

ADDING HUMIDITY TO TRACE CONCENTRATION GAS STANDARDS

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ABSTRACT

A key, but often overlooked, factor in the behavior of gas sampling & measuring systems is the effect of relative humidity (RH) on performance of the system. RH can have a significant effect on the sensitivity and stability of a sensor system. Even for sensors that are not sensitive to RH, the RH level may affect the efficiency of sample delivery to the sensor. Systems sampling ambient air should be calibrated with standards that simulate ambient air.

This paper discusses the various techniques for adding humidity to trace concentration gas standards without compromising the accuracy of the standard.

INTRODUCTION

Humidity is often a key player in analyses. It may affect measurement sensitivity, offset measurement values, affect peak location in chromatograms, or interfere with the actual measurement. Analytical methods for samples that may contain humidity generally include some method of eliminating humidity, or at least controlling the sample humidity. But what is the effect if that methodology is not working properly?

The most effective approach is to make multiple calibration checks using the same concentration calibration gas, but with different levels of relative humidity (RH). However, creating humidified mixtures without disturbing the trace concentration is not easy.

If there is contact with liquid water, or condensation, any soluble component will be lost to the water. An original known concentration can be diluted with a saturated diluent to avoid contact with liquid, but then one must be able to maintain that concentration while adding different levels of humidity. With dynamic dilution systems, the problem is further complicated by the need to work at extremes of both total flow and RH simultaneously.

A BRIEF REVIEW: WHAT IS %RH?

Relative humidity - %RH - is the ratio of the partial pressure of water in a mixture to the vapor pressure of water.

$$\%RH = \frac{P_{(water)}}{Vp_{(water)}}(100)$$

P is the partial pressure of water in the gas

Vp is the saturation vapor pressure of water

Obviously, %RH depends on both the temperature and pressure of the gas. We work with %RH because it represents what is actually happening in the mixture.

It also illustrates why a cylinder gas mixture will always be 'dry'. For a cylinder with 2000 psig and saturated at 22°C, the water content of the gas is only about 0.02%, or about 0.5%RH. At 50 psig cylinder pressure the water content will be 0.8% or about 20%RH, but the %RH in the cylinder will remain 100%.

ADDING MOISTURE TO A MIXTURE

There are two fundamental methods for adding water to the mixture without the mixture contacting the liquid water; Direct Injection of vapor or microscopic droplets and the Divided Flow technique where a clean diluent is saturated and mixed with the dry flow of mixture.

Direct Injection

The direct injection technique is very useful concept if there is no way to use divided dilution flow. One might nebulize water to create micro droplets and vaporize them. This requires controlling microliters/minute water flow, Alternatively, steam could be used and added as a gas. But if the 'steam' approach is used one must maintain an elevated temperature (above 100°C) and then be able to adjust and control steam flow rates of only a few cc/min. This is practically impossible, especially over a wide range of flow and %RH values.

A relatively new technique using 'inkjet printer technology' does show promise. Here the dry trace concentration standard flows past an inkjet type nozzle where water is introduced and vaporized. By varying the introduction rate the %RH can be varied over a wide range. Currently this method is limited to low flows, but it does show promise.

Divided Dilution Flow

For applications involving trace concentration mixtures there is usually a need to further dilute a primary mixture. In this case our interest is primarily permeation tube standards, so the divided dilution flow method was chosen. In the permeation tube method, component vapor is emitted from the tube at a constant rate. That vapor is mixed with a dilution gas to form the gas standard. Adjusting the flow of dilution gas sets the concentration. By dividing the dilution flow before addition of the component, one portion of the dilution gas can be saturated with water vapor with no contact of the component with liquid water. Rejoining the streams creates a humidified standard. Humidity can be adjusted by adjusting the split ratio. A schematic of the method is shown in Figure 1 below.

