



Generating Calibration Gas Standards

with Dynacal® Permeation Devices

Permeation devices provide an excellent method of producing known gas concentrations in the PPM and PPB level for calibration of analytical instrumentation. The basic requirement of any calibration system is to maintain the permeation device at a constant temperature in a known carrier flow. When the permeation rate at that temperature and the dilution flow rate are known, the concentration of the calibration stream can be calculated.

Calibration Systems

Basic U-Tube Holder

A simple calibration system can be assembled utilizing an existing constant temperature water bath and a simple “U” tube holder (**Figure 1**), which can be made or purchased. An external pump is required to provide a carrier flow through the calibration chamber, with the total dilution flow adjusted so that there is an excess of calibration gas furnished to the analyzer inlet. If 200 cc/min meets the required sample flow, the *minimum* dilution flow for generating the calibration stream is 200 cc/min plus 20-50% excess (240 ~ 300 cc/min). Increasing the total dilution flow to 3000 cc/min gives a dynamic range of 1 to 10.

Calibration Instruments

For easier operation and greater precision, use one of our Dynacalibrators or assemble an instrument with the following features (**Figure 2**):

1. A constant temperature chamber with 0.1°C temperature control
2. Fixed carrier flow through the chamber
3. Additional dilution air which can be adjusted to give a 10:1 dilution
4. An overflow outlet for excess gas
5. Valve, calibration chamber, and sample line surfaces of glass, stainless, or Teflon®.

Additional System Considerations

Minimization of Pressure Variations

Since some analyzers are sensitive to the variations in pressure which can occur when dilution flows are changed, a “T” connection must be inserted between the calibration system and the analyzer to vent the excess calibration gas. Pressure variations can be further minimized by connecting the analyzer probe line perpendicular to the span gas flow. If problems persist in spite of these precautions, feed the calibration gas into a larger diameter tube or gas mixing bulb, with the analyzer probe inserted into the larger tube or bulb.

