

ADDING RELATIVE HUMIDITY TO TRACE CONCENTRATION GAS STANDARDS IN A PERMEATION SYSTEM

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ABSTRACT

Gas sensor sensitivity levels have increased in equipment where atmospheric conditions, such as relative humidity, directly affect test results. Calibrating for changes in relative humidity in trace level gas concentrations has generated the need for effectively adding relative humidity to the output gas of a permeation system. There are several techniques available for adding known levels of humidity to pure gas streams, but those techniques do not directly apply to the dynamics of a permeation system.

Specific factors have to be considered for controlling broad ranges of relative humidity in varying dilution gas streams without compromising the concentration of other analytes in the output of the permeation system. Relative humidity can be added to the calibration gas stream without affecting the final concentration requirement by incorporating a module that utilizes a split-flow technique with variable pressure control and variable flow control. This module can be used in different permeation system scenarios or bypassed when a dry calibration gas is needed.

INTRODUCTION

The requirement to calibrate for ppb concentration ranges of gas mixtures in a matrix containing percent levels of relative humidity has become crucial in many industries (1). The nanotechnology, pharmaceutical, and semiconductor industries have quality issues and must test

for trace gas contaminants in the presence of varying relative humidity (2, 3). A problem arises when humidity interferes with the analysis. Typically, the humidity either gives a false response or it effects detector sensitivity. Calibration must be done in the presence of humidity, in either case.

Many methods for creating relative humidity in air or nitrogen gas streams are available, and are extremely useful for calibrating humidity sensors and hygrometers directly (4,5). However, none of these methods apply to adding humidity to calibration gas mixtures containing trace level analyte concentrations. Generally, contact of the trace concentration calibration mixture with the moisture source results in loss of the trace analyte.

Permeation systems are known for producing accurate gas standards at low concentrations. An effective means of calibration is creating standards that closely parallel real analysis. Generating humidity in a permeation system satisfies the need for trace gas calibration with humidification if done without compromising the calibration gas. This paper reviews current methods used for creating relative humidity, the factors involved in humidifying a calibration gas stream from a permeation system, and explains an effective technique for adding humidity to the output of a permeation system.

METHODS OF CREATING RELATIVE HUMIDITY

Relative humidity (RH) is expressed as a percentage and is the ratio of the amount of water vapor present in air to the amount of water vapor that could be present in air at saturation (6,7). Common methods for generating specific relative humidity values include saturated salt solutions, split flow or divided flow saturation chamber, two-temperature humidity generator, two-pressure humidity generator, and the bubbler method (8-12). A short description of each method provides background for a technique that works with a permeation system.

SATURATED SALT SOLUTIONS

Lewis Greenspan reported data related to this method for different salt solutions (8). A closed chamber is partly filled with a saturated salt solution to generate relative humidity. Depending on the amount of relative humidity required different salts are saturated in water (8,9). This method is reported to be effective in calibrating humidity sensors (8), but limitations restrict applying it to a flowing calibration gas stream such as a permeation system (12).

SPLIT FLOW OR DIVIDED FLOW SATURATION CHAMBER

A dry air or nitrogen stream is split into two flows. One flow goes through a saturation chamber where it is saturated with water vapor and the other flow remains dry. Relative humidity is adjusted by accurately adjusting the mixing ratio of the two air streams in a measuring chamber with a mass flow controller. A humidity sensor inside the chamber measures percent relative humidity. (9-11) This technique can be useful if controls are accurate and it can be applied to a flowing calibration gas as created with a permeation system. A key factor with this method is that the split flow ratio and the total moisture in the humidified portion determine the maximum

RH attainable in the final mixture. Higher RH can be obtained by elevating the saturation temperature of the humidified portion. Another key factor in working with a permeation system is that the total flow is varied to adjust the concentration. Thus the problem of split ratio constraining the maximum RH is further complicated by the need to also vary the total flow.

TWO-TEMPERATURE HUMIDITY CHAMBER

Vapor saturated air or nitrogen is cooled in a chamber to the dew point temperature corresponding to the desired relative humidity. Excess vapor is condensed and the vapor partial pressure equals the saturation partial pressure. Saturated air is heated get the vapor partial pressure corresponding to the desired RH. Two to three chambers are needed to perform this method and precise temperature control is required (9).