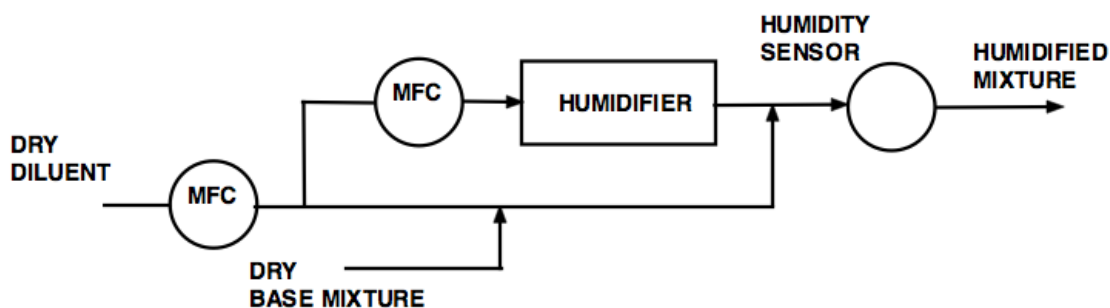


Figure 1
DIVIDED FLOW METHOD

FORMING THE SATURATED STREAM

Having chosen the divided dilution flow method the question becomes “how to saturate the wet stream?” Three methods are available; bubbling, headspace saturation, and permeation.

Bubbling

Bubbling is a simple sounding technique that is difficult to actually operate. The gas to be saturated bubbles through water held at the desired saturation temperature and presumably exits as a saturated gas. The first problem is in the bubbling process. As flow is increased to raise the final %RH the bubbling is more violent and entrainment of droplets becomes an issue. Additionally the effective contact varies with the depth of water in the saturator. This leads to the question, “what is the actual saturation

temperature?" It is advantageous to use both elevated temperature and pressure in the bubbler.

The second problem is in delivering the gas. It must be kept above the saturation temperature and not subject to any pressure fluctuations. Those problems are common to all methods, but more serious with bubblers because of the direct involvement with the water. Finally, a small error in operation or application can lead to flooding the entire system.

Headspace Saturation

Headspace Saturation is also a popular technique and works very well. This technique creates a laminar flow over the surface of the water. Surface cooling from evaporation is a key problem, especially at high flow rates, so the water must be heated and constantly stirred.

Both the bubbling and headspace saturation techniques have the advantage that the final %RH at target conditions can be theoretically calculated from the saturation temperature and pressure and the final mixing ratio of wet-to-dry gas.

Permeation

In the permeation saturator the liquid water is separated from the gas by a membrane that is extremely permeable to water. Since there is no contact with the liquid there are no problems of entrainment or flooding the system. As with other methods, the saturation temperature must be controlled. The gas is preheated to supply the heat of vaporization.

A key factor with the permeation technique is that the saturator must be sized to fit the application. The membrane limits the flow of water, so if it is too small it will not be able to supply enough water to saturate the gas and the final %RH will not be achieved.

ADDING ADJUSTABILITY

The %RH of the final mixture can be adjusted by three means: changing the wet-to-dry gas flow ratio, adjusting the saturation temperature of the wet gas, and adjusting the saturation pressure of the wet gas. Examining each of the factors we find that all of them must be used to generate a wide %RH range in the varying total flow rates expected.

Using Wet/Dry Flow Ratio

Using the divided flow technique, one must first find the total flow required. Then, the %RH is set approximately by adjusting the portion of that dilution flow that is saturated. The problem then becomes the rangeability of the flow control devices.

For example, if we use a saturation temperature of 22°C and have a flow controller range of 5lpm, then the minimum controlled flow is about 250 ccs per min. Suppose we decide to make a mixture containing 90% RH at 5lpm total flow. There will be no problem. The wet gas flow required will be about 4500 cc/m and the dry gas about 500 cc/min. But if the total flow is only 1000cc/min we would need 900cc/min wet flow and only 100cc/min dry flow – well out of the flow control range.

The highest %RH possible for the 1lpm case is 75%. The lowest total flow for which we could add 90%RH would be 2500cc/min with 22°C saturation. In this case the dry gas flow sets the limit. The effect is similar at low %RH values but the wet gas flow becomes the controlling factor.

Using Saturation Temperature

Table 1 below shows the vapor pressure of water at various temperatures.

°C	mmHg	°C	mmHg
20	17.546	31	33.730
21	18.663	32	35.700
22	19.841	33	37.769
23	21.085	34	39.942
24	22.395	35	42.221
25	23.776	36	44.613
26	25.231	37	47.121
27	26.763	38	49.750
28	28.376	39	52.506
29	30.071	40	55.391
30	31.855		

Table 1
VAPOR PRESSURE OF WATER

From Table 1 it is clear that at an ambient temperature of 23°C and a saturation temperature of 20°C one could never get above about 80%RH. Additionally, since the flow rate requirement for saturated gas varies substantially, and heat must be added to supply the heat of evaporation, there is always the possibility that the wet gas flow will not be completely saturated.

