

Using Permeation Tubes to Prepare Trace Moisture Standards in Reactive Gases

Jim McKinley

Kin-Tek Laboratories, Inc., 504 Laurel St., LaMarque, TX 77568, U. S. A.

E-mail: jmckinly@kin-tek.com, FAX +1 409 938 3710

Abstract

The measurement of trace concentrations of water vapor in reactive gases has become very important in the semiconductor manufacturing industry. Techniques for measuring low ppm and ppb moisture in NH_3 , HCl, and other reactive gases have been developed, but producing standards for system calibration and data validation remains a problem.

Permeation tubes have proven to be an effective method for creating trace moisture standards in inert process gases such as nitrogen. This paper describes adaptation of the permeation tube method to produce trace moisture standards in reactive matrices.

Introduction

Trace moisture contamination is a serious problem in many high purity industrial gases, affecting yield and product quality in the chemical industry, weld integrity in the aerospace industry, and yield, product quality, and tool life in the semiconductor manufacturing industry. For inert gases measuring and calibration techniques are well developed.

Similarly, techniques have been developed for measuring trace concentrations of moisture in a variety of reactive gases. But none of these techniques is absolute. Additionally, at very low concentration levels, moisture monitoring systems in industrial applications are often non-linear. Calibration and frequent data validation are essential to successful monitoring in these applications.

Gas standards with known moisture concentration are required for effective calibration. Several techniques have been used for producing standards in inert gases such as nitrogen. Producing standards in reactive gases, however, remains a problem because standard techniques are not applicable in a reactive matrix gas. For example, the dewpoint/frostpoint method cannot be used because many of the gases condense at the temperatures required to get trace moisture concentrations. See Table 1. Additionally, many of the reactive gases are extremely soluble in water, so that even when temperature is not a problem the matrix will contaminate the water resulting in an unpredictable vapor pressure.

Another problem is establishing a "zero" reference. In the dewpoint/frostpoint method water vapor would be either added or removed to establish water concentration in the mixture. Other methods simply add water vapor to the preexisting concentration in the matrix. Reactive gases are much more difficult to purify than inert gases, so an effective calibration method must be able to deal with a non-zero reference point.

Permeation Tube Method

Permeation tubes have been shown to be an effective tool for dynamically blending trace concentrations of a wide range of gases and vapors in an inert matrix such as high purity nitrogen. With some adaptation this method can also be used to create trace concentration mixtures in reactive matrix gases.

A permeation tube is a device that uses the permeation of vapor through a solid membrane to produce a very small, very stable gas flow. Figure 1 shows a diagram of basic permeation tube. Essentially it is a length of Teflon® tubing with water sealed inside. Water vapor passes slowly

through the tube wall and into the surrounding atmosphere. Passing a known flow of clean dry gas over the tube adds the emitted water vapor to that flow. The water vapor emission rate is measured by measuring the rate of weight loss while the tube is held at operating conditions. Figure 2 shows the concept of using a permeation tube to generate a calibration mixture. The concentration generated is given by:

$$C = \left(\frac{f}{f + F} \right) 10^6 \quad 1$$

where

C is the concentration in ppm (v/v),
 f is the flow of water vapor,
 F is the flow of dilution gas.

Since the flow of water vapor is extremely small (nanoliters/minute) compared to the dilution gas flow (typically liters/minute), equation 1 reduces to

$$C = \left(\frac{f}{F} \right) 10^6 \quad 2$$

The flow of water vapor from the tube is given by:

$$f = K(T) \frac{A \Delta p}{t} \quad 3$$

where

f is the flow of water vapor from the tube,
 $K(T)$ is the permeability of the membrane tube as
a function of temperature,
 A is the surface area of permeation,
 Δp is the partial pressure difference of water vapor
across the membrane,
 t is the thickness of the membrane.

