance represents. For a gas, it can be calculated based on its weight or the volume it occupies. For example, 34 g of ammonia is equal to 2 moles (34 g/17 g) of ammonia; therefore, its mole number is 2. At 0°C and standard sea-level atmospheric pressure of 760 mm of mercury (Hg), these 34 g of ammonia with a mole number of 2 would occupy a volume of (2 × 22.4) 44.8 liters.

4.1.2 Ideal Gas Law

The Ideal Gas Law, also known as Boyle's Law, characterizes the behavior of an ideal gas. An ideal gas is a hypothetical gas with negligible molecular size and intermolecular forces. Boyle's Law states that for an ideal gas, the relationship among its pressure (P), volume (V), and absolute temperature (T in Kelvin) can be expressed as:

$$PV = nRT \tag{4.1}$$

where n is the number of moles of the gas, and R is the molar gas constant (8.3143 joules per Kelvin per mole). For n moles of an ideal gas, Equation 4.1 can be rearranged as follows:

$$nR = \frac{PV}{T} \tag{4.2}$$

Equation 4.2 states that for a certain amount (n moles) of an ideal gas, the relationship among P, V, and T remains constant under various temperature and pressure conditions. Therefore,

$$nR = \frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \tag{4.3}$$

Equation 4.3 can be expressed simply as

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \tag{4.4}$$

Example 4.1

As stated above, 1 mole of an ideal gas at 0°C and 1 atm (760 mmHg) will occupy a volume of 22.4 l. At room temperature (25°C, or 298 K) and 1 atm, the volume

(V_1 in the following equation) for 1 mole of ideal gas can be calculated using Equation (4.4) as 24.45 l:

$$V_1 = \frac{T_1}{P_1} \times \frac{P_2 V_2}{T_2} = \frac{298(\mathrm{K})}{760(\mathrm{mmHg})} \times \frac{760(\mathrm{mmHg}) * 22.4(\mathrm{l})}{273(\mathrm{K})} = 24.45(\mathrm{l})$$

The volume of a vapor is directly dependent on temperature, but is inversely dependent on external pressure. In other words, a gas will expand and occupy a larger volume as the temperature is increased or when the external pressure is reduced.

4.1.3 Vapor Concentration

The concentration of a vapor is generally expressed as either volume concentration of parts per billion (ppb) or parts per million (ppm), or as weight concentration such as milligrams per cubic meter. At concentrations higher than 0.1% (>0.1% v/v), volume percentage is normally used instead of ppb or ppm. In this book, except those specially noted, volume concentrations are expressed as ppm, ppb, or percentage (%) concentration. For example, the concentration of ammonia in a gas mixture containing 1 μl (microliter) of ammonia in 1 cubic meter ($1\ \mathrm{m}^3 = 10^9\ \mu\mathrm{l}$) of the gas mixture is $1\ \mu\mathrm{l}/10^9\ \mu\mathrm{l}$ or 1 ppb. If the gas mixture contains 1 ml of ammonia, the concentration is 1 ppm. One liter of ammonia gas in 1-m^3 gas mixture will produce a concentration of 1000 ppm that is equivalent to a 0.1% concentration.

Concentration can also be expressed as weight-per-volume (w/v) concentration, such as milligrams per cubic meter. The weight-per-volume concentration expresses the actual amount of the substance contained in a fixed volume. The expression is applicable for any pressure and temperature condition. The weight-per-volume concentration and volume concentration can be converted by applying the gas law and mole volume constant explained earlier. Appearing below is an example that illustrates the relationship between volume concentration and weight concentration.

Example 4.2

Assume 1 liter of a 1% ammonia gas mixture. What are the equivalent weight concentrations (in milligrams per cubic meter) at 0°C and 25°C? First, we determine the equivalent volume of ammonia in a liter of the 1% ammonia mixture that is equivalent to 0.01 l. The molar volumes at 0°C and 25°C are 22.4 l and 24.45 l, respectively, as discussed earlier. The mole numbers of ammonia in this gas mixture at the two temperatures can be calculated as follows:

$$n = \frac{V}{MV}$$

where MV is the molar volume at 0°C (22.4 l) and 25°C (24.45 l).

Table 4.1 Calculated Equivalents of 1 Liter of 1% NH_3 (Results for Example 4.2)

Temperature (°C)	Mole Number	Weight (g)	Concentration (mg/l)	Concentration (mg/m^3)
0	0.000446	0.007589	7.589	7589
25	0.000409	0.006953	6.953	6953

Given that the molar weight of ammonia is 17 g, the weight of ammonia under the two conditions is calculated as

$$W = n \times MW = 17n(g)$$

By converting the weight to milligrams and the volume to cubic meters, the weight concentrations in milligrams per cubic meter are obtained. Results are listed in Table 4.1.

The above example shows that even though the stated volume concentrations are the same at different temperatures, the amounts of substance (weight) contained in fixed-volume concentration gas mixtures are different.

Similarly, weight concentration (milligrams per cubic meter) can be converted to volume concentration. To do this, the above calculation is reversed. The weight is converted into a molar number first, and then, based on the given temperature and pressure, its volume and volume concentration are calculated. Table 4.2 lists the conversion factors for common CWAs and high-hazard TICs. The factors can be used to easily calculate the weight-volume concentration from volume concentration. For example, suppose that the concentration of generated GA vapor is 0.02 ppm at 25°C, the weight-volume concentration is calculated at equal to 1.33 mg/m^3 by knowing that 1 ppm of GA at 25°C is equal to 6.63 mg/m^3:

$$C = 0.02(ppm) \times 6.63(\frac{mg/m^3}{ppm}) = 1.33(mg/m^3)$$

4.2 VAPOR GENERATION

A chemical vapor generation system consists of the vapor source and volume dilution through a mixing device. The controlled vapor from the vapor source is introduced into the dilution flow and mixing device to achieve the desired concentration. The process is very simple. Precise control of various flow blends and understanding pertinent basic physical chemical laws determine the suitability of a given dissemination technique.

Several vapor generation methods use direct contact of the liquid with a carrier gas stream. These include sparging (the carrier gas bubbles through the liquid); syringe injection of the liquid material directly into a carrier gas-flow stream; and head-space vapor saturation. Solid-state vapor generation exploits the use of vapors

Table 4.2 Conversion Factors for CWAs and Selected TICs at Three Temperatures

Chemicals	MW (amu)	Conversion Factor at Selected Temperature ([mg/m^3]/ppm) 0°C	25°C	40°C
GA	162.13	7.24	6.63	6.31
GB	140.10	6.25	5.73	5.46
GD	182.12	8.13	7.45	7.09
GF	180.2	8.04	7.37	7.02
VX	267.38	11.94	10.94	10.41
HD	159.08	7.10	6.51	6.19
HN-1	170.08	7.59	6.96	6.62
HN-2	156.07	6.97	6.38	6.08
HN-3	204.54	9.13	8.37	7.96
L	207.35	9.26	8.48	8.07
AC	27.03	1.21	1.11	1.05
CK	61.48	2.74	2.51	2.39
CG	98.92	4.42	4.05	3.85
DP	197.85	8.83	8.09	7.70
Ammonia	17	0.76	0.70	0.66
Arsine	77.93	3.48	3.19	3.03
Boron trichloride	117.2	5.23	4.79	4.56
Boron trifluoride	67.8	3.03	2.77	2.64
Carbon disulfide	76.1	3.40	3.11	2.96
Chlorine	70.91	3.17	2.90	2.76
Diborane	27.7	1.24	1.13	1.08
Ethylene oxide	44.1	1.97	1.80	1.72
Fluorine	38.0	1.70	1.55	1.48
Formaldehyde	30	1.34	1.23	1.17
Hydrogen bromide	80.9	3.61	3.31	3.15
Hydrogen chloride	36.5	1.63	1.49	1.42
Hydrogen fluoride	20.0	0.89	0.82	0.78
Hydrogen sulfur	34.1	1.52	1.39	1.33
Nitric acid (fuming)	63.0	2.81	2.58	2.45
Phosphorus trichloride	137.4	6.13	5.62	5.35
Sulfur dioxide	64.1	2.86	2.62	2.50
Sulfuric acid	98.1	4.38	4.01	3.82
Tungsten hexafluoride	297.9	13.30	12.18	11.60

Note: Concentration in milligrams per cubic meter = concentration in parts per million × conversion factor.

preadsorbed onto high surface-area solids below saturation capacity in order to greatly reduce the equilibrium vapor pressure of liquids and thus permit direct generation of vapors at lower flows and concentrations. Similarly, liquid materials can be diluted, using a noninterfering solvent, to reduce substance's volatility to achieve similar results. Other "indirect" methods, where a barrier is introduced between the liquid and vapor such as permeation, diffusion, and effusion can also be employed. For chemicals with very low volatility, vapor generation may not produce the concentrations required to effectively evaluate a given detection device. Aerosol generation is an alternative technique. Aerosols can be generated using nebulizer spray or vapor condensation techniques. For some gaseous compounds, chemical reactions may be necessary if analytically prepared cylinders are not commercially available.

Agent concentration generated by various methods must be analyzed to verify and determine the reliability of each technique. Theoretically calculated concentrations can only be used as estimates of the generation process. They cannot substitute for actual concentrations because of the adsorption and absorption effects by generator plumbing and the efficiency to deliver the saturated vapor before dilution. Sample collection techniques and some pertinent analytical methodologies will be discussed. It should be noted that many analytical methodologies are currently used by laboratories and researchers for diverse chemicals. In this chapter we present techniques that have been successfully used for many years.

4.2.1 Vapor Generation Methods

Several methods to generate controlled vapor concentrations that are currently in use are briefly described in this section. Each vapor generation technique serves a specific purpose. The most important difference among these techniques is the range of the vapor concentration generated.

4.2.1.1 Evaporation Method

The most direct method of vapor generation is to pass all or part of a carrier stream through a liquid reservoir to produce the vapor concentration. Since the chemical continually evaporates into the carrier gas stream, vapor containing the chemical is constantly generated for the test. The vapor concentration in the resulting carrier stream depends on the vapor pressure of the liquid, and the efficiency of the carrier stream used for the sparger generator. This method has been used extensively to generate airstreams containing CWAs and simulants to characterize the destructive efficiency of low space-time catalytic oxidation reactors.

The evaporation method used for a liquid or solid chemical is based on the evaporation rate or volatility of the chemical. Concentration of the vapor generated with this method may be very high for highly volatile compounds. On the other hand, it may not produce sufficient vapor from low-volatility liquids or solids. To use this method, the suitable dilution gas, such as dry air or nitrogen, is introduced to a gas dispersion bottle containing the chemical to be tested. The gas that passes over or through the liquid will carry the substance vapor that is used as the source vapor for the vapor generation. Figure 4.1 shows an example of a type of gas dispersion bottle that is used to generate vapor with the evaporation method.

Vapor concentration depends on several factors such as the size of the dispersion bottle, the temperature of the liquid, and the carrier gas flow rate. It can be expected that the carrier gas at a higher flow rate may not be vapor saturated at the outlet since it is constantly passing through the liquid without sufficient residence time to reach liquid — vapor equilibrium. Increasing the volume above the liquid or decreasing the flow rate of the dilution gas prolongs residence time and increases the saturation level of the generated vapor at the outlet. If equilibrium can be established,

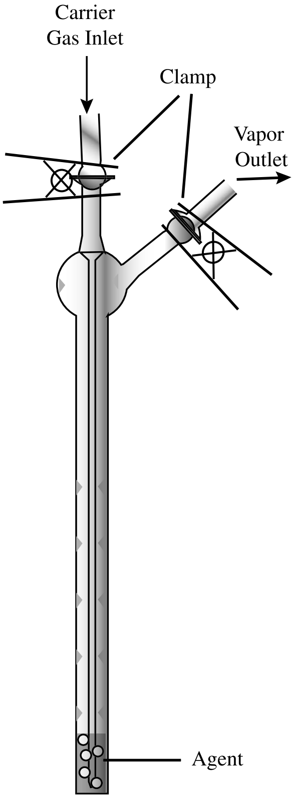

Figure 4.1 Example of gas dispersion bottle.

the concentration of the substance in the carrier gas after it passes through the liquid is estimated as follows:

$$C(\text{ppm}) = \frac{VP(\text{mmHg})}{760(\text{mmHg})} \tag{4.5}$$

where VP is the substance's vapor pressure at a certain temperature. This estimation is based on the assumption that the vapor is saturated with the target chemical. In general, this equation overestimates vapor concentration. The carrier gas may not be saturated with the chemical vapor at high carrier flows.