TWO-PRESSURE HUMIDITY GENERATOR

Dry air or nitrogen is saturated at a given pressure and temperature and then isothermally brought to chamber pressure to produce known humidity levels. The advantage is the result relies on the measurement of pressures and temperatures within the chamber and not on the direct measurement of water vapor. However, inaccuracies in temperatures and pressures cause reliability problems and there are long stabilization times (9,13).

THE BUBBLER

This method simply uses air or nitrogen bubbled through water to create a level of humidity based on ambient or measured conditions. A humidity sensor is usually placed inside the humidifying area to verify relative humidity. The flow rate of air, bubble size and temperature determine the resulting RH. This works fine if using only clean air or nitrogen and if accuracy and stability of RH are not extremely important. Soluble analytes will dissolve and be lost from the final mixture if the calibration gas mixture is bubbled through water.

Each method previously described may be appropriate for creating levels of humidity depending on the specifics of the application, but limitations in some prevent them from being useful with a permeation system (or other calibration gas source).

TYPICAL PERMEATION SYSTEM

Typically, a basic permeation system consists of an oven chamber with accurate temperature control, a flow-measuring device or a flow meter, flow controllers, and the permeation tube or tubes as seen in Figure 1. The permeation tube is placed inside the oven chamber and held at a constant temperature (14). The permeation tube emits (or permeates) pure analyte gas at a steady rate called the emission rate. The manufacturer establishes the emission rate of the tube, usually by a weight loss method and reports it in a unit such as nanograms per minute. Slight changes in temperature directly affect the emission rate of the tube, so temperature stability is crucial. An inert carrier gas such as nitrogen or air picks up the analyte emitting from the permeation tube and combines it with metered dilution gas to carry it out of the system for use as a calibration gas (15).

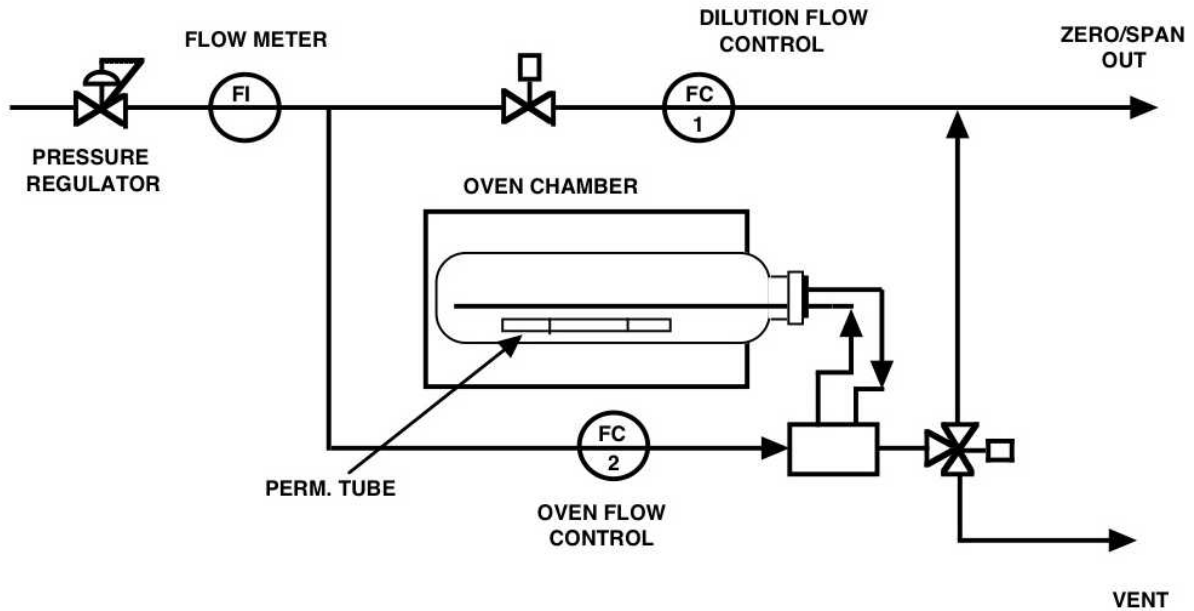


FIGURE 1 – PERMEATION SYSTEM FLOW DIAGRAM

Figure 2 shows the emission rate of the tube (f), along with the metered dilution flow rate (F), which is used to calculate the final concentration (C). Assuming the oven temperature is stable, the rate of dilution flow determines the final concentration value of the calibration gas stream.