Typically a system is operated at a fixed temperature and choosing a tube with appropriate membrane area and thickness sets the moisture addition rate. Additionally, changing operating temperature can change the addition rate from any tube.

Design Considerations

There are three special problems associated with trace moisture calibration. First, it is practically impossible to obtain a true zero reference for moisture, so standards prepared by simply adding water vapor to a “dry” gas actually have unknown uncertainty. Second, water is very polar and interacts with virtually all materials. Thus a change in concentration may require a long stabilization time, and worse, changes in operating conditions may result in transient concentration changes. Third, water is pervasive in our atmosphere, so it is very difficult to prevent contamination of a standard (or sample) in the delivery process.

With reactive matrix gases the problems may be accentuated. Additionally, there are problems due to interactions between the matrix gas and the water source, and even with the water vapor itself. With permeation tubes the matrix gas can affect the output in three ways. First, if the matrix is very

soluble in the membrane material, the dissolved matrix gas may change the permeability of the membrane to water (or any other analyte component). Second, the matrix is also permeating backward through the membrane to the interior of the tube. If the matrix is very soluble in water its ever-increasing presence will lead to changes in water vapor pressure and thus, unstable emission rate from the tube. Finally, even if the vapor pressure of the water did not change, the flow of matrix into the tube would distort the rate of weight loss making it impossible to accurately measure the emission rate of the tube.

Flow Path Design

Figure 3 shows a flow diagram of a system that addresses the problems noted. The concept is to base calibration on the difference in analyzer response caused by the addition of a known amount of water to the matrix gas. Using the “standard addition” technique minimizes the “no zero reference” problem.

To circumvent the problems caused by interaction of the permeation tube with the reactive matrix, the system uses two flow paths. The water vapor is added to a flow of extremely dry, inert gas such as high purity nitrogen to form a primary mixture. A small flow of this primary mixture is added to a controlled flow of “dry”, reactive, matrix gas to form the final standard.

The dual flow path method is not new. This technique has been used extensively for adding oxygen sensitive organic compounds to ambient air. In the current application, however, the reactive matrix may actually interfere with the water vapor measurement. In this case, dilution of the reactive matrix may alter sensitivity of the method or result in a false analytical signal. To minimize this effect the design shown in Figure 3 allows the water vapor concentration to be varied while minimizing the inert gas dilution and keeping the dilution constant.

The primary mixture flow passes divides into two parts. A small carrier flow, typically about 0.1 lpm, goes through FC-2 and passes over the permeation tube where it picks up the emitted water vapor. This flow can either be added to the primary mixture or discarded to vent, thus allowing the primary mixture to be either “span” or “zero” gas.

The main portion of the primary mixture flow passes through flow controller FC-1 and out to vent through backpressure controller BPC-1. Typically this flow will vary from about 0.25 – 5 lpm. Varying this flow changes the primary mixture concentration over a 20:1 range. A small portion of the primary mixture is split off through FC-4 and mixed with the reactive matrix. Typically the FC-4 flow will be in the 0.01 – 0.1 lpm range. If the reactive matrix flow is in the range of 5 lpm, the resulting dilution with inert gas will be 2% or less.

Toggling the carrier flow in and out of the primary stream creates a step change in moisture in the mixture, and allows calibration under “zero” conditions that are identical to the “span” conditions.

To minimize the effects of trace water vapor adsorption effects, the flow components are heated and temperature stabilized, and mixtures are maintained under controlled backpressure.

Operation

In the design shown three distinct moisture concentrations are formed. The highest concentration is the base gas formed by passing the carrier stream over the permeation tube.

$$C_B = \frac{1.24E(\text{ng/min})}{F_2(\text{ml/min})} \quad 4$$

where

C_B is the base mixture concentration,
 E is the permeation emission rate in ng/min.
 F_2 is the carrier gas flow rate.