Many practitioners also calculate average concentration based on the gravimetric method during a test. The gravimetric method measures the weight change after a test period. The evaporation rate (R_{eva}) of the chemical is calculated as follows:

$$R_{eva} = \frac{W_0 - W_1}{t} \tag{4.6}$$

where W_0 is the weight (g) of the chemical at the beginning of the test, W_1 is the weight (g) of the chemical at the end of the test, and t (minutes) is test duration.

When the flow rate of the carrier gas is controlled as a constant during the test and temperature change is minimal, concentration can be calculated as

$$C(g/l) = \frac{W_0(g) - W_1(g)}{t(\text{min})} \times \frac{1}{F(l/\text{min})} \tag{4.7}$$

where F is the flow rate of the carrier gas (in liters per minute). This gravimetric method of determining concentrations is also applicable to permeation and diffusion methods of vapor dissemination, which are discussed later in this chapter.

Varying the temperature of the reservoir can change vapor pressure of the substance within. For example, by placing the dispersion bottle in a temperature-controlled hot-water bath (Figure 4.2), the vapor pressure of the substance is increased and, consequently, the concentration of the substance in the carrier gas is increased.

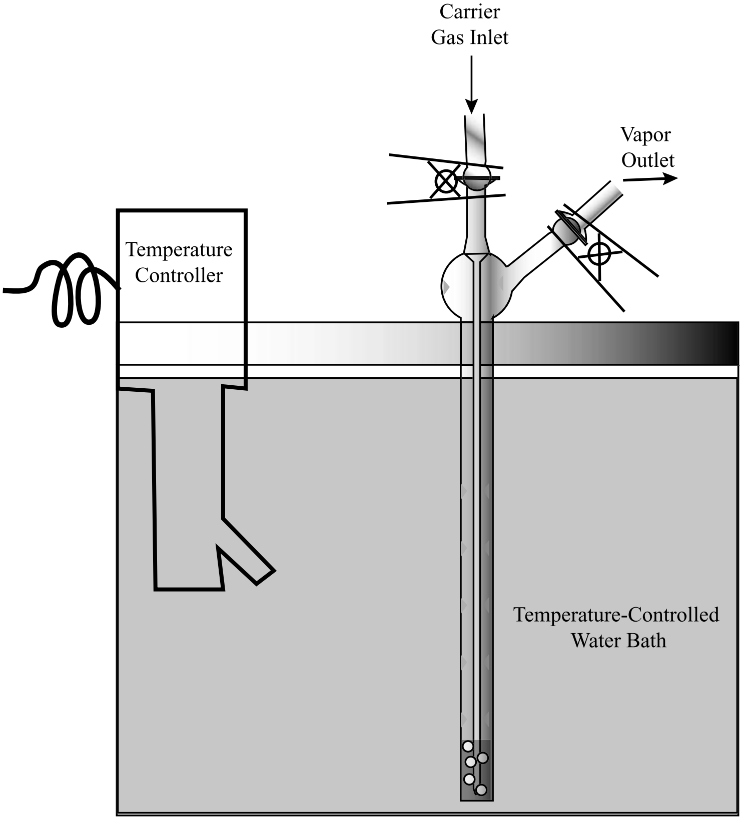

Figure 4.2 Water bath used with gas dispersion bottles for vapor pressure control.

Often a solution of high-vapor-pressure substance in a low-vapor-pressure solvent is used as a vapor source to control and lower the generated vapor concentration. The volatility of the high-vapor-pressure substance (the solute) can be reduced substantially to permit generation of lower concentrations without having to use large volumes of dilution air. Certain important issues should be considered when using this method, however. The vapor generated from the solution will contain not only the substance of interest but also the solvent. The chosen solvent must not interfere with the test. Since evaporation rates of the substance and the solvent are different, the vapor pressure of the substance continually changes with time as it is being depleted at a much higher rate than the solvent. Thus, the concentration of the solution changes during the test. Calculating the concentration based on the gravimetric method may not be appropriate.

4.2.1.2 Saturation Method

The heart of a vapor generation process is the ability to consistently carry the vapor from the substance source. Ideally, the carrier stream carries the substance vapor in its saturate form. Degree of saturation depends on relative flow rate and substance volatility. Two types of saturator will be described. First, the delta tube saturator is used for low total flow applications where a high-purity vapor stream is required. Second, a more conventional multiple-pass saturator equipped with a high surface-area wicker facilitates evaporation for greater flow demands.

4.2.1.2.1 Delta Tube Saturator

The delta tube generation system described here is primarily used for testing of small detection devices in the laboratory. The sparger or "bubbler" type of generator described above is replaced by a triangular shaped "delta tube," and a small drop (e.g., ≤100 μl) of agent is used. The carrier gas stream sweeps over the liquid or solid surface rather than through it to carry the vapor for further dilution (Figure 4.3). A two-stage dilution technique can be employed depending on the targeted concentration range and the volatility of the compound of interest.

The delta-tube generator system is the most useful generation system for point-sample detector testing. It permits generation of very low concentrations of highly purified vapor using minimal dilution flows. The use of the delta tube design has also eliminated the dangerous backsplash of toxic substance that was possible when using bubbler generator types. Because of internal pressure within the vapor generator system, malfunction or disconnection upstream from the sparger in the flow system could cause the substance in the bubbler to flow backward and thus cause backsplash. The delta tube generator system is constructed using commercially available components. Corrugated Teflon lines, Swagelok® fittings, and glass ball-and-socket joints are used to minimize sorption losses and maximize installation flexibility.

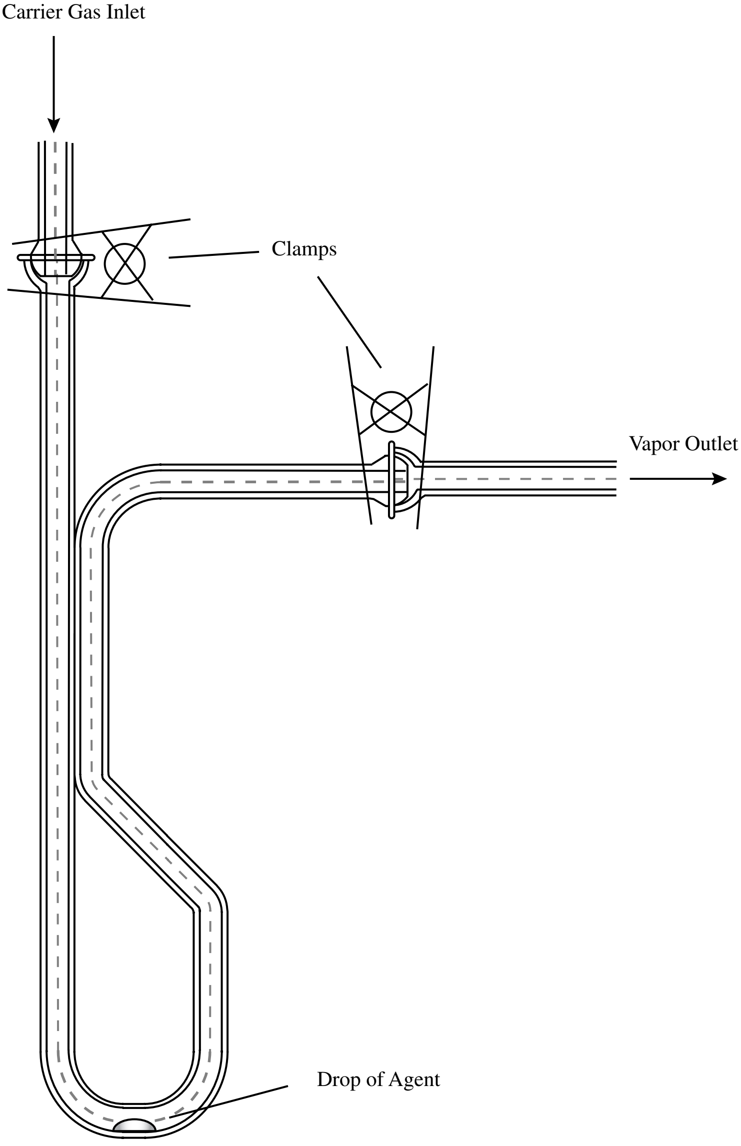

Figure 4.3 Delta tube.

4.2.1.2.2 Large-Scale Saturator

This device is similar to the delta tube used to generate vapor for various applications, including physical property (vapor pressure) measurements and filter testing. This larger version is shown schematically in Figure 4.4. Comprised of concentric glass and ceramic tubes up to 5 cm in diameter and 15 cm long, it has been used to

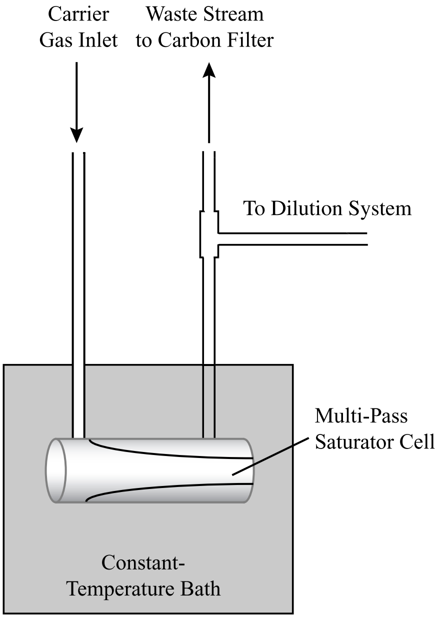

Figure 4.4 Large-scale saturator.

generate flow rates up to 10 l/min. Larger systems can be scaled down to less than 0.1 l/min, and can hold up to 100 g of liquid. These larger generators and liquid samples make it more difficult to purify low-volatility agents such as VX, however. Other than that, these saturators have proven to be extremely stable and easy to operate. Large-scale saturators have been used extensively to generate challenge streams for CWAs and simulants studies where as much as 10 g per experiment are needed to assess filtration performance.

4.2.1.3 High-Pressure Injection Method

During recent laboratory and subscale tests of a pressure-swing adsorption (PSA) filtration system (Causey and Buettner, 1996), it became necessary to introduce a controlled mass (dose) of medium-volatility vapors, including the nerve agent GB, into a high-pressure, high-flow feed stream, and to ensure evaporation prior to filter entry. The liquids are injected into a large (200-gallon) mixing chamber that is then pressurized to the feed condition (approximately 65 psi). Sufficient time is allowed for the liquid to evaporate and mix prior to injection. After the premixed sample is prepared, the experiment was initiated by feeding high-pressure air to the PSA feed stream. Once the PSA system achieved steady state at the desired feed humidity, the flow was diverted through the mixing chamber prior to entering the PSA test rig.

4.2.1.4 Diffusion/Effusion Method

Molecules tend to move from a high-concentration area toward a low-concentration area, and the flux is a function of the concentration gradient. Therefore, by creating and keeping a concentration gradient near the surface of the source chemical, it will be continually released into the dilution gas stream through the diffusion process.

The diffusion method can be used to deliver higher-concentration vapor than the permeation method (discussed in next section) but lower concentration than the evaporation method. It can produce vapor with concentration in the parts-per-billion to 100-ppm range and is used for generating vapor from liquid chemicals.