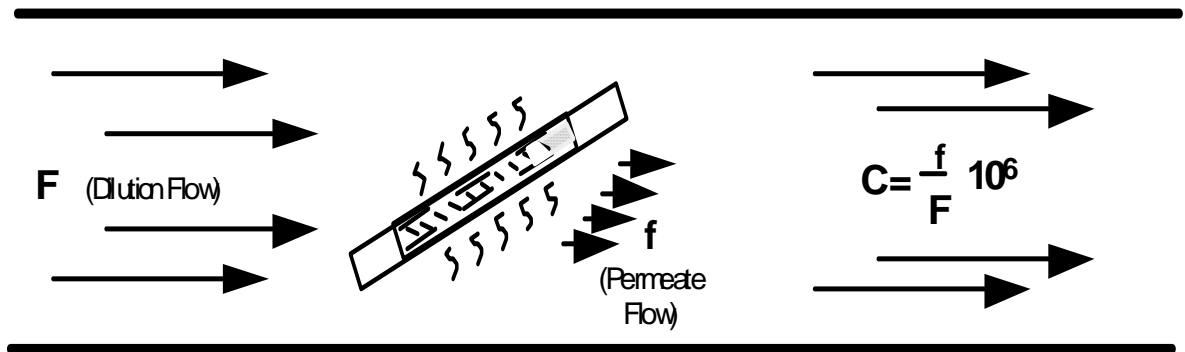


FIGURE 2 – OPERATION OF A PERMEATION TUBE

Increasing dilution flow decreases calibration gas concentration, and decreasing dilution flow increases concentration. Any inaccuracies in metered flow or any leaks in the permeation system can cause discrepancies in the final concentration values (15).

HUMIDIFICATION MODULE

When a calibration gas is created using permeation tubes, the total dilution flow determines the final mixture concentration. Adding RH must be done without affecting the desired concentration. Also, dilution gas passing over the permeation tube must be dry and clean. Factors such as pressure and temperature must be measured and noted for calculating the final RH when the water vapor is added.

A humidification module has been designed to work with a typical permeation system so that humidity can easily be added to a span mixture. The modular design allows for easy installation to existing permeation systems. Total dilution flow is split between the permeation system and the humidification module. One portion of the clean, dry dilution flow goes over the permeation tube and mixes with the emitted analyte. The other portion goes directly to the humidification module, is saturated with water vapor and then recombined with the analyte portion to form the final mixture. There is no contact of the analyte gas with liquid water. Varying the ratio of the wet/dry dilution gas or adjusting the saturation pressure adjusts the relative humidity level in the final mixture (16).

SYSTEM DESIGN

Figure 3 shows a flow diagram of the humidification module connected to a typical permeation system. Dry dilution gas is regulated to 50 psig as it enters the permeation system and subsequently is split twice. Figure 3 shows that the first split (S1) in the dilution flow provides enough flow to carry the emitted permeation tube gas from the oven and combine it with metered dilution flow for generating the calibration gas concentration. The second split (S2) provides dry dilution gas to the adjacent humidification module for saturation. Dilution flow entering the humidification module during operation passes through a mass flow meter and is controlled before entering a pre-heater. A pre-heater raises the saturation temperature of the dilution gas and supplies heat for surface “evaporation” of the permeating water. A highly permeable membrane immersed in water saturates the preheated dilution flow with water vapor. A water reservoir and pump system supply water to the saturator and prevents the saturator from becoming dry or damaged. A variable backpressure regulator adjusts the saturation pressure to provide additional control, and an inline pressure transducer measures the saturation pressure. Humidified gas combines with the dry analyte bearing portion and exits as humidified calibration gas. A humidity/temperature sensor in the mixing chamber monitors the final RH of the mixture (16).