Raising the saturation temperature solves these problems and also shifts the limiting rates to higher values. Operating around 30°C is the optimum range for most applications.

Using the above example, but with (approximately) 30°C saturation temperature one could expect:

At 90%RH (at 22°C) in 5000cc/min

$$\text{wet flow} = (20/30)(0.9)5000 = 3000 \text{ cc/min}$$

$$\text{dry flow} = 5000 - 3000 = 2000 \text{ cc/min.}$$

and at 1000cc/min

$$\text{wet flow} = (20/30)(0.9)1000 = 600 \text{ cc/min}$$

$$\text{dry flow} = 1000 - 600 = 400 \text{ cc/min}$$

All flow rates are in range and the minimum total flow is now ~600 cc/min.

At 20%RH the calculation is similar but we go below the flow range for wet gas when at the 1000 cc/min total flow.

Saturation Pressure Control

The third control on %RH is the pressure at which the gas is saturated. Doubling the saturation pressure reduces the amount of water in the wet gas by one half. Gas saturated at 30°C at atmospheric pressure contains about 4% water. Raising the saturation pressure to 14.7psig reduces the concentration to 2% water.

Using the pressure control is a convenient way to fine tune the humidity in the final mixture and also allows humidity-total flow combinations that could not otherwise be obtained. Changes in saturation pressure are seen immediately, whereas changes in saturation temperature may require hours.

Figure 2 shows a schematic of a system incorporating the elements discussed above.

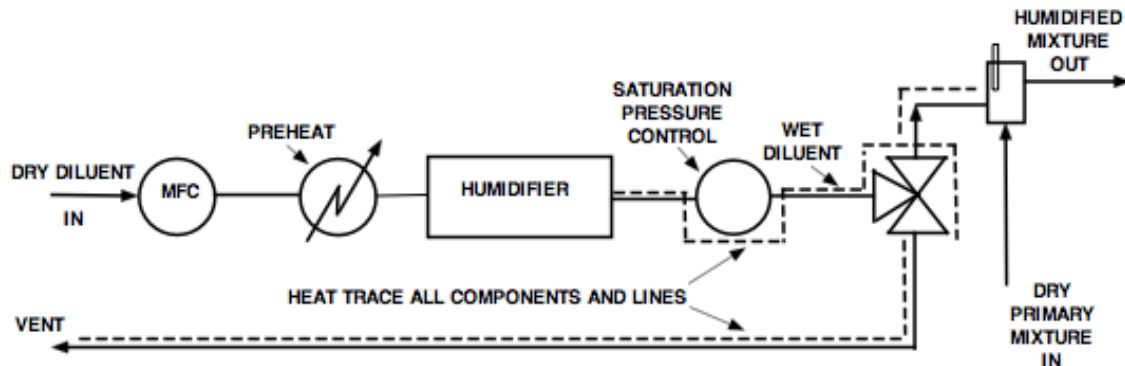


Figure 2
HUMIDIFIER FLOW DIAGRAM

STABILIZING THE MIXTURE

To maintain stability the saturated gas must be held above the saturation temperature until mixed with the dry gas. Furthermore, all components in the flow path must be heated. One cool tube fitting can cause condensation and result in inability to control the %RH.

It should be noted that the temperature of the humidified mixture will always be above ambient, and the %RH observed at the instrument outlet will be the %RH at that temperature. For example, suppose 90%RH at 22°C is desired and actually created. But if the temperature of the exiting gas is actually 27°C where the %RH measurement is made, it would be indicated as 67%RH. For best results the %RH measurement should be made as near the application temperature as possible.

A specific %RH can be created manually by setting the three controls. But since the controls are interactive and there are so many factors that affect %RH it is far better to put humidification under computer control. By sensing at the application one can assure that the desired value is actually being delivered to the application.

CONCLUSIONS

Adding humidity to trace concentration mixtures requires keeping the trace components free of any contact with liquid water. The most convenient way to add humidity is to dilute a base mixture with already humid gas. Using 30°C saturation temperature for the diluent is optimum for most applications. Controlling the saturation pressure extends the range and is convenient for fine tuning and controlling %RH.

Adding humidity, and particularly automating humidification is one of the most difficult jobs in creating trace concentration gas standards that simulate actual samples.