Figure 4.5 shows an example of a diffusion device. A small vial containing the source chemical is placed in a larger container in a temperature-controlled oven.

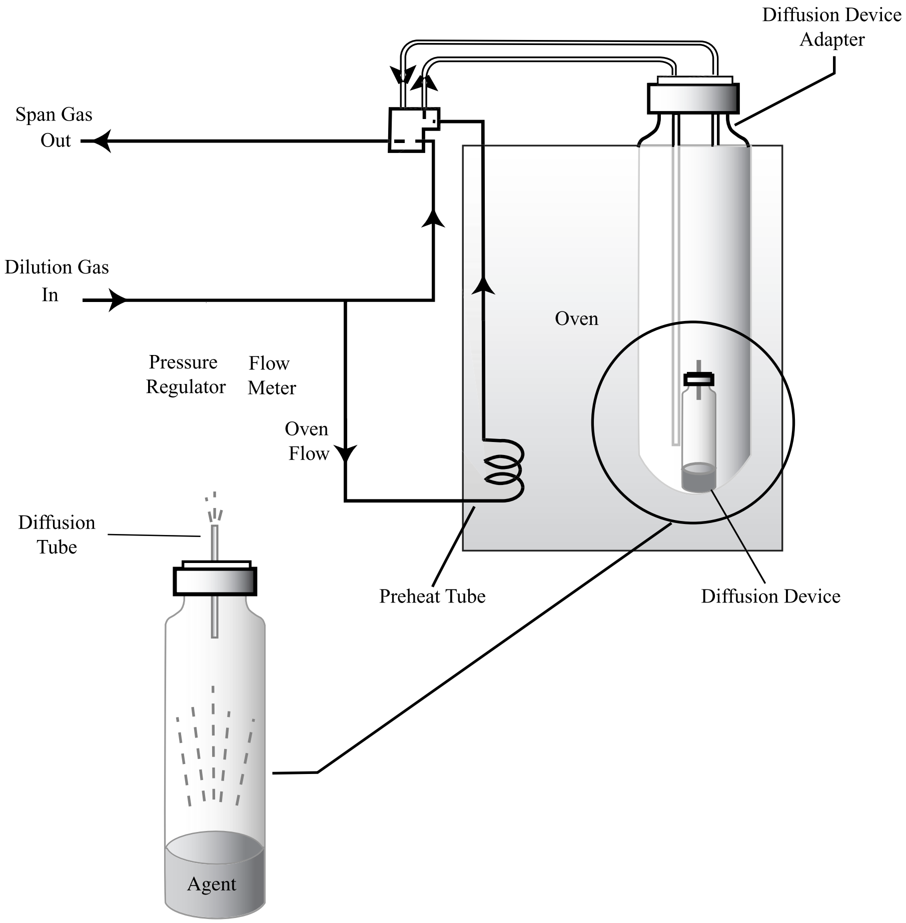

Figure 4.5 Diffusion device.

The substance in the vial diffuses out of the vial through the diffusion tube as the vapor source is swept away by the dilution gas. Changing the temperature of the oven or diameter of the diffusion tube will change the diffusion rate. Higher temperature and larger diffusion tube diameter will permit faster diffusion. Increasing the diffusion tube length, conversely, reduces diffusion flux. Manipulation of these combined effects permits controlled vapor generation.

4.2.1.5 Permeation Method

The permeation method is based on the slow penetration or permeation of molecules through a polymeric membrane. The permeation rate of the compound is determined by physical characteristics of the chemical and the membrane. Permeation is pressure and temperature dependent. Higher vapor-pressure compounds will have a higher permeation rate. Similarly, high temperature will create high internal vapor pressure that leads to higher permeation rate.

Under suitable conditions, permeation tubes can be used as the source for generating low-vapor concentrations. The mass flux of a substance through the wall of the permeation tube is constant at a given temperature, and produces a predictable concentration as a function of the carrier flow rate. Figure 4.6 is a schematic of a permeation tube generator, showing a system in which the tube temperature and flow rate are controlled in order to achieve the desired final concentration.

Controlled and predictable concentrations over a wide flow rate range are readily achievable. The generator uses a small diameter tube (e.g., 1/4 in. O.D.) made of a suitable membrane material such as polytetrafluoroethylene (pTFE) loaded with the liquid agent. The compound contacts the inside surface of the membrane and the vapor slowly permeates.

When the permeation tube is held at a constant temperature, a steady flux flow of compound vapor is emitted. This output can be measured by weight loss over a period of time to determine the permeation or emission rate. The permeation rate is generally expressed as number of nanograms per minute (ng/min). Weight-loss measurements can be taken at various temperatures to produce different emission rates for the same tube. The emission can be diluted with a known flow of dilution air to achieve the desired concentration.

Permeation tubes for many liquid chemicals, such as acetone and certain CWA simulants can be purchased commercially. However, permeation tubes for CWAs or TICs are not readily available and must be fabricated in the surety laboratory. Figure 4.7 shows a piece of Teflon tubing (e.g., 10 to 20 cm long and 1/4 in. diameter) is sealed with a Teflon plug at one end (Figure 4.7b). The chemical is then injected into the tube to fill about half of the tubing length from the other end (Figure 4.7c) and sealed with another Teflon plug (Figure 4.7d). The seal must be tight so that the chemical cannot leak from the ends.

The permeation rate is determined by the gravimetric method. The permeation device, after it has been assembled, is weighed and then placed in a temperature-controlled cavity with constant flow of nitrogen or clean air to sweep away the permeated chemical vapor. After a period of time, perhaps days, the tubing is weighed again and the permeation rate is determined by weight loss over elapsed time. Since

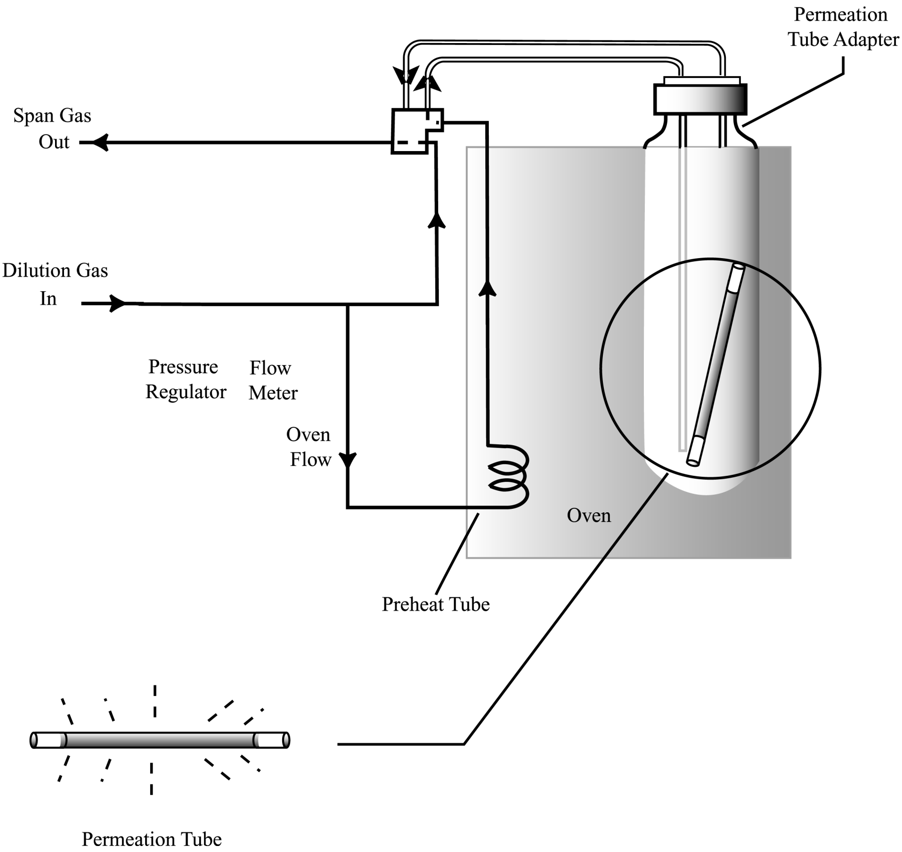

Figure 4.6 Permeation device.

the permeation rate is a constant at a constant temperature, during tests, increasing of the dilution flow rate decreases the generated vapor concentration.

4.2.1.6 Syringe-Pump Injection Method

The syringe-pump injection method has been used for a variety of applications mainly to produce higher concentration and volume generations that may not be achieved through usual volatilization techniques. The technique is accomplished by directly injecting the liquid into a carrier stream through a syringe at a fixed rate. Low-concentration streams are generated by injecting as little as 0.1 mg/min of GB into an air stream at a 1000 to 1500 l/min flow rate for a final concentration of approximately 0.1 mg/m^3.

A similar vaporization method has been developed by forcing liquid into a stream of heated air. If enough heat is applied, the liquid will be instantaneously evaporated. This method has been used to generate a high-volume stream of simulant for large-item testing in the chamber. Concentrations of 100 mg/m^3 or higher can readily be generated and maintained using this method.

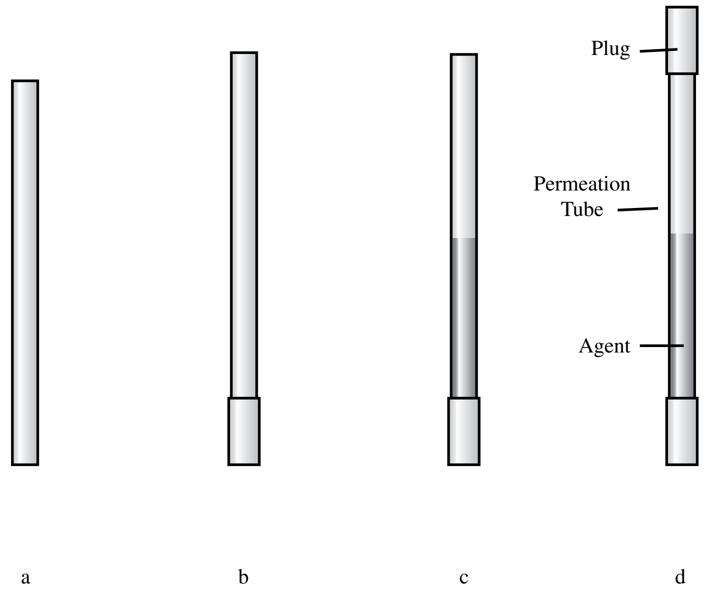

Figure 4.7 Procedures to assemble permeation tube.

This method generates vapor at a rate of 400 cubic feet per minute (cfm), which is equivalent to approximately 11.3 m^3, using an electric blower attached to the end of a 6-in.-diameter aluminum pipe. Two 208-V heater elements are mounted inside the pipe. This length of pipe is then inserted into the side of an 8-in.-diameter length of pipe roughly at a 45° angle. The 6-in. pipe is inserted into the 8-in. pipe at least 0.5 in. to prevent any liquid simulant from entering the pipe containing the heaters. The length of 8-in. pipe is mounted vertically in a stand. Then, the simulant, which is volume controlled by a needle valve, is pumped through an orifice mounted near the top of the 8-in. pipe to form a spray on its sides. The spray is vaporized by the hot air created by the heater elements and forced through the generator by the blower motor. Temperatures of 52°C (125°F) have been shown to vaporize nearly all the simulant put into the system. Since not all the simulant will vaporize, a drain must be installed in the bottom of the 8-in. pipe to recover liquid for reuse. An approximate material balance can be calculated if the airflow and simulant injection and recovery rates are measured.

Simulant vapors released into the test chamber are stirred with fans to produce a uniform challenge. The feed is monitored with proper analytical devices and data acquisition system. This system has been employed to generate a high volume of vapor in a large chamber for testing the protection efficiency of unhardened collective protection shelters. These shelters typically use filtered air to overpressurize the inside of the shelter to preclude infiltration of unwanted vapors.