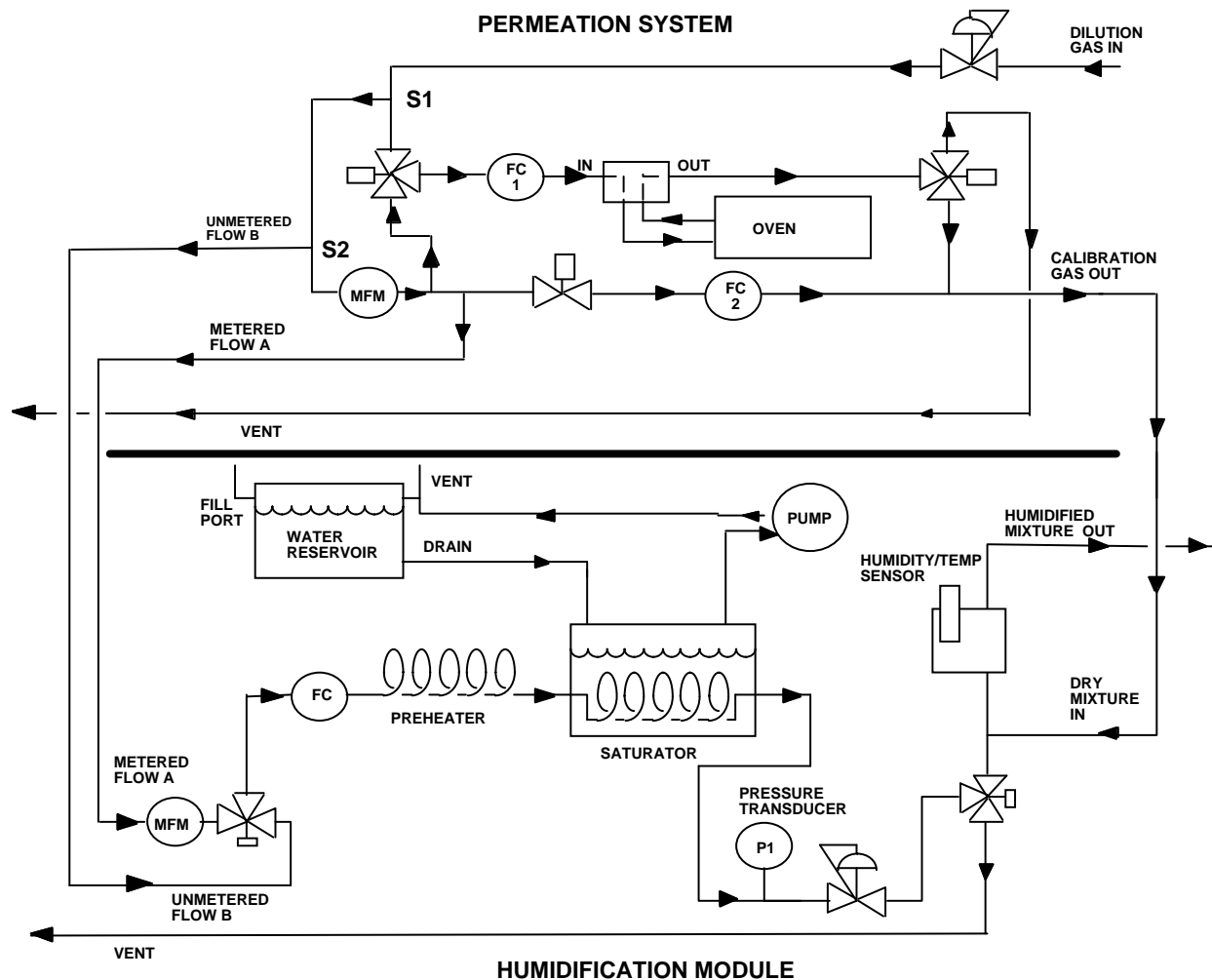


FIGURE 3 – FLOW DIAGRAM OF PERMEATION SYSTEM CONNECTED TO HUMIDIFICATION MODULE

The amount of dilution flow sent through the saturator is added back to the final calibration gas. Total dilution-flow and pressure settings needed for a specific RH depend on total flow required to achieve calibration gas concentration from the permeation system. Calculation of total dilution flow requires calculation of the split flow needed for the dry portion of the dilution gas and calculation of the split flow needed for the humidified portion of the dilution gas (16).