This concentration may range from about 12 to 2,500 times higher than the final concentration. Usually this concentration will be 50 to 500 times higher than the final concentration. Maintaining a relatively high concentration at this point is very advantageous, since this is the only point where atmospheric moisture leaking into the system is undetectable. Since the concentration here is high, small leaks become insignificant.

The second concentration is the primary mixture. By varying the primary flow the concentration of this stream can be varied. Typically, this concentration 10 to 100 times higher than the final concentration. The actual concentration here is the sum of the concentration created by the permeation tube emission and the background concentration in the high purity dilution gas.

$$C_P = C_B \frac{F_2}{F_1 + F_2} + C' \quad 5$$

where

C_P is the primary mixture concentration,
 C_B is the base mixture concentration
 C' is the background contamination in the gas,
 F_1 is the main primary dilution flow,
 F_2 is the carrier flow.

Since high purity gas is used for the primary dilution, one would expect that the background moisture concentration C' is very low and perhaps negligible. In any case it will ultimately be accounted for in the standard addition method.

The final concentration is the actual span mixture in the reactive gas.

$$C_S = \frac{1.24E}{F_2} \left(\frac{F_2}{F_1 + F_2} \right) \left(\frac{F_4}{F_3 + F_4} \right) + C_0 \quad 6$$

where

C_S is the final span mixture concentration,
 C_0 is the total background moisture concentration,
 F_3 is the dilution flow of reactive matrix gas,
 F_4 is the flow of primary mixture added to the span gas.

The reactive matrix gas should also be as dry a possible. The unknown background concentration can be estimated from the standard addition technique.

Calibration By Standard Addition

To use the standard addition method, first set the system to the “zero” state. Observe the analyzer response to the background moisture concentration in the matrix gas. This response is R_0 . Then set the system to the “span” state, and add a known amount of water vapor to the matrix gas. Allow the analyzer to stabilize and observe the response R . For a linear system, calculate the sensitivity factor S . See figure 4 for a graphical explanation.

$$S = \frac{\Delta R}{\Delta C} \quad 7$$

The term ΔC is the concentration added from the permeation tube. The background concentration, C_0 can then be calculated.

$$C_0 = \frac{R_0}{S} \quad 8$$

Substituting this value for C_0 into equation 6 gives an improved estimate of span gas concentration. For nonlinear systems several standard additions must be made and the sensitivity function estimated from that data.

Table 1 Properties of Some Common Reactive Compounds

Compound	Boiling Point (°C)	Solubility (wt. %)
Ammonia	- 33.35	42.8
Arsine	- 62.5	0.09
Carbon Dioxide	-78.5	
Chlorine	-34.	0.73
Ethylene	-103.7	0.03
Hydrogen Bromide	-66.8	49.
Hydrogen Chloride	-85.	82.3
Nitrogen Trifluoride	-129.	<i>i</i>
Phosphine	-87.7	0.04
Propylene	-47.7	0.08
Silane	-112	<i>i</i>