A variation of this method is to inject liquids with low boiling points directly into process streams by virtue of their own head pressure. Cyanogen chloride (ClCN), for example, is frequently used to test developmental and fielded filtration materials and systems. It boils at 12.8°C. Therefore, it has an inherent high vapor pressure at room temperature. Thus, it can be injected directly into process streams operating near atmospheric pressure. The flow rate of ClCN is controlled using a regulator, and care must be exercised to ensure that the ClCN container maintains sufficient temperature to keep its total pressure above that of the process stream. The ClCN cylinder is commonly placed in a controlled heater bath to offset the cooling caused by the evaporation of ClCN during the test.

4.2.1.7 Solid-State Vapor Generator

The principal method of air purification for low-volatility vapors relies on physical adsorption of vapors onto high-surface-area adsorbent materials such as activated carbon. The solid-state vapor generator (SSVG) method reverses this procedure by initially contaminating a high-surface-area material with a small amount of the target chemical. Vapor generation is effected after purging the adsorbent particles containing the adsorbed vapor using dry air, nitrogen, or other carrier gas to reach a vapor loading equilibrium. A schematic depiction of this generation system is shown in Figure 4.8. This approach is highly effective in suppressing the equilibrium vapor pressure of the adsorbed material owing to the strong interactions between the vapor and the adsorbent. Studies have shown that the equilibrium vapor pressure of GB is suppressed by nearly 10 orders of magnitude using a mass ratio of 1% GB to coconut-shell carbon (CSC). The degree of suppression depends strongly on the mixing (vapor loading) ratio, and approaches the vapor-liquid equilibrium limit as the loading approaches the saturation limit of the adsorbent (0.4 g GB/g CSC). These observations immediately lead to the ability to precisely control the generation rate and concentration over an extremely wide range between direct generation of sub-parts-per-trillion concentration levels at very low flow rates. A generation rate of 100 femtograms (10^{-15} g) per minute for GB was observed. The generation rate measurements are limited on the low end by the detection technology used, not by generator conditions (loading ratio and temperature, primarily), which could have been further reduced.

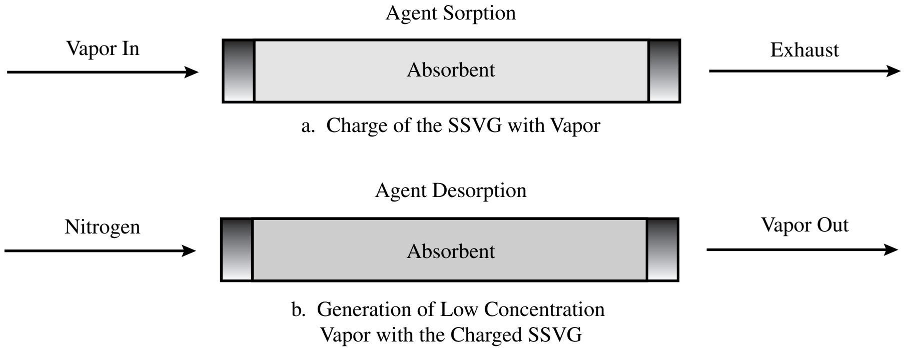

Figure 4.8 Solid-state vapor generator.

4.2.1.8 Compressed Gas or Gas Mixture

Using pressurized gases or gas mixtures is another way to generate vapors for TICs and other chemicals that are gaseous at room temperature. Pressurized gas can be purchased as pure gas or gas mixture at different concentrations. This gas can be blended directly with the dilution air in a dilution system to achieve the desired concentration. A special regulator may have to be used with each gas or gas mixture. When compressed cylinder gas is used, adjusting the flow rates from the pressurized vapor source and the dilution air stream governs the concentration. In general, because of the high volatility of this type of vapor, the concentration can be directly calculated. Adsorption losses can be considered minimal or negligible given their characteristic high volatility.

4.2.1.9 Chemical Reaction Method

Generation of chemical vapor through chemical reaction is an alternative method used to generate chemical vapors that are difficult to obtain commercially or are unstable under normal storage, or for other special purposes. For example, generation of a GB vapor can be achieved using the binary chemical reaction method. Vapor can also be generated via the decomposition of a chemical as well. The decomposing chemical serves as the source chemical. With this method, the emission rate is relatively easy to control using similar methods as discussed above, such as permeation and diffusion. For example, formaldehyde vapor could be generated using its water solution. But, water and methanol in the solution may interfere with the detection devices under testing. Thus, an alternate source of formaldehyde that would not interfere with the testing process must be used. The decomposition of paraformaldehyde releases formaldehyde without other byproducts. Therefore, formaldehyde vapor can be generated using paraformaldehyde contained in the permeation or diffusion device. The advantage of this formaldehyde source over the solution source is that it eliminates possible effects associated with water and methanol in the solution. Similarly, ammonia vapor could be generated using various ammonia-containing compounds, such as ammonia carbonate. The decomposition of ammonia carbonate releases ammonia as the source for generation.

The reaction of various chemicals is another way to generate chemical vapors. For example, SO_2 is released when HCl reacts with $Na_2S_2O_5$:

$$\mathrm{HC1} + \mathrm{Na_2S_2O_5} = \mathrm{SO_2} + \mathrm{NaHSO_3} + \mathrm{NaCl} \tag{4.8}$$

Difficulties associated with the reaction method are controlling the reaction that governs the release rates of the vapor, and the potential interference from multiple chemicals in the reaction during testing. Each and every reaction may require a special apparatus and settings.

4.2.2 Dilution and Mixing System

Having presented various techniques for providing a vapor source for generation, we will discuss ways of diluting vapor into the desired concentration and conditions for effective detector evaluation. Under normal circumstances, vapor concentration from the source can be accomplished with a dilution system to satisfy experimental needs. A single-stage dilution system is usually sufficient for most compounds to provide detectable concentrations for current detection devices. When very low concentration is desired, further dilution is required. A multiple-stage dilution system is then used.

Moisture in the air has been found to pose frequent undesired effects in many detection devices. Therefore, evaluating the moisture effect is one of the more important steps in evaluation. One way of mitigating the moisture effect is to include the humidity level in the generated vapor sample that is similar to the ambient condition. By so doing, the effect of moisture can be evaluated or negated. Therefore, the method for humidifying the vapor stream is presented along with discussion of dilution methods.

4.2.2.1 One-Stage Dilution System

A simple one-stage dilution system is shown in Figure 4.9. The vapor from the source, controlled with a regulated flow meter, meets the dilution airflow that is also controlled with a regulated flow meter into the mixing manifold. Diluted sample exhausts from the mixer can be used to test the detector directly or as a source for the next stage of dilution. The excess flow then passes through a charcoal canister to remove the toxic component before exhausted. The sample vapor concentration can be calculated as

$$C(\mathrm{ppm}) = \frac{C_s(\mathrm{ppm}) \times F_s(1/\mathrm{min})}{F_s(1/\mathrm{min}) + F(1/\mathrm{min})} \tag{4.8}$$

where F_s is the flow rate of the source vapor, C_s is the source vapor concentration, and F is the flow rate of the dilution air. This single-stage dilution serves as the basic generation system from which later generator systems followed with added features. This dilution system is a simplified version leading to the two-stage dilution system described in the next section. The function of each component in this dilution system is similar to that in the two-stage dilution system, and is explained in the next section.

4.2.2.2 Two-Stage Dilution System

Figure 4.10 is an example of a two-stage dilution system. An air generator (6) provides the clean and dried air used for the carrier stream. This pressurized air is split into five streams, each controlled by flow meters equipped with appropriate needle valves (7, 11, 12, 19, and 20). Flow meters (11), (12), (19), and (20) control the two parallel humidity dilution streams. These are identical for ease of operation. The flow meter (7) is used to provide a dry airstream for the first-stage dilution.

For the two-stage dilution apparatus, the agent carrier gas (1) for the first dilution is supplied from a nitrogen tank and is controlled by a flow meter equipped with a

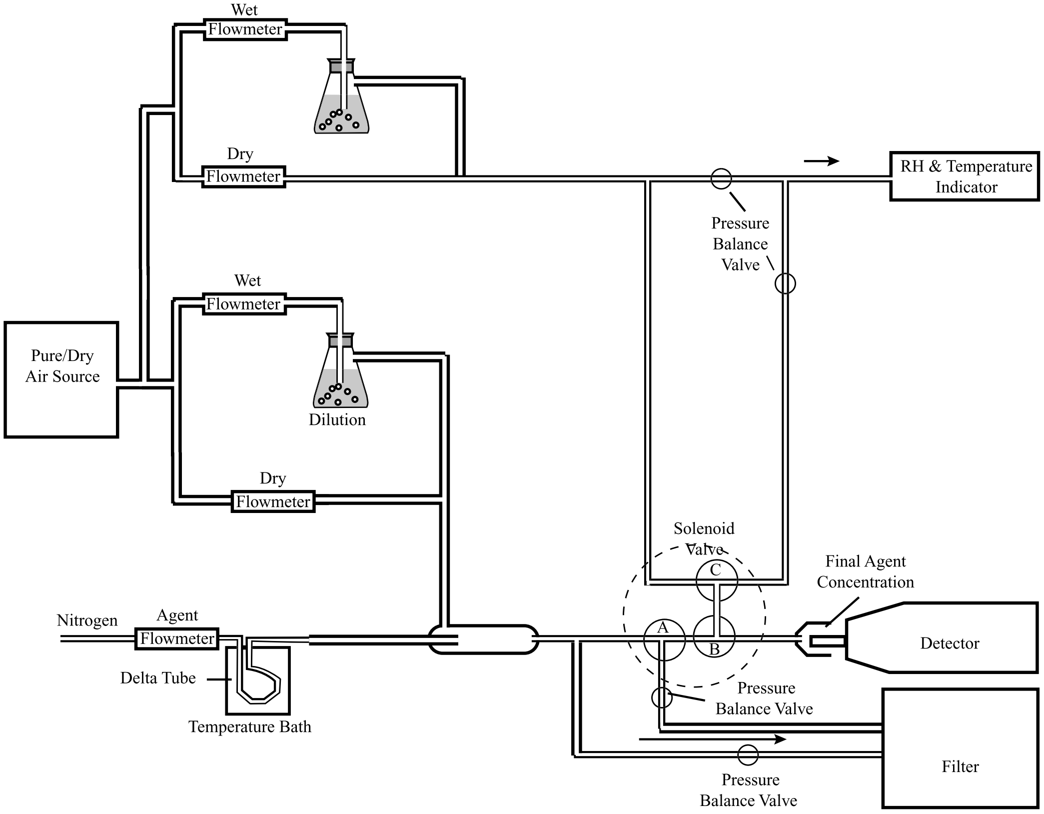

Figure 4.9 One-stage dilution system.