When a disposable permeation tube is used, the calculation for total dilution flow (F_T) required to achieve a specific calibration gas concentration from the permeation system is as follows:

$$F_T = (E \times K_o) / C \quad (1)$$

Where F_T = Total dilution flow (cc/min)

E = permeation tube emission rate (ng/min)

K_o = factor specific to the analyte compound in permeation tube

C = desired concentration of calibration gas (ppmv)

Once the total dilution flow is determined, calculate the amount of dry calibration gas flow required from the permeation system (F_{dry}), and the portion of flow that will be sent through the saturator in the humidification module (16).

$$F_{dry} = [1 - (\%RH \times P_w) / 100 (P_d)] F_T \quad (2)$$

Where F_{dry} = permeation system mass flow meter setting (cc/min)

$\%RH$ = desired relative humidity value

P_w = vapor pressure of water in mmHg at reference temperature (17).

P_d = delivery pressure reference for the $\%RH$

F_T = total dilution flow value calculated from equation (1) in cc/min

The amount of flow sent through the humidification module to achieve desired $\%RH$ is calculated as:

$$F_H = (\%RH / 100) F_{dry} \quad (3)$$

Where F_H = humidification module mass flow meter setting (cc/min)

$\%RH$ = desired relative humidity value

F_{dry} = value calculated from equation (2) in cc/min

A multi-channel switch displays four parameters on the humidification module; 1) The gas temperature ($^{\circ}C$) before it exits the system, 2) percent RH of the final mixture at that temperature, 3) the saturation pressure (psig) and 4) the metered flow of saturated dilution gas (liters/min). Each of these parameters is important for realizing the $\%RH$ at given conditions. The gas temperature and relative humidity readings are taken before the humidified gas exits the module. Adjustments of F_H and F_{dry} are possible for adjusting the relative humidity as well as varying the calibration gas concentration. Adjusting the saturation pressure also adjusts the relative humidity without affecting the final calibration gas concentration (16).

DESIGN CONSIDERATIONS FOR THE HUMIDIFICATION MODULE

Calculation of $\%RH$ is performed using equations (1-3) based on parameters measured within the system. The RH value produced is the RH at “module conditions” which may be different from “application (delivery) conditions”. It is important to correct to delivery conditions, as needed. The humidification module relies on manual adjustment for changes in flow and pressure, and manual calculation of final $\%RH$ making it a very “hands-on” system. Fluctuations in laboratory temperature results in RH drift, so it is important to monitor the instrument readout regularly and adjust as required to maintain delivery conditions. Regulating

gas temperature and measuring humidification and temperature at the point of gas analysis will help, but can be cumbersome.

The addition of a pump to the humidification module was an upgrade from an earlier design and proved to be essential for stable operation. Circulating the water sweeps gas bubbles from the permeation tube surface, avoids air bubbles in the water lines, and prolongs the life of the saturator. It also helps stabilize temperature drift due to the heat vaporization losses in the humidification process. The water reservoir is heated but the temperature is not controlled. Water temperature affects the RH output, so controlling water bath temperature and/or regulating water level may improve RH stability. The stabilization time of the humidification module is 2 to 4 hours. The time is not an issue since permeation tubes need to equilibrate within a permeation system, but any broad changes in %RH may take some time to stabilize during calibration procedures.

An upgrade to the humidification module design has recently been made for a larger based permeation instrument. The system is computer controlled and performs calculations through integrated software based on sensor feedback flow control. The upgraded design can be operated remotely and allows users to set up calibrations of extensive or simple calibration gases at various concentration levels. Humidity can be added or bypassed without manual adjustment at each level. The humidification system design is custom built inside a large multi-oven permeation system and at this time is specific to that system only. Tests are being conducted on the performance of the feedback control in relation to the overall permeation system and data is inconclusive at this time.

CONCLUSIONS

An add-on module for adding humidity to trace concentration mixtures from a permeation system has been designed. The humidification module is capable of adding up to 80% RH over a wide flow range and up to 90% for a restricted range. The split flow – remixing design of the humidification module makes it possible to humidify calibration gases of highly soluble compounds at ppb concentrations that would be lost in contact with water. Preheating the dilution gas and circulating the water proved essential to stable operation. A computer controlled version has been designed and tested, but is only available for use in conjunction with a much larger permeation system.

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