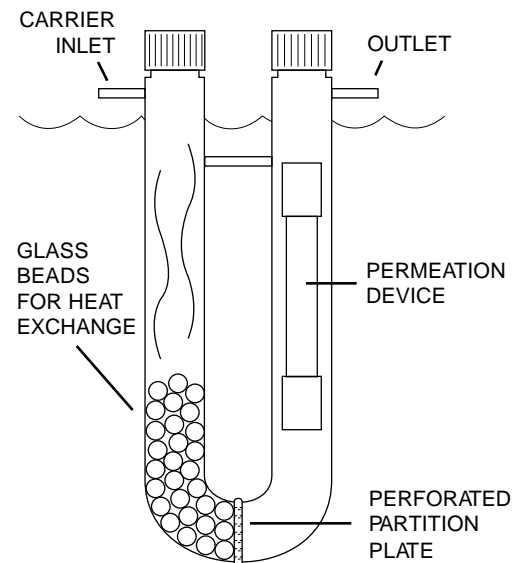


Figure 1: Simple U-tube holder

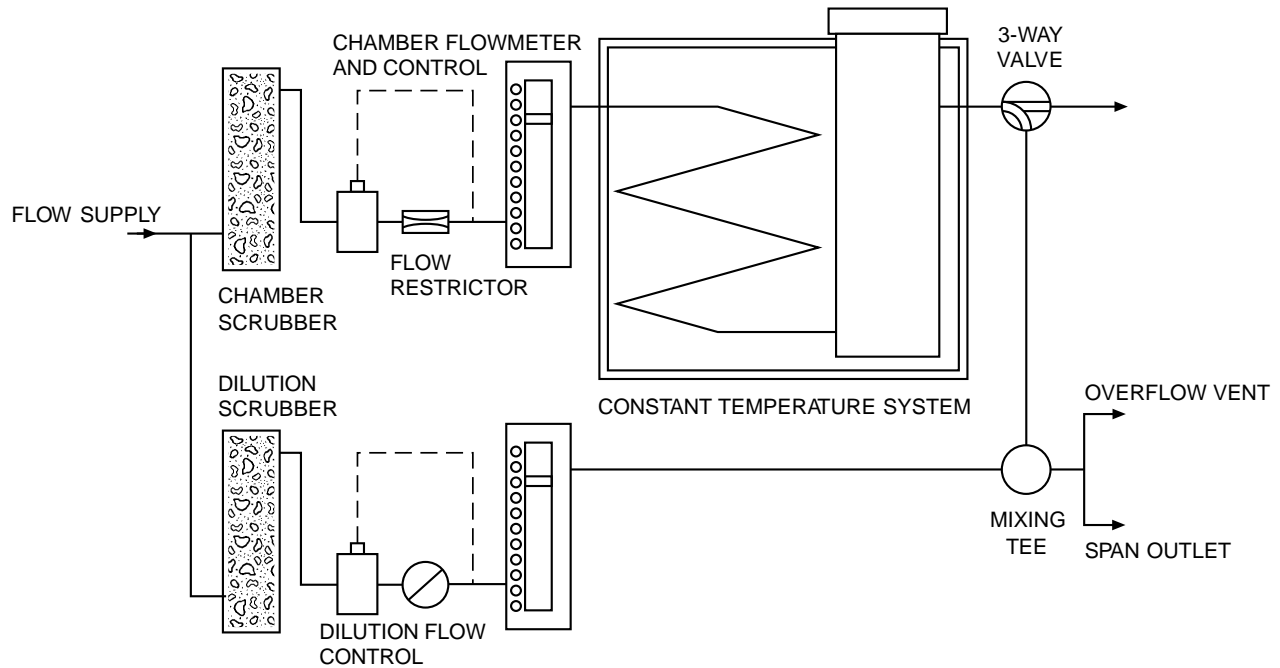


Figure 2: Schematic of Basic System

Special Carrier Flow Requirements

If the chemical fill of the permeation device is subject to deterioration upon exposure to substances in the carrier flow, special scrubbers or carrier gases should be used. For example, NO_2 and Cl_2 permeation devices require a dry carrier stream - any moisture in the system will build up on the tube surface and form corrosive deposits on the stainless steel crimp band under the label. Hydrogen sulfide devices should be operated in a flow of nitrogen for best long-term stability. Otherwise, oxygen from the air will back-diffuse into the tube, reacting with the H_2S and depositing sulfur in the tube wall. The observed effect is a gradual rate increase leading to premature failure.

Permeation Device Characteristics and Limitations

Equilibration

Prior to their use, permeation devices should be conditioned at the calibration temperature and carrier flow to bring the rate to its equilibrium value. Most devices require 30 minutes to 3 hours to reach equilibrium. Heavy wall tubes, low vapor pressure compounds, and halogenated compounds typically take longer. The best procedure is to set up the calibration system the day before it is needed, allowing the system to equilibrate overnight. Conduct repeated tests over a period of time to insure that equilibrium has been achieved.

Lifetime

The formulas at right are based on the assumption that the devices have a 75% liquid fill and that the chemical fill is stable under the conditions used. "Rate" is the permeation rate in ng/min per cm, ρ is the liquid specific gravity at the control temperature (for an approximate calculation, assume $\rho = 1$), and L is the active length in cm.

Device type	Lifetime in months
High emission tubular	$[5600/\text{rate}] \times \rho$
Standard emission tubular	$[1400/\text{rate}] \times \rho$
Low emission tubular	$[3125/\text{rate}] \times \rho$
Extended life tubular	$[23000/(\text{rate} \times L)] \times \rho$
Wafer	$[11000/\text{rate}] \times \rho$

Temperature Limitations

The temperature is usually limited by the control instrument, but the permeation devices do have limits. Temperatures which create vapor pressures in excess of the following cannot be used:

Device type	Pressure limit
High emission tubular (1/4" OD x .030" wall)	70 psi
Standard emission tubular (1/8" OD x .030" wall)	200 psi
Low emission tubular (3/8" OD x .090" wall)	300 psi
Wafer (.030" thickness)	450 psi
Wafer (.050" thickness)	700 psi

Caution:

The limits in the table above are guidelines only - use them with caution. The strength of Teflon decreases as the temperature increases, so greater safety factors should be used.

Rate Change with Temperature

To estimate the permeation rate at a different temperature when you know the rate at a given temperature, use this rule of thumb: each 1°C increase in temperature increases the rate by 10%. For a precise calculation, use this equation:

$$\text{Log } P_1 = \text{log } P_0 + \alpha (T_1 - T_0)$$

where P_0 = Rate at temp T_0 (°C), P_1 = New rate at temp T_1 (°C), and α = the temperature coefficient (0.030 for high emission tubes, 0.034 for standard emission tubes).

CAUTION:

Do not use temperatures which would produce a pressure greater than the limits listed in the table above.

Size Limitations

Once again, the limitation is usually with the device holder. Few systems can accommodate tubes longer than 20 cm, or more than 3 tubes. Check the overall length and inside diameter of the permeation device holder. If a desired rate requires a tube too long to fit it, the options are: higher temperature, multiple tubes, lower dilution flow, or diffusion tubes.