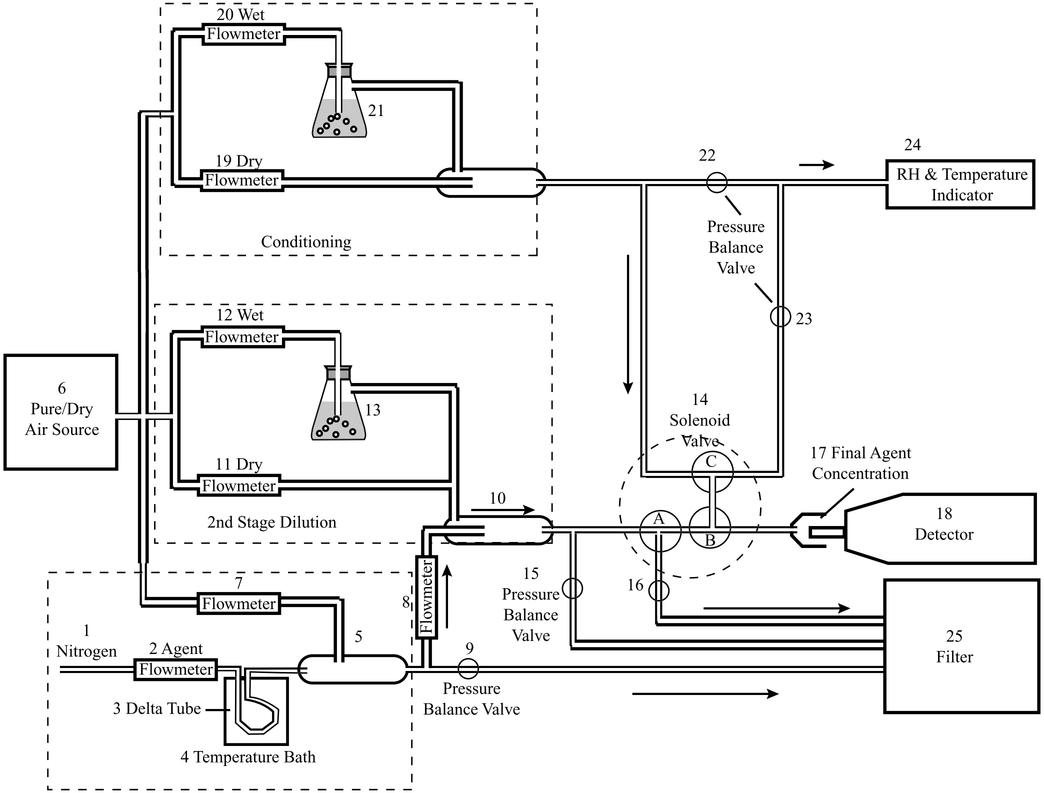

Figure 4.10 Two-stage dilution system.

high-accuracy needle valve (2) into the agent reservoir or the delta tube (3). The delta tube is immersed in a temperature-controlled bath (4) to maintain a constant temperature. The nitrogen carries the chemical vapor as it sweeps over the chemical and enters into a glass manifold (5) where it is met with a stream of dry air from the pure air generator through the flow meter (7) to provide the first-stage dilution.

A portion of the resulting first-stage agent vapor flow is forced through a flow control meter (8) and valve (9) into the manifold (10). It is met and further diluted with the humidity-tempered air from the combined streams from flow meters (11) and (12), as desired. The resulting relative humidity (RH) is controlled by varying the ratio of the dry air (0% RH) from flow meter (11) and the wet (100% RH) air stream from flow meter (12) bubbling through the humidifier water reservoir (13). The RH is estimated and is compared with the RH and temperature indicator (24) installed in the system's conditioning airstream. The humidified chemical vapor airstream is then split into two streams. One stream is directed to the solenoid valve assembly (14) consisting of three 3-way solenoid valves. The second stream is directed through a regulating valve (15) into a charcoal canister (25) to remove excess toxic chemical vapor.

A sample port (17) is connected directly to the solenoid assembly to minimize the delay when switching from conditioning air to agent air during a challenge. The glass cup has slots to release the excess flow that is delivered to the detector inlet area. The detector samples the agent vapor without having to attach directly to the sample port. Usually, the delivered flow is approximately twice the detector demand to ensure that the detector is not starved. This approach precludes detector response from pressure biasing.

This two-stage dilution system provides easily controlled, low-concentration level generation when limited airflow is required. It should be noted that the detector inlet is not hard coupled to the sample port and that the generated vapor is flowing over the inlet for the detector to sample; the flow must be in excess of detector demand. Total air delivered to the sample port must be minimized to ensure that toxic vapor released into the surrounding environment is minimal. The flow to the detector inlet, however, must be maintained in excess of detector demand. The reason for this type of sampling is to avoid generator flow from influencing the detection process through an induced pressure differential that could occur in directly coupled sampling.

Staged dilution extends the operating range to extremely low concentration levels while keeping total flow volume low. Presently, detection instrumentation limitations make it unnecessary to require more than a two-stage dilution for even the most volatile materials of interest. For example, GB is one of the most volatile liquid chemical agents tested routinely. Single-stage dilution can produce a final concentration near 0.1 mg/m^3 when the delta tube is held at 0°C at a total dilution flow rate of 3 l/min. Adding a second stage extends concentrations to below 0.0001 mg/m^3 while maintaining a final flow rate of 3 l/min.

However, if the concentration of the vapor source is very high and the target concentration is very low — for example, when a parts-per-billion level of Cl_2 vapor is generated with 99.99% Cl_2 gas — a multiple-stage dilution system may have to be used. A portion of the sample from the mixer of the first-stage dilution system is used as the source of the next stage of dilution and mixes with the second-stage dilution air similar to that demonstrated in the above example. A portion of this vapor is then diluted with anther dilution flow. This procedure greatly reduces vapor concentration and achieves the desired low concentration.

The following example shows the advantages of multiple-stage dilution over single-stage dilution. Let's assume that the starting concentration from a gas source cylinder is at a concentration of 1% and the estimated limit of detection is at the 1-ppm level. The generator system, therefore, must be able to generate vapor at that concentration level. Let's further assume for the sake of simplicity that the minimum reliable flow rate reading of the flow meter is 1 ml/min. To reach the 1-ppb vapor concentration using a single-stage dilution system would require a total flow rate (F_{total}) of

$$F_{total} = \frac{C_s \times F_s}{C_r} = \frac{1\% \times 1(\text{ml/min})}{1(\text{ppb})} = \frac{10,000(\text{ppm}) \times 1(\text{ml/min})}{0.001(\text{ppm})} \tag{4.9}$$
$$= 10,000,000(\text{ml/min}) = 10(\text{m}^3/\text{min})$$

Therefore, the required dilution flow is 1 ml/min less than 10 m^3/min. Such a large amount of flow, greatly in excess of detector needs, creates undesirable side effects. Because CWAs or TICs are highly toxic, their release into the atmosphere should, if possible, be kept to a minimum to avoid excessive contamination. Therefore, the excess exhaust from the generation process must be contained via trapping or filtering through an activated charcoal filter to capture toxic material from the stream before it is exhausted.

A flow of contaminated air at 10 m^3/min has created safety concerns when such a large volume of toxic vapor is being continuously created. Higher volume usually leads to higher system pressure, more toxic substance being consumed, large-area contamination potential, and a larger apparatus requirement. All of these factors create additional hazards for operators. This flow cannot be easily controlled or disposed of through a small-size filter in the laboratory setting. Use of large filtering system drastically increases operational logistics and costs.

Furthermore, the use of large volumes usually increases the system's internal pressure. Consequently, the flow through system plumbing could create undesired artifacts when sampled by the detection device during testing. The internal pressure effect could become drastic when the detector is directly connected to the sample port. Such effects may drastically affect the detection algorithm of many detectors. A preferable method is to use a smaller amount of excess vapor around the detector inlet through a sample cup so that the detector will draw in the amount it needs without being influenced by the relative flow velocity from the generator system.

When a two-stage dilution system is used, the concentration is first reduced to, for example, the 3-ppm level by using 1-ml/min source vapor and 2999-ml/min dilution air:

$$C_1 = \frac{10,000(\text{ppm}) \times 1(\text{ml/min})}{3000(\text{ml/min})} = 3.3(\text{ppm}) \tag{4.10}$$

We can, then, take 1 ml/min of this diluted vapor and dilute it with again with 3000 ml/min of dilution air to reach the desired 1 ppb second-stage concentration in a total flow of 3 l.

$$C_2 = \frac{3.3(\text{ppm}) \times 1(\text{ml/min})}{3000(\text{ml/min})} = 1.1(\text{ppb}) \tag{4.11}$$

This total 3-l/min flow can be controlled much more effectively using a small filter. Thus, the two-stage generator provides an effective means to produce a desired concentration of these toxic materials for laboratory testing purposes.

4.2.2.3 Other Generation Techniques

Besides the discussed methods of vapor dissemination for subsequent dilution to achieve the desired agent concentration, there are several additional techniques that are worth mentioning. Vapor generation from low-volatility compounds may not provide a sufficiently high concentration using the delta tube, diffusion, permeation tube, or solid adsorbent techniques. The use of a syringe pump and subsequent evaporation at a small flow volume does not produce easily controllable concentrations in the laboratory. To overcome such problems and provide an adequate, stable, generated concentration, an aerosol generator would be necessary.

An aerosol generator, unfortunately, will produce aerosol or particles together with a vapor. In the case of low-volatility liquids or solid compounds, such a practice of producing a test concentration is considered acceptable. More than likely, the dissemination of low-volatility compounds would be in the form of aerosols to produce the desired concentration. In the case of low-volatility liquid compounds, the use of a nebulizer to produce a spray of fine mist for subsequent dilution can produce the desired concentration. Figure 4.11 presents a flow schematic for a typical aerosol generation system. A push-pull system is required to aid aerosol movement along the tube. Based on the nebulizer, dilution flow rates, and viscosity relationships, the lighter aerosols will be carried into the dilution stream while the larger sprays will hit the wall of the nebulizer envelope and flow back into the liquid.

In addition to the use of a nebulizer, another specially designed apparatus has been used for generating specific concentrations from solid compounds is a vapor condensation aerosol generator (Figure 4.12). The solid is melted in a reservoir immersed in a heated silicone oil bath controlled at above the melting point of the substance. Similar to vapor generation, the nitrogen stream passes through the molten substance to carry the vapor as well as the aerosol produced by the bubbling effect to meet with the dilution airflow. The dilution airflow can be conditioned with proper humidity, as in the case of delta tube vapor generation. The cooler dilution air will condense the hot vapor and form aerosols of fine solids. Depending on the flow of the carrier and the dilution, a desired concentration can be achieved. The heavier particles that were not carried to the end of the vertical tube because of the flow relationship will fall back into the agent reservoir where they are recycled.

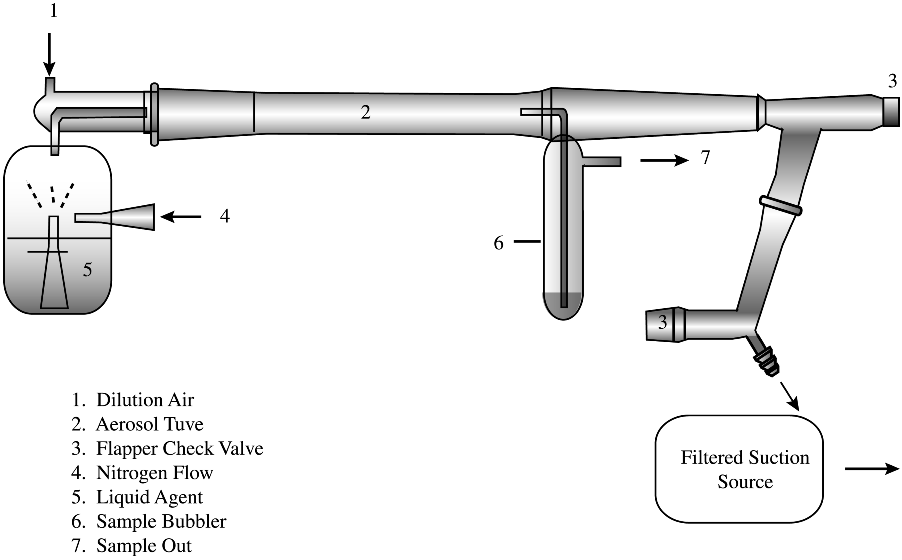

Figure 4.11 Liquid aerosol generator.

To maintain the flow of aerosolized particles from dissemination toward the sample port and eventually the exhaust, it is necessary to provide a suction source at the end of the tube to equate the amount of air used for the generation process. This balancing of input and exhaust facilitates aerosol movement through the tube, which prevents aerosol fallout due to generator's internal pressure resistance that causes droplet coagulation.

