Permeation Tubes:
A Simple Path To Very Complex Gas Mixtures

By Jim McKinley

As applications requiring gas mixtures become more sophisticated, the mixtures required become progressively more complex. Permeation tubes can supply miniscule flows of a wide range of analyte vapors while compensating for background contamination in the matrix.

Introduction

A complex gas mixture may contain a few or many components; however, there is typically another factor that makes the mixture difficult to prepare and impractical (and often impossible) to store. For example, the requirement that a mixture be delivered at a specific relative humidity (RH) moves any mixture into the "complex" category. The RH value is a function of both temperature and pressure, so storage of the humidified mixture is out of the question.

Some other factors resulting in "complex" mixtures are (1) extremely low concentrations (parts-per-billion, parts-per-trillion, etc.) particularly of reactive or polar compounds, (2) high concentrations of high boiling compounds, (3) trace concentration mixtures prepared in a matrix contaminated with an unknown concentration of the contaminant, i.e., a non-zero matrix, (4) mixtures prepared in a highly reactive matrix, and (5) mixtures of components that react (however slowly) with each other.

Typically, such complex mixtures must be dynamically blended and used immediately. But dynamic blending presents its own set of problems. To create a 1 ppm volume (ppmv) mixture by direct blending in a single stage requires measuring and controlling 1ml/min of component vapor and blending it into 1,000 l/min of matrix gas! Obviously, this is not a practical solution; multiple dilution stages are required and each stage adds additional error. But even then the problem remains of accurately controlling a small flow of the component vapor.

Permeation tubes offer a simple path for avoiding many of the problems encountered in creating complex gas mixtures. They are particularly useful for two of the most

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common complex mixture problems: preparing extremely low concentration mixtures and preparing known mixtures in a non-zero matrix.

Description of Permeation Tubes

Permeation tubes are devices that act as a flow control mechanism for dispensing a very small flow of permeate vapor through a polymeric membrane (usually TFE or FEP Teflon®). Figure 1 shows a schematic of the basic disposable, liquid-filled permeation tube. The component compound is held in contact with one side of the polymeric membrane. Component vapor flows through the membrane at a rate determined by the permeability of the membrane and the vapor pressure of the component compound. The membrane permeability is a function of membrane temperature, so when the component is a liquid sealed inside of a permeation tube, the component vapor flow (emission rate) is set by the operating temperature of the tube. Matrix gas flowing over the other side of the membrane (i.e., around the tube) mixes with the emitted vapor to form a trace concentration mixture. For a stable component compound, the emis-

sion rate is extremely steady as long as there is visible liquid in the tube.
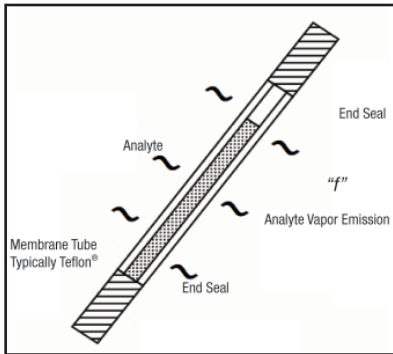

Figure 1. Typical Permeation Tube

To measure the emission rate, the tube is held at operating temperature in a steady flow of carrier gas and weighed periodically over carefully timed intervals. The rate of weight loss is the emission rate of the tube. If the temperature and weight loss measurements are traceable to NIST, then the emission rate is also traceable.

Using Permeation Tubes

Permeation tubes are extremely simple devices, and are very easy to use. Essentially one needs only to accurately control the tube temperature and the matrix gas flow to create a known, reproducible mixture. Careful attention to a few details in the instrument system, however, can greatly improve its overall utility. Figure 2 shows a flow schematic of an effective permeation tube blending system.

The flow path should provide a continuous, uninterruptible, fixed carrier flow over the permeation tube. With fixed carrier flow, the component concentration is steady and surfaces in the system equilibrate assuring rapid response while minimizing bias in the system. In the absence of carrier flow the permeation chamber and surrounding elements are quickly contaminated with a high concentration of component compound, so it is essential that the carrier flow be continuous.

It is also desirable to be able to isolate the permeation tube in the system by switching the carrier flow to vent. The matrix flow is then "zero

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gas" allowing an on-line demonstration that the system is clean and free of component contamination. This feature is essential when working with a non-zero matrix gas as described in the final section below.