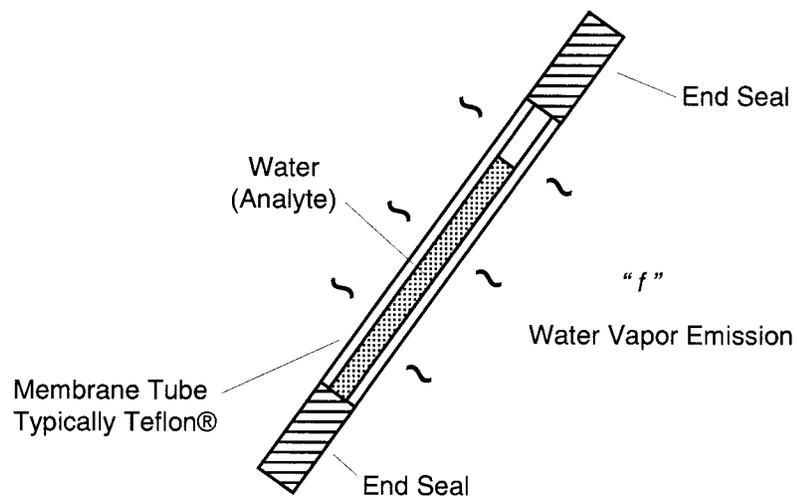


FIGURE 1
DISPOSABLE PERMEATION TUBE

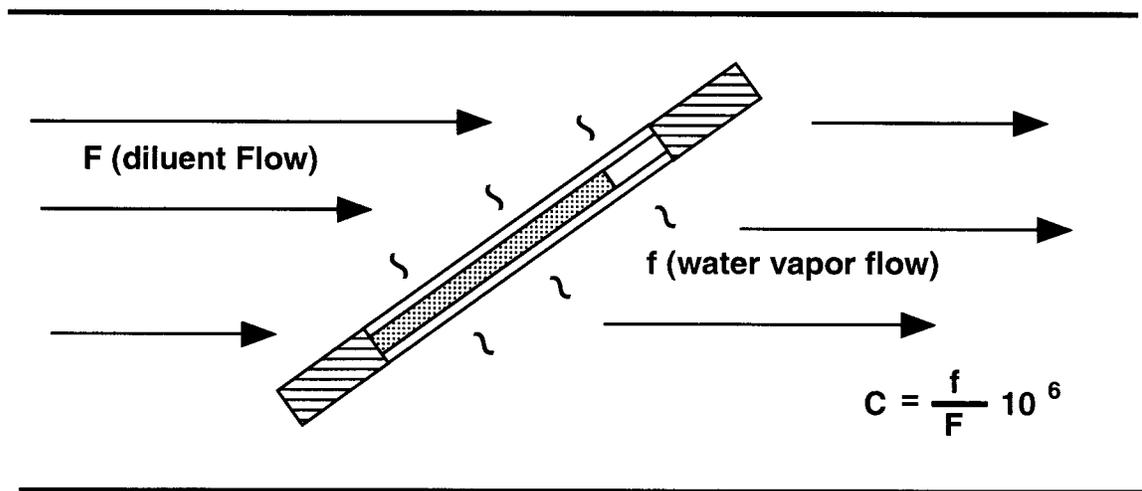


FIGURE 2
USING A PERMEATION TUBE

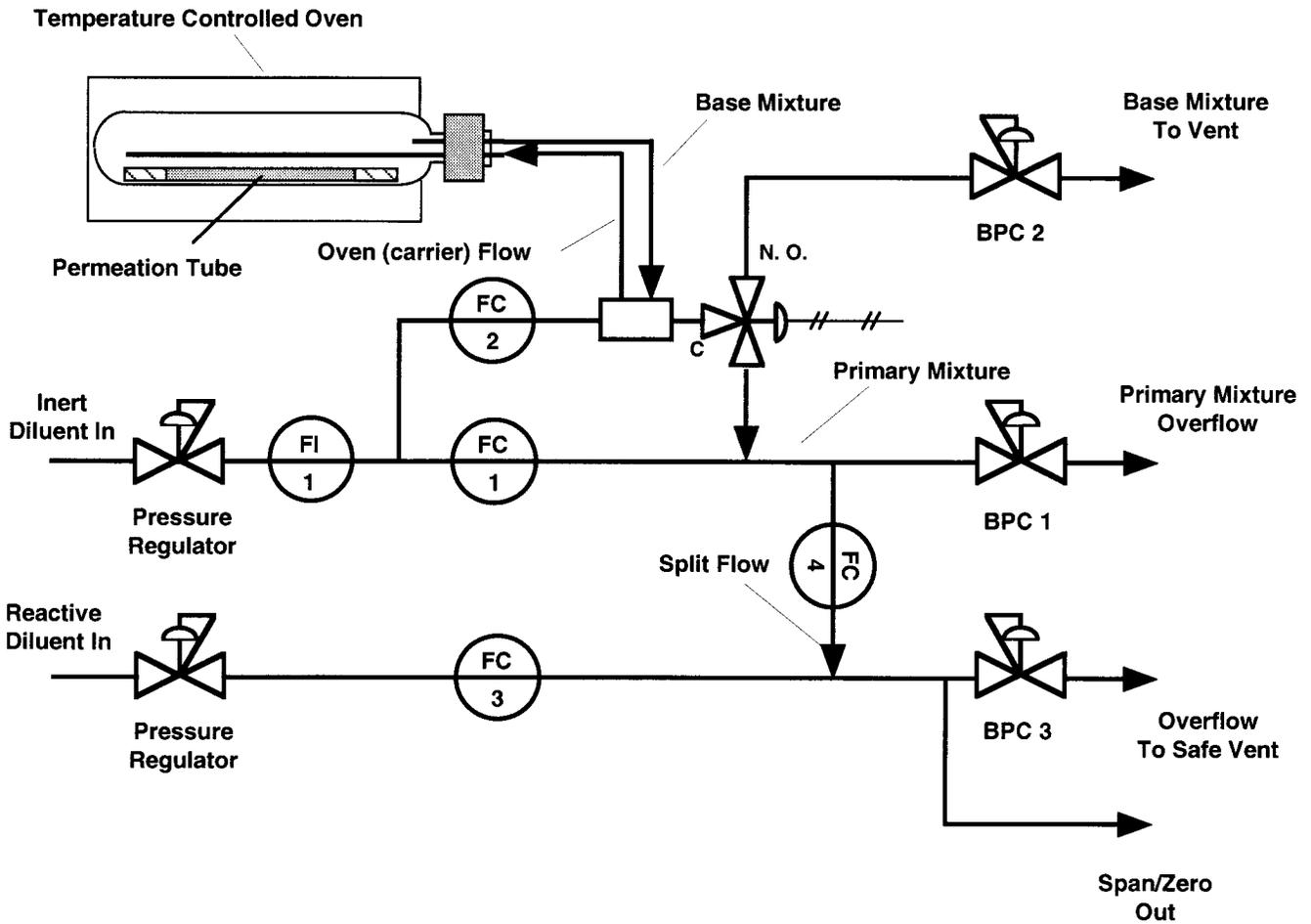
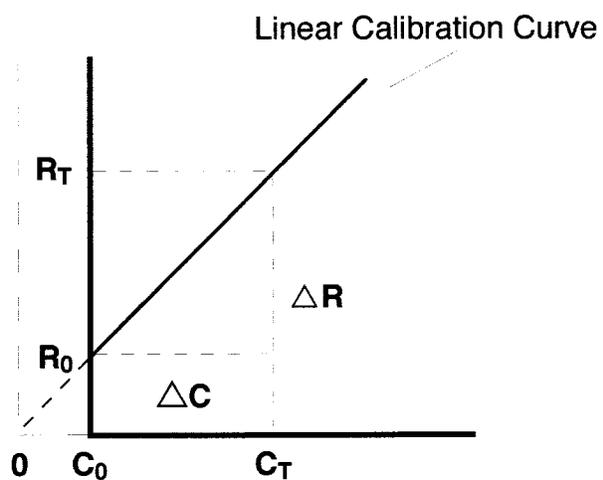


FIGURE 3
FLOW DIAGRAM
SYSTEM FOR ADDING TRACE MOISTURE TO A REACTIVE MATRIX



$$\frac{\Delta R}{\Delta C} = S \text{ (System Sensitivity)}$$

$$\Delta R = R_T - R_0$$

$$\frac{C_0}{R_0} = \frac{C_T}{R_T} \text{ (for linear response)}$$

$$C_0 = \Delta C \frac{R_0}{\Delta R} = \frac{R_0}{S}$$

$$C_T = C_0 + \Delta C$$

FIGURE 4
CALIBRATION BY STANDARD ADDITIONS