4.2.3 Comparison of Generation Techniques

Spargers have been widely used for generating a high-flow airstream. This method has general utility, but is subject to the unintended release of liquid in the event of pressure transients downstream of the generator. This possibility presents a serious problem for generation of high-toxicity vapors, and extraordinary safety measures (e.g., pressure relief valve and liquid trap) must be used to preclude liquid release when used for CWA vapor generation.

Another difficulty experienced when using the sparging method is the possibility of unintended aerosol production and transport with the vapor. Expedient measures can be implemented to remove aerosols from the product stream, including aerosol filtration and maintaining the sparger at subambient temperature; however, this phenomenon reduces the operator's ability to establish predictable concentration with the generator's operating conditions.

The use of a delta tube saturator and the two-stage dilution system described above has the capability of generating highly purified agent vapor in a small controlled volume of conditioned air within the limits imposed by their physical properties. The small agent quantity permits rapid purging of the higher-volatility impurity materials that may interfere with generation of the target vapor. This is the only

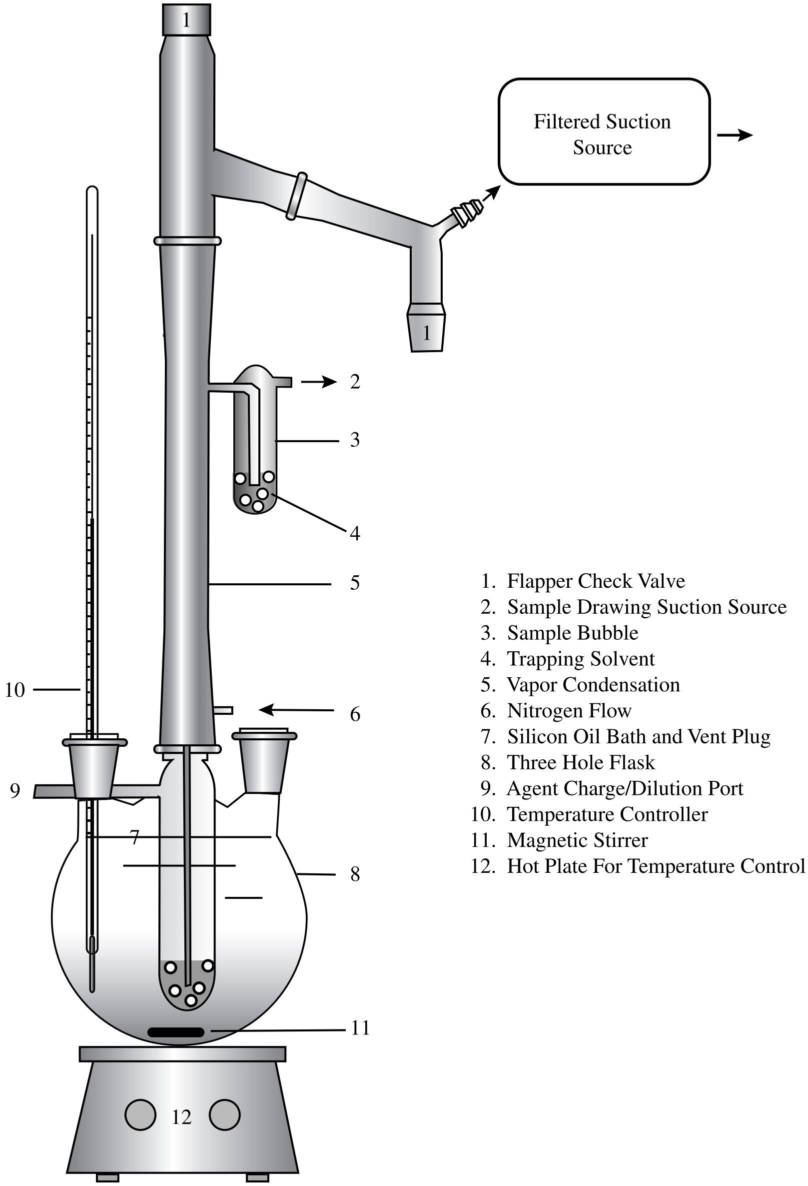

Figure 4.12 Solid aerosol generator.

method that can produce highly purified target vapor where highly volatile impurities cause interference.

The delta tube behaves similarly to the diffusion generator except that it has a more positively controlled carrier flow that can overcome the generator's internal system pressure. A diffusion system, which the vapor from the substance passively diffuses depending on flow dynamics of the system, can be quite unpredictable due to changes in internal pressure. The flow rate of the carrier gas in the delta tube generation system can be precisely controlled using a needle valve. More importantly, the use of the delta tube prevents dangerous backsplashing of the agent that can occur when an impinging sparger is used improperly. Backsplashing is an area of major safety concern when dealing with lethal substances.

The use of a two-stage dilution system expands the range of achievable concentrations while keeping the final dilution flow rate to a minimum as required by the experiment and safety considerations, without having to resort to high-volume dilution to reach low-concentration generation. The two-stage system also facilitates generation and control of RH and vapor concentrations. Only the last-stage RH needs to be controlled. Raising or lowering the final concentration can be achieved by varying the agent flow rate of the first stage, while keeping the same second stage flows, therefore, retaining the same RH condition in the final stage.

Saturator systems can produce the desired concentration very rapidly with minimal manipulation. Because pure substance is used, the resulting vapor is of the highest purity without solvent influence. In cases where higher generation rates are needed, a high-capacity multiple-pass saturator (Figure 4.4) or parallel addition of delta tubes (Figure 4.13) together with higher bath temperature can be implemented.

Syringe pump methods work well and are generally applicable for a wide variety of materials. However, this method has disadvantages and limitations that should be recognized by the potential user. Containment difficulties arise for low-boiling-point liquids. Also, the ability to generate vapors at very low rates is limited currently to greater than 0.1 mg/min or 0.1 ml/min by available equipment. Additionally, since this method involves liquid injection, care must be taken to ensure that complete evaporation and mixing are achieved prior to sampling the product stream. Cooling due to liquid evaporation can be an exacerbating factor for the latter, particularly at high injection rates owing to the low heat capacity of air. For example, injection of liquid water into a dry airstream at 25°C to achieve a 10% RH product will result in an airstream at approximately 19°C and 15% RH unless the stream is reheated to restore the original temperature. This effect will be less significant for low-humidity, low-flow conditions, since the heat of evaporation will be low. The effect will become more pronounced at high-flow, high-humidity conditions.

Permeation tube generators are predictable, safe, and convenient to operate. The two principal disadvantages are low generation rates and long equilibration time as compared to delta tube methods. Applications are limited to a smaller range of compounds. VX, for example, has not been successfully generated using a permeation tube owing to effects caused by impurity vapors that interfere with VX permeation. Impurities within the VX, although in very small percentages as a liquid, have much higher vapor pressure values than VX. This vapor pressure phenomenon greatly altered the ability to effect proper VX permeation. The higher vapor pressure impurities that permeate at faster rates thus overwhelmed VX concentration. Only the delta tube method is capable of producing high-purity VX vapor.

The SSVG method is ideally suited for direct generation of low flux streams (i.e., low concentration and low flow rate) without the need for further dilution. Another potential advantage of this method, which has not been explored yet, is the ability to reduce head pressure over a high-volatility vapor or gas that might normally

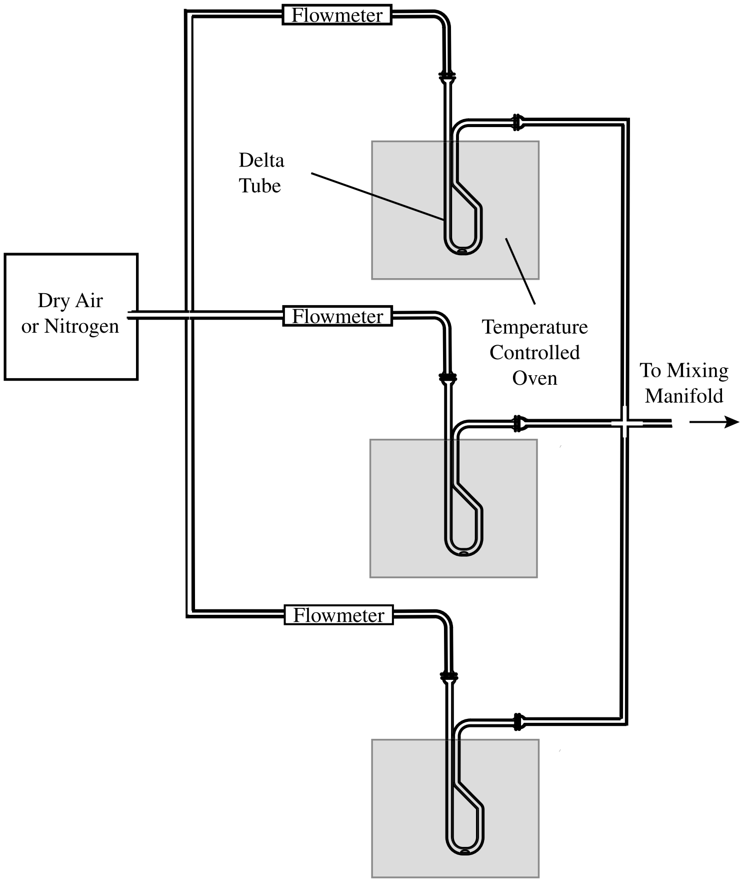

Figure 4.13 Setup of parallel delta tubes.

be dispensed from a high-pressure container. This safety feature might be particularly useful for field dissemination of CWAs such as cyanogen chloride and arsine for detector calibration, but its greatest utility should be realized in industrial applications such as gas (hydrogen) storage. The wide range of available generation rates and control parameters using this method make it ideal for a wide range of applications. In addition, storage of highly toxic vapors on a solid adsorbent can significantly reduce the safety risks associated with handling these materials.

Potential problems associated with the SSVG method include decomposition of the adsorbate as a result of intimate contact with adsorbent reactive sites. This effect has been observed for adsorbed HD and VX recently, and seems to be exacerbated by the presence of water vapor. Efforts to minimize this effect include use of low-ash adsorbents, operating at as low a temperature as possible, and avoiding the presence of water. The latter includes sample preparation methods to reduce water contamination and use of ultra-dry carrier streams since water vapor in the carrier even in the parts-per-million range will eventually be concentrated on the surface of the adsorbent and potentially lead to hydrolysis.

The high-pressure vapor injection method has the distinct advantage that a known dose of chemical is delivered to the test rig. Also, the integrated concentration time (Ct) challenge can be determined if the flow rate is known. Often, however, test planners desire step function challenges, that is, rapid establishment and removal of the feed concentration over the test duration. In the present case, the feed concentration rises rapidly but tails off slowly due to mixing effects inside the mixing chamber. On the other hand, this injection method more closely approximates what might be expected under field dissemination. In fact, mixing effects in the field will most likely be more pronounced than observed in the test configuration.

Under suitable conditions where rapid change of generated concentration is not required, permeation tubes can be used as the source of low concentrations of gases and vapors. Once the system becomes equilibrated, the same concentration can hold for a long period of time. The disadvantage is the longer lag time for achieving different concentrations. Thus, this method of generation would be best suited for routine testing using the same concentration.

Syringe pump generation has a low-concentration generation limit, injecting as little as 0.1 mg/min of GB into an airstream at a flow rate of 1000 to 1500 l/min to reach a final concentration near 0.1 mg/m^3. It is not suitable for low-concentration generation.

4.2.4 Humidification of Generated Vapor

Generating humidified vapor streams using air as the carrier to simulate an operational environment for detector testing is a must. Moisture often causes changes in detector behavior. In this case, an added complication arises due to the interaction between water vapor and the target vapor. Ideally, Raoult's Law limits the sum of relative pressures (ratio of partial pressure to single-component vapor pressure at the measurement temperature) of all vapors in a mixture to 1.0. For example, an air stream at 50% RH can only hold up to 0.5 relative pressure of the target vapor. Deviations from Raoult's Law can be significant, especially for mixtures involving nonmiscible liquids.