Device type	Active length	Total length	Max. diameter
Standard emission	0.5 to 20 cm	add 3.5 cm	0.64 cm
High emission	0.5 to 20 cm	add 3.5 cm	0.98 cm
Low emission	1.0 or 2.0 cm	3.7 cm	0.98 cm
Low emission #2	1 to 15 cm	add 3.5 cm	0.98 cm
XLT	0.2 to 10 cm	add 9.5 cm	0.64 cm
XLT #2, #3	0.2 to 10 cm	add 7.3 cm	0.98 cm
Wafer	.030 - .090" thick	4.6 cm	1.60 cm

Critical Temperature Limitations

The device must maintain a two phase equilibrium at above room temperature. This eliminates the use of chemicals with a critical temperature below room temperature, such as CO, NO, and methane.

Output Limitations

It is difficult to achieve high PPM concentrations at flows over 1 L/min.

Answers to a Few More Frequently-Asked Questions

“Does the permeation rate go down as the amount of liquid decreases?”

No. As long as there is any liquid remaining in the device, there will be a two-phase equilibrium with a constant internal vapor pressure.

“Does the permeation rate change with a change of external pressure?”

No. The permeation rate does not change with altitude or external atmospheric pressure changes. The partial pressure of the chemical at the outer wall or membrane surface is assumed to be zero – a valid assumption when the tube is in a chamber with a purge flow. The permeation rate is a function of the pressure gradient of the chemical fill from the inside to the outside surface. There would have to be a relatively high concentration around the tube before the pressure gradient would change to the extent that a rate change would be detectable.

“Does tube orientation make a difference?”

No. Vapor pressure and solubility of the chemical in the permeable membrane are affected only by temperature. They do not change as a function of liquid/surface contact area.

Calculations

Concentration

Concentrations are expressed both in mass per unit volume and parts per unit volume (PPM or PPB). Since the volume of a gas varies with the temperature and pressure, standard conditions must be used in the computation and comparison of pollutant concentrations. Reference conditions are defined as 25°C and 760 mm Hg (1013.2 MB). To compute the concentration of a calibration gas generated by a permeation tube in a dynamic carrier flow, use the following equation:

$$C = \frac{P \times \left(\frac{24.46}{mw} \right)}{F_C}$$

where C = the concentration in PPM by volume, P = the permeation rate in ng/min, mw = the molecular weight of the pollutant gas, F_C = the total flow of the calibration mixture in cc/min, corrected to the reference conditions defined above (see next section). The constant 24.46 is the molar volume at the reference conditions.

Correcting the Flow Rate

If necessary, correct the flow rate to the reference conditions with the following equation:

$$F_C = F_m \left(\frac{P}{760} \right) \times \left(\frac{298}{(t + 273)} \right)$$

where F_C = the flow rate at the reference conditions, F_m = the measured flow rate, and t = the temperature in °C. *Note:* the measured conditions are those pertinent to the flow measuring device, not to the chamber where the permeation tube is held.

Many types of flow measuring devices are used to determine flow rate, and the specific type should be considered when applying temperature and pressure corrections. For positive displacement types such as bubble flowmeters and wet or dry test meters, the standard corrections are used. However, for rotameters that use a floating ball, a different flow principle is involved. The height of the ball in the flowmeter is a function of the gas density, viscosity, and momentum. For air, the following equation is used to correct the measured flow to standard conditions:

$$F_C = F_m \sqrt{\frac{P}{760} \times \frac{298}{(t + 273)}} = 0.626 F_m \sqrt{\frac{P}{T}}$$

where F_C = the flow rate at the reference conditions of 25°C and 760 mm Hg and F_m = the indicated flow at the observed temperature ($t^\circ\text{C}$) and pressure (P mm Hg).

Sample Problem

What PPM concentration is being generated in this scenario?

An H_2S analyzer is located in an instrument shelter at 5000' elevation. The shelter temperature is 15°C. The permeation tube source is a 4 cm certified tube maintained at 30°C, with a rate of 2050 ng/min. A flow of 200 ml/min is passing into the constant temperature chamber, which is further diluted with a flow of 2000 mL/min dilution air. Both flows are measured with a flow metering device that is in equilibrium at the shelter temperature.

The first step is to correct the flow rate to the reference conditions. If a barometer is not available, the pressure at the particular elevation in the U. S. Standard Atmosphere can be used for a suitable approximation:

$$P = 760 \left(1 - \frac{.0065Z}{945} \right)^{5.2568}$$

or, 632 mm Hg at 5000 feet, where z = altitude in feet and p = pressure in mm Hg. Plugging this value into the equation for correcting the flow gives:

$$F_C = (2000 + 200) \left(\frac{632}{760} \right) \times \left(\frac{298}{(15 + 273)} \right)$$

or, 1893 mL/min at 25°C and 760 mm Hg. Now we can plug the values into the formula for determining concentration:

$$C = \frac{(2050) \left(\frac{24.46}{34} \right)}{1893}$$

or, 0.78 ppm.

References

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