The temperature of the permeation tube must be carefully controlled. The

emission rate from a liquid fed permeation tube typically varies about 10% per degree Celsius, so a stable operating temperature is essential for mixture accuracy and stability. Control to ± 0.1°C assures emission accuracy within ± 1%. Higher accuracy temperature control has limited value because other error sources then dominate the overall accuracy of the final mixture.

Measurement and control of the matrix gas flow is often the most significant error source, especially when the matrix is some gas other than nitrogen. Common practice is that flow meters are actually calibrated for nitrogen (or air), and accuracy is specified as a percent-of-full-scale reading. For example, a 5 l/min flow meter may show 5 l/min ± 50 cc/min (1%) at full scale, but at 0.25 l/min the accuracy is still ± 50 cc/min resulting in ± 20% error. Even more troublesome is using the flow meter for a non-nitrogen matrix. Common practice then is to apply a "flow factor," or correction factor to compensate for the physical characteristics of the matrix gas on the flow meter. The flow factor correction is based on the ratio of physical factors to those of nitrogen. The result is that the error band is no longer well defined.

Flow meters used for permeation systems should be calibrated at 5 or more points to assure ± 1% flow measurement accuracy of the full meter range. When used with a non-nitrogen matrix, the meter should be calibrated with the actual matrix gas.

The great strength of the permeation tube method is that the permeation tube itself solves the most difficult flow control problem—controlling the miniscule flow of a wide range of vapors used as component gases.

Creating Extremely Low Concentration Mixtures

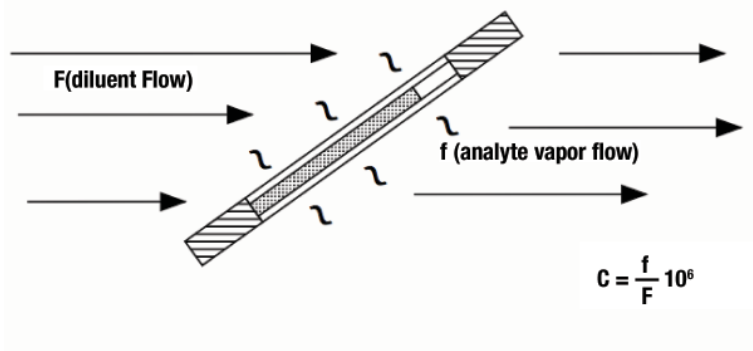Permeation tubes can be used to make concentrations that are quite low with single step dilution. For

$$C = \frac{f}{F} \cdot 10^6$$

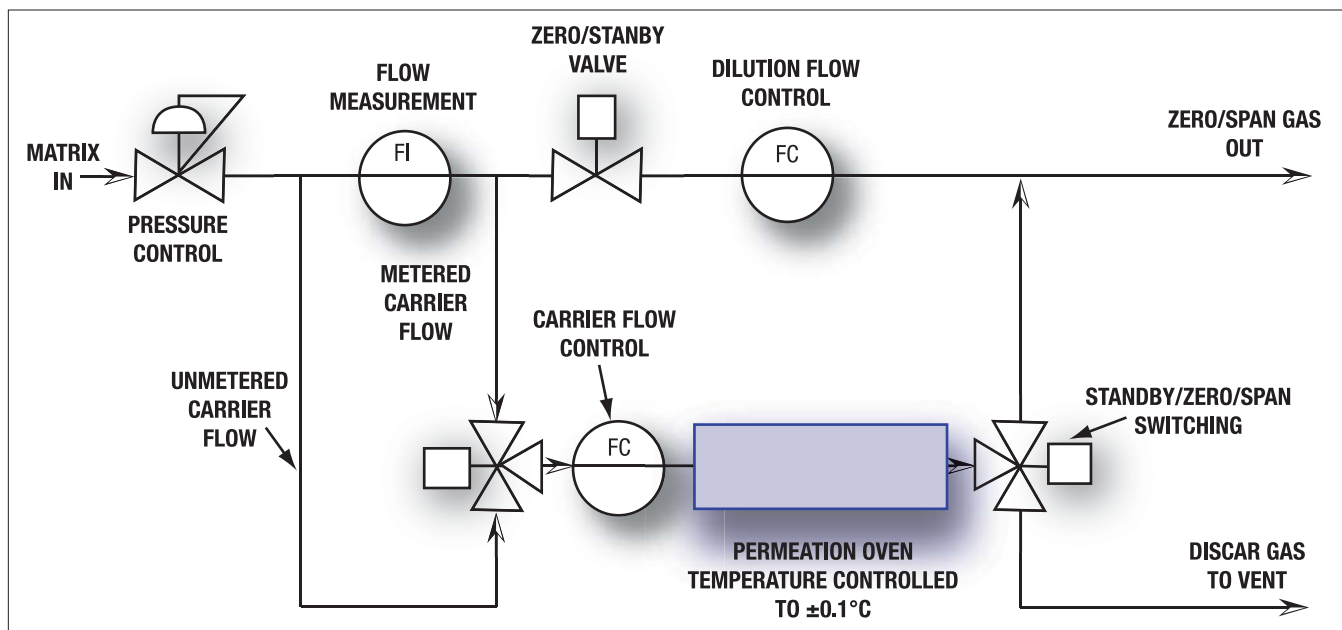*Figure 2. Schematic of an effective permeation tube blending system*