As mentioned earlier, detection devices should be tested under diverse environmental conditions. Therefore, the basic generator system was modified to include humidification of the vapor stream. Since moisture will degrade the source substance, the carrier stream passing over the substance must be kept at zero moisture content to prevent sample degradation. Thus, only dilution air streams can be humidified. Fortunately, the amount of carrier flow through the source is much less than the amount used for subsequent dilution, except for very low volatility compounds. That permits generation of a vapor stream with controlled RH.

The one- and two-stage dilution apparatuses discussed earlier include the humidifier devices shown in Figures 4.9 and 4.10. The following humidifying process discussion is based on the more complete system shown in Figure 4.10. The conditioning side of the generator described serves as an example of a humidifying method. The humidifying stream uses the flow from flow meter (19) that is set equal to the combined flows through flow meters (8) and (11). This dry airstream is combined with the flow from flow meter (20) that is set equal to the flow from flow meter (12), through the humidifier (21), to form the conditioning air stream. This stream is also split into two streams similar to that described in the chemical vapor generation section. One stream passes through the regulating valve (22) and is released. The other stream is directed to solenoid (B), and through solenoid (C) into the sampling cup (17), while the solenoids are not energized. Challenge with the chemical vapor is effected when all three of the solenoid valves (14) are energized. The conditioning air stream exhausts through solenoid (C) and a regulation valve (23) to the RH and temperature indicator (24) for an indication of the RH and temperature conditions. This arrangement permits a wider range or regulation of flows to meet test demands. Because flows for controlling humidity of the two sections are matched with identical flow rates, readings obtained from the humidity indicator can be considered as equal to the RH condition of the chemical vapor-generating section.

To ensure that the air is saturated when it passes through the water reservoir kept at the same temperature as the environment, the flow is maintained at the minimum level to provide adequate volume (e.g., 3 l/min is adequate for most detectors). Saturation efficiency needs to be considered when higher flows are used, however. By keeping the humidifier water at the same temperature as the environment, the relationship will hold. The air passing through the humidifier can only become saturated at the same temperature and thus, when it is mixed with the dry air, the percentage of RH is directly proportional to the ratio of wet and dry flows. This technique minimizes the need to manipulate flow adjustments to control RH if and when a heated water source is employed. It also eliminates condensation problems associated with heated water or steam injection techniques.

While the described generation system uses dual humidified streams, the humidity of the toxic vapor stream is not measured. The RH is considered the same, for practical purposes, as that of the conditioning side by use of similar flow settings. The RH on the conditioning side is measured when detector testing is underway. Quite often, detection sensors have been found to be grossly affected by humidity differences between the conditioning and the challenge airstreams. RH mismatch could cause large changes in baseline signals. Therefore, it is necessary to provide identical RH to both the conditioning and subject vapor streams. To ensure that there is no RH deviation between the two streams, the generation apparatus is modified to use a single humidifier rather than two separate humidifiers (Figure 4.14).

4.3 GENERATION OF CWA OR TIC VAPOR WITH INTERFERENT VAPOR

The ban against outdoor testing using toxic chemicals prompted the need to generate toxic vapors together with a potential interfering vapor under laboratory engineering controls for detector testing. In general, the potential interference vapor is introduced to the vapor generation system immediately before the vapor stream enters the sample cup. The interference vapor source can be disseminated through

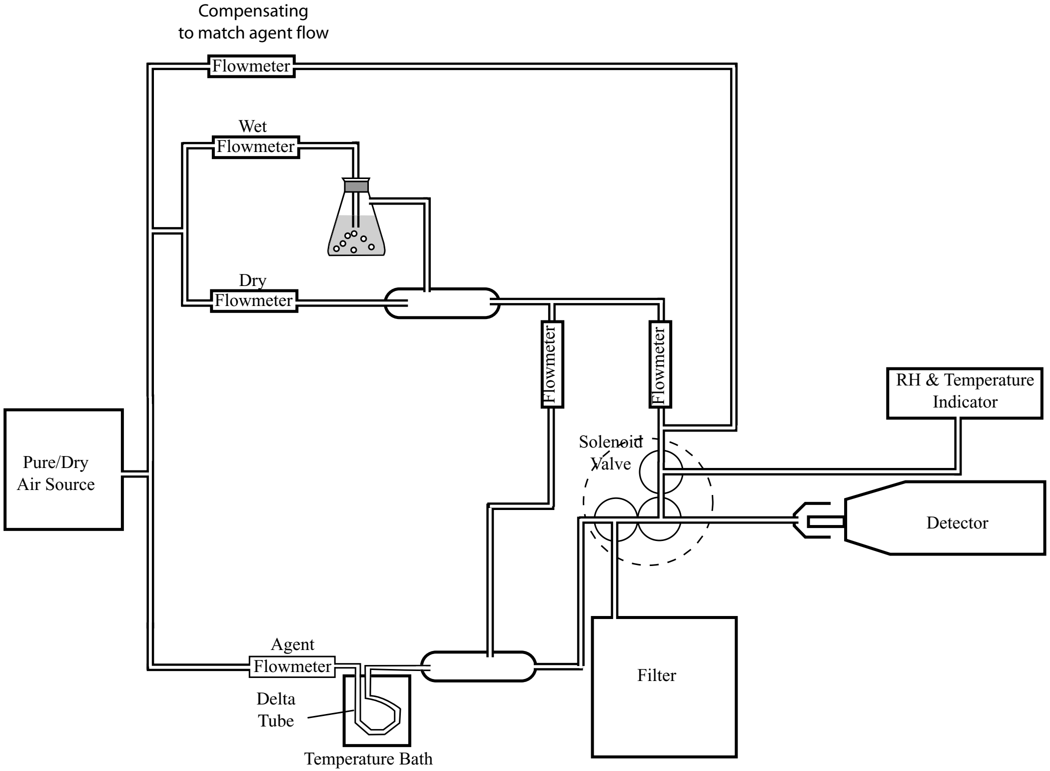

Figure 4.14 Single humidifier for condition and agent generation.

several methods, including delta tube, impinging bubbler, compressed gas cylinder, engine exhaust, and burning apparatus.

The flow passing through the delta tube or impinging bubbler containing the liquid interference sample is controlled to carry the saturated headspace concentration of the substance. Figure 4.15 shows the diagram of a two-stage dilution system coupled with a gas dispersion bubbler that generates necessary interference. In general, passing the air through the liquid in a bubbler is an efficient way of saturating the air with a given substance. However, many substances foam readily by the bubbling action. A delta tube can then be used so that the air only sweeps above the liquid surface to carry the headspace vapor for dilution. Depending on the total flow of the basic vapor generation system, the flow through the interferent delta tube or impinging bubbler is adjusted to produce the desired volume dilution. For example, when the final flow of the generation system is set for 3-l/min, the amount of flow through the interferent will be 30 ml/min to achieve the 1% headspace concentration.

Similarly, the flow from a compressed cylinder can be properly converted to provide the desired parts-per-million concentration when diluted with the flow from the generation system (Figure 4.16). Gasoline engine and diesel engine exhaust can be piped into the laboratory and the flow can be controlled by use of a stopcock to give the proper volume dilution.

To generate smoke from burning materials requires much more manipulation. Figure 4.17 shows a laboratory smoke generator. It is necessary to provide airflow to support the combustion necessary to properly burn the sample (e.g., with diesel fuel, kerosene, jet propulsion fuel, etc.). A small amount of the sample is placed in the cup attached to the center stem. A cotton string, used as a wick, is lit. The fixture is inserted into the flask where a stream of air is provided to maintain combustion. Once the proper combustion is achieved by regulating the amount of air into the flask, the flame is extinguished. The stopcocks are then adjusted to force the desired volume of air toward the vapor generation system while exhausting the rest of the combustion air. Once this relationship has been reached, the wick is again lit and testing can then begin.

To test the effects of the interferent on the detection ability of a device, the following procedure can be adopted. A generation system equipped with parallel conditioning and vapor streams connected to three solenoid assemblies is used. The interferent stream mixes with the stream from the solenoid assembly prior to the sample cup where the detector draws in the vapor sample. The detector is first being conditioned by sampling the conditioning air. After a period of conditioning, the solenoids are energized and the detector then draws its sample from the vapor stream to ensure that it detects the target substance of interest. These took place before the interference is connected or introduced.

Once the detector has shown proper response to the subject vapor, it is allowed to clear under the conditioning air. After clearing, the interference vapor is introduced and mixed with the conditioning air to observe the effect on the detector. If the detector responds with an alarm to this interference vapor, it could be misconstrued as the presence of the target toxic chemical.

If exposure to the interference vapor does not cause a false positive response, the conditioning air is replaced with the subject vapor air. The detector is now

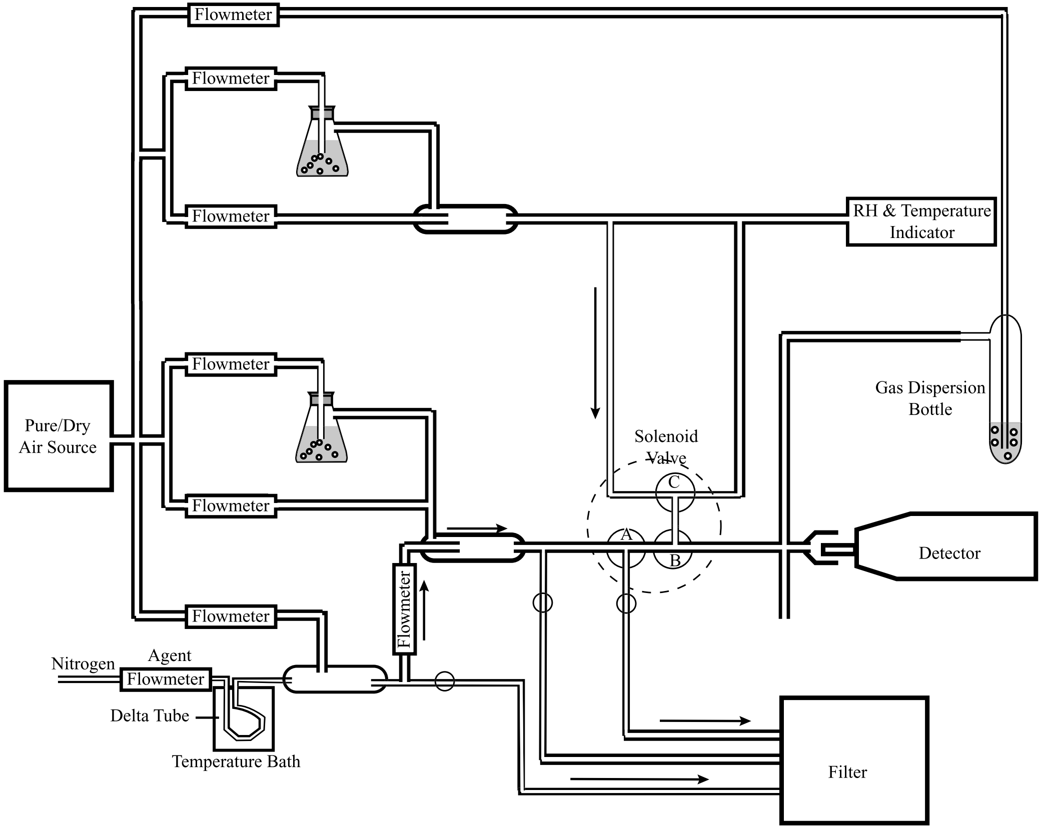

Figure 4.15 Two-stage dilution system with gas dispersion bottle as interference source.

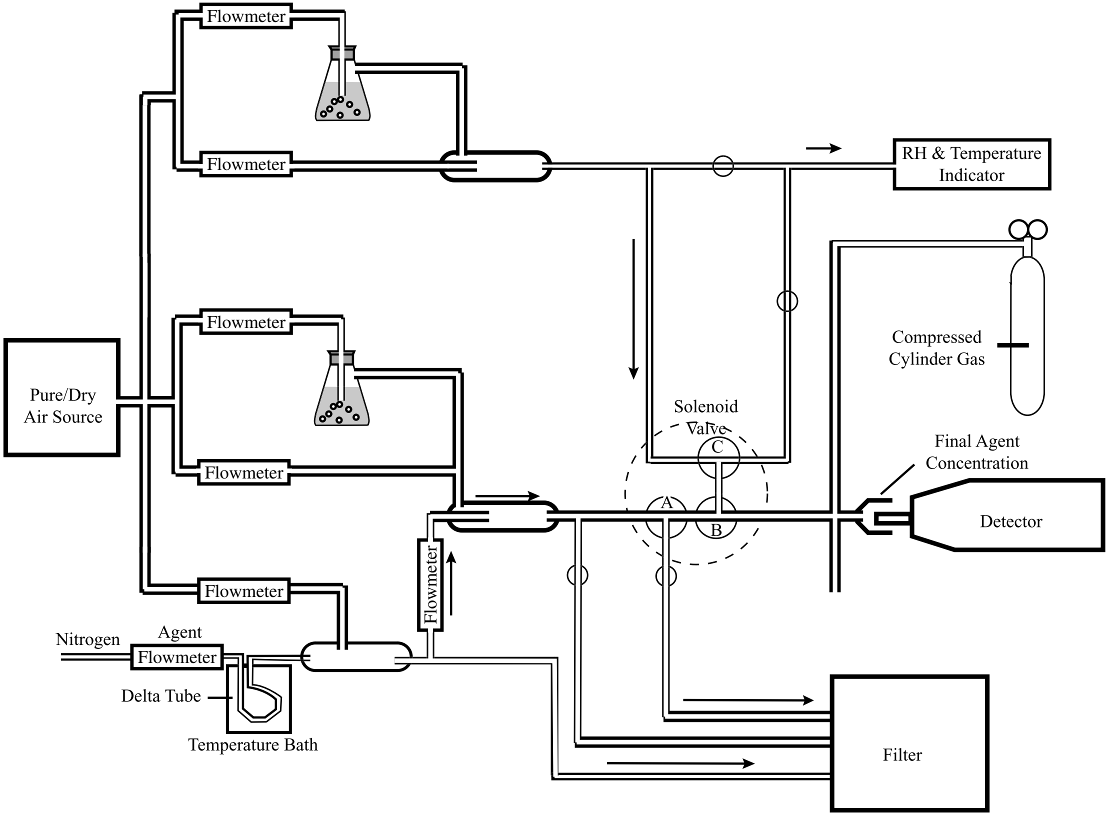

Figure 4.16 Two-stage dilution system with compressed gas as interference source.

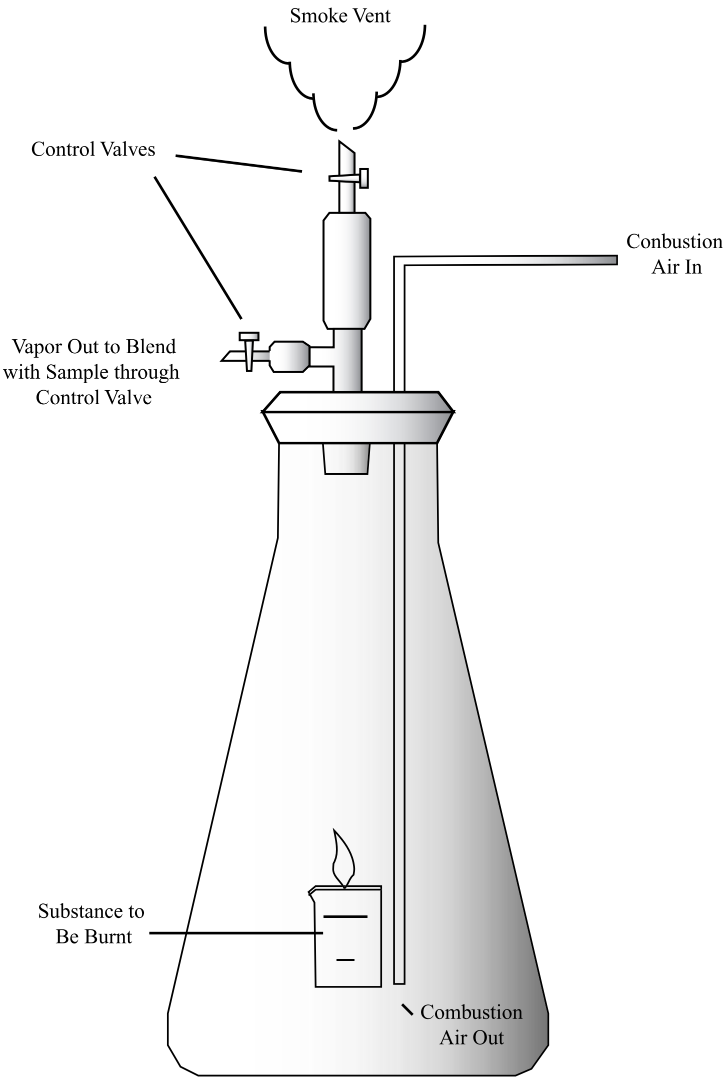

Figure 4.17 Smoke generator.

sampling the subject vapor together with the interference vapor. If it can properly respond to the subject vapor, the detector is considered not affected by the presence of the interference vapor. If, however, the detector fails to respond with an alarm, the effect is considered false negative; although the interference vapor does not cause the detector to generate false positive alarms, it interferes with the detection algorithm to prevent proper detection of the target vapor. This effect is considered more harmful than a false positive response. While false positives are a nuisance, false negatives could be fatal.

Laboratory testing is limited due to a variety of restraints. For instance, laboratory equipment often creates undesired artifacts that produce misleading results.

Mismatches in RH and pressure influence during sampling are the most common artifacts. Care must be exercised to identify and minimize or eliminate such artifacts during any evaluation. Rigorous evaluation of toxic chemical detection devices is crucial to ensure that they are reliable, that is, that they meet their design objectives.

4.4 CWA SIMULANTS

Detectors and protection equipment should be tested with actual CWAs or TICs during the development stage to ensure performance. While it is possible to obtain various TICs from commercial vendors, tests with actual CWA agents are generally limited to a few surety-qualified laboratories and government agencies. Open-air tests with CWAs have been banned since the sheep killing incident in Utah linked to VX leakage in 1969. Hence, CWA simulants are used as alternatives. Studies have been conducted to evaluate the properties of protective clothing with simulants. (Reports can be accessed at http://hld.sbccom.army.mil/ip/reports.htm#detectors or www.cdc.gov/niosh/nppt1/simulppjul31.html.)

To be qualified as a CWA simulant, the chemical should mimic the behavior of the CWA it simulates. It must be relatively nontoxic if the simulant is intended for outdoor dissemination. The chosen substance must be environmentally benign. If the simulant is intended for use under laboratory control conditions, substances with some toxicity can be used. Simulants are chosen based on structural, vapor pressure function group similarities to respective CWAs. When the simulant is used to evaluate detector performance, choosing the simulant that closely matches the type of detection methodology used by the detector is of the utmost importance. For example, if the detection device is an ion mobility detector, the simulant chosen must have similar ionization affinity, function group, and structure size so that its mobility is similar to the CWA.

Tables 4.3 and 4.4 list several substances that have been used to simulate the nerve agent GB and blister agent HD, respectively, in detector testing. The listed chemicals in Table 4.3 are similar to GB in some aspects. For example, the structure of dimethyl methylphosphonate (DMMP) is very similar to that of GB. Both contain the CH_3-P=O group. The main difference between them is that the simulant does not have the more active fluoride (-F) function group, and thus, its toxicity is much lower than GB. Both compound molecules contain phosphorous. Therefore, it is possible to use DMMP as a simulant to evaluate the performance of a flame photometric detector, ion mobility detectors, or surface acoustic wave detector.

Table 4.4 lists various chemicals that have been used to simulate the behavior of mustard gas. For example, dibutyl sulfide (DBS) has a similar structure, and is used as a simulant of mustard gas for detector evaluations.

However, no matter how closely simulants mimic respective agents, they are not the real thing. Simulants should only be used in preliminary studies. For example, during development of a flame photometric detector, DMMP and DBS can be used to generate the necessary signals for the flame photometric detector. DMMP contains phosphorous and DBS contains sulfur atoms; therefore, they are suitable for simulation of the G and H agents, respectively. The use of these

Table 4.3 GB and Simulants

Chemical	Structure	CAS	Notes
GB	$CH_3P(O)(F)OCH(CH_3)_2$	107-44-8	
Dimethyl methylphosphonate (DMMP)	$CH_3P(O)(OCH_3)_2$	756-79-6	Vapor pressure (mmHg) = 1.2 mm Hg at 25°C
Diethyl methylphosphonate (DEMP)	$CH_3P(O)(OC_2H_5)_2$	683-08-9	
Diethyl ethylphosphonate (DEEP)	$C_2H_5P(O)(OC_2H_5)_2$	78-38-6	
Diisopropyl methylphosphonate (DIMP)	$C_7\text{-}H_{17}\text{-}O_3\text{-}P$	1445-75-6	Vapor pressure = 13 mmHg at 10°C. Diisopropyl methylphosphonate is a chemical byproduct resulting from the manufacture of sarin (GB).
Triethyl phosphate (TEP)	$(C_2H_5O)_3P(O)$	78-40-0	

Table 4.4 HD and Simulants

Chemical	Structure	CAS
Bis(2chloroethylethyl)sulfide (HD)	$Cl(CH_2)_2S(CH_2)_2Cl$	505-60-2
Dibutyl sulfide (DBS)	$CH_3(CH_2)_3S\ CH_3(CH_2)_3$	544-40-1
1,6-Dichlorohexane (DCH)	$Cl(CH_2)_6Cl$	2163-00-0
Di-n-butyl disulfide (DBSS)	$CH_3(CH_2)_3S_2(CH_2)_3CH_3$	629-45-8
Bis 4-chlorobutyl ether (BCBE)	$Cl(CH_2)_4O(CH_2)_4Cl$	6334-96-9
2-Chloroethyl phenyl sulfide (CEPS)	$C_6H_5SCH_2CH_2CL$	5535-49-9

chemicals for development purposes will make the process easier and more efficient because of the limited CWA availability for testing. Tests with actual CWAs must be performed periodically during developmental stages. Occasionally, the results observed in testing using simulants do not match those derived from using the actual agents.

A simulant that is acceptable for one purpose may not be useful under different conditions. Light emission from the excited S_2 through burning of dibutyl sulfide (DBS) makes it a suitable candidate to serve as a viable HD stimulant for flame photometric detectors. If a device is designed for detecting Cl clusters formed by decomposing HD molecules, the use DBS as an HD simulant will not work. There is no chloride contained in DBS. Another substance that contains chloride, such as CEES, would then be proper. Therefore, deciding on the correct simulant requires a thorough understanding of the unique characteristics of the target CWA and potential simulants.

It is very important to note that although the toxicity of the chemicals listed in Tables 4.3 and 4.4 is much lower than CWAs, some of them are still quite toxic and are considered controlled substances. For example, diisopropyl methylphosphonate (DIMP) is a byproduct of GB production. Before using any of the chemicals listed in the tables as a simulant in a given situation, substance toxicity and impact on the environment must be considered. The U.S. Army Edgewood Biological and Chemical Center maintains an extensive database containing structural, physical, chemical, toxicological properties, and applications information on chemicals that have been tested or proposed for use as CWA simulants.