Figure 3. Typical Permeation System Flow

example, a tube emitting 50 nanoliters-per-minute (nl/min) mixed into 1 liter-per-minute creates a 50 ppbv mixture. Diluted into 5 l/min, the same emission gives a concentration of 10 ppbv.

Theoretically, one could choose a 1 nl/min tube and dilute it in 10 l/min to get a 100 pptv mixture (10^{10}:1 dilution) in a single dilution step. But, as with all great schemes, there are practical limits. With permeation tubes, the basic limit is the minimum emission rate that can be actually measured. As mentioned above, emission rate is usually determined by measuring the rate of weight loss. A typical disposable permeation tube weighs 10 – 15 gm, so the static weight is well within the range of a semi-micro balance (but beyond the 2 gm range of most micro-balances). The minimum readable weight change is 0.01 mg, and a weight change of 1 mg is needed to assure the possibility of measuring weight loss at ± 1% accuracy. For a 100 ng/min emission rate, the minimum interval between weighings is 7 days. At 10 ng/min the minimum interval is over 2 months! The minimum time for emission rate certification is then about 8 months.

Measuring extremely low weight loss rates is difficult even using a micro-balance. The problem then shifts to cleanliness and gas purity. During the certification process the Teflon membrane develops a static

charge, which attracts any particles in the sweep gas flowing over the tube during the emission measurement process. This introduces additional error. The practical limit for single stage dilution using permeation tubes is about 10^8:1.

Best practice is to use a secondary dilution step for lower concentrations. Figure 3 shows a secondary dilution system. Here, a small portion of the primary mixture (i.e., the mixture produced directly from the permeation tube) is split off and diluted into an additional flow of matrix gas. This method can give 10^3:1 to 10^5:1 additional dilution. Thus, single digit ppt mixtures can be prepared with only 2 dilution stages with a total matrix gas consumption in the 2 – 10 l/min range.

As concentrations go ever downward, the ultimate problem is often the purity of the matrix gas. Unknown background contamination can introduce large random errors.

Making Known Standards In A Non-Zero Matrix

The method of standard additions can be used to avoid the non-zero matrix gas problem. To use this method, first observe the detection system response to the matrix gas alone, i.e., the "zero addition response." Then add the permeation tube output to the matrix gas and observe the response due
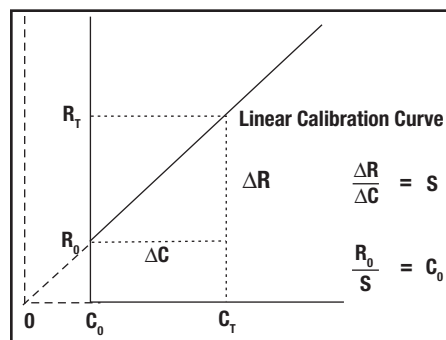

Figure 4. Calibrations by standard additions

to the added component compound. Since the concentration in the matrix is constant, several "standard addition responses" can be obtained by varying the matrix gas flow. Using the difference between two known addition responses, calculate the sensitivity of the system to the known addition.

$$S = \frac{\Delta R}{\Delta C}$$

where

ΔR is the change in detection system response, and

ΔC is the change in concentration due to the standard addition.

Apply this response factor S to the observed zero addition response R_0 and estimate the original background concentration C_0.

$$C_0 = \frac{R_0}{S}$$

Using this estimate of the background

concentration the calibration curve can be adjusted to more accurately reflect true concentration. Figure 4 illustrates this estimation graphically.

If only one standard addition is used the method assumes linearity of the response curve through zero. Generally, the error introduced by this assumption is small (at least compared to the error due to unknown background concentration). Multiple standard additions can be used to estimate response linearity or define nonlinear response curves. **G&I**

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