Chilled Mirror Hygrometry, a Technology for Process and Lab

By Dr. Gerald Schultz

Abstract

Of all the instrumental methods for measuring the water vapor content of gases, chilled mirror hygrometry (CMH) is one of the most useful owing to its inherent accuracy, unparalleled wide dynamic range, ease of operation, and low maintenance. For instance, the dynamic range of CMH technology spans six orders of magnitude from 0.1 ppm to over 100,000 ppm with an accuracy of 1% or better. Since the chilled mirror hygrometer employs a platinum resistance thermometer (PRT) to measure the saturated vapor pressure of water, the measurement can be made traceable due to the known stability and lack of hysteresis of PRTs. This is especially important in critical industrial processes involving humidity in gases. CMH can be designed using chemically resistant materials when it is to be deployed in corrosive environments. The article will describe how the measurement of dew/frost point is made by the chilled mirror hygrometer and how other humidity related quantities such as relative humidity, and mixing ratio can be calculated using the dew/frost point along with gas temperature and pressure. The preferred humidity unit is application specific. Finally, the article will discuss how a chilled mirror hygrometer can be used in conjunction with a humidity generator to measure and control the humidity of lab gases. This system can then be used to calibrate secondary humidity sensors such as polymer and inorganic oxide- based sensors, which are subject to drift and therefore not strictly traceable due to a broken chain of measurements and associated uncertainties.

Introduction

The humidity content of a gas is a critical measurement and control parameter in many industrial processes and laboratory operations. This is because of the anomalous phase and chemical behavior of water i.e., an unusually high boiling and melting point for its molecular mass, as well as its ability to chemically react with key industrial gases, generating acids and bases such as hydrogen chloride, hydrogen fluoride, ammonia, carbon dioxide, nitrogen dioxide, hydrogen sulfide, sulfur dioxide, and sulfur trioxide. This behavior can lead to mechanical and corrosion damage to process equipment, and alteration of chemical process parameters with the attendant loss of production quality and throughput.

There are various technologies available to measure the humidity of gases, and they fall into two general categories. The first measures the inherent physical properties of water like optical extinction coefficient, electrolysis current, and saturated water vapor. Examples of such technologies include spectroscopy (as in TLDS, CRDS), coulometry (using phosphorous pentoxide), and optical chilled mirror, respectively. The second type of technology measures the reversible interaction of water vapor with an hygroscopic material followed by the change in the bulk electrical or other property. This type of technology is not readily traceable because the hygroscopic material is subject to changes leading to drift in the sensor's standard response function and therefore a broken chain of measurements with its associated uncertainties. Such sensors are also subject to hysteresis, which degrades system accuracy. Examples include polymer humidity sensors, and oxide humidity sensors ,for exmple, aluminum oxide and silicon oxide. These humidity sensors have the advantage of relatively lower cost and can therefore be deployed at multiple locations along the process line, which is a distinct advantage when process lines are long with many valves and supply ports, typically found in electronic fabs, and industrial and natural gas facilities.

Of the fundamental measuring means, chilled mirror hygrometry (CMH) is the most versatile owing to its exceptionally large dynamic range of measurement e.g. (0.1 ppmv to over 100,000 ppmv), high accuracy, ease of maintenance, and ability to operate over a wide temperature range. The various definitions of humidity are described below; all of them can be calculated from the measured dew/frost point. Dew/frost point is the fundamental measurement unit of a chilled mirror hygrometer.

Humidity Units

A chilled mirror hygrometer measures the dew or frost point in a gas mixture of water vapor and a carrier gas. The measurement is performed automatically through opto-electronic means, which will be described below.

For any ideal gas mixture the mixing ratio, %RH, and ppmv are functions of *dew point* (or the frost point below zero) as follows:

$$e_w = 10^{[8.07131 - 1730.63/(233.426+T_d)]} \quad \textbf{(1)}$$

$$m.r.\ (gr/lb) = 4366.2\ (e_w) / (P_{total} - e_w) \quad \textbf{(2)}$$

$$\%RH = (e_w / e_{w\ saturation})\ x\ (100\%) \quad \textbf{(3)}$$

$$ppmv = (e_w / (Ptotal - e_w)) \times 10^6 \qquad (4)$$

where:

t_d = measured dew point (frost point below 0°C)
P_{total} = total pressure
e_w = water vapor pressure
$e_{w\ saturation}$ = saturated water vapor pressure at the ambient temperature
m.r. = mixing ratio in air
ppmv = parts per million water vapor by volume
%RH = the relative humidity of the gas system

By knowing the dew point, total system pressure and ambient temperature, the %RH, mixing ratio, and ppmv water vapor can be determined. Mixing ratio and ppmv are units that describe the water vapor concentration, while %RH describes the tendency for water vapor to condense into a liquid or solid phase. The process gas industry routinely uses and understands ppmv, and dew/frost point; natural gas process people are familiar with mixing ratio and dew point, while food processing and HVAC folk think in terms of %RH. In the final analysis, as the above equations show, all units are interchangeable when one knows the dew/frost point, which is directly obtained from a chilled mirror hygrometer.

Operating Principles of Chilled Mirror Hygrometry

The temperature at which water vapor in a carrier gas condenses onto a plane surface as liquid water or solid ice is called the dew point temperature or the frost point temperature, respectively. The dew or frost point temperature is declared when the condensed layer is in equilibrium with its vapor phase. The CMH determines this temperature by opto-electronic means; when light reflected off of the mirror surface is non-changing in time, signifying that the condensed layer is neither growing nor diminishing.

The schematic diagram in Figure 1 depicts the CMH system. Figure 2 is an example of a chilled mirror hygrometer configured in an insertion probe used in process or lab applications . Accuracies of chilled mirror hygrometers can be 0.1°C dew/frost point over a temperature range of 90°C to -90°C with no hysteresis. This is accomplished by means of a very sensitive opto-electronic system and a platinum resistance thermometer (PRT) that measures the temperature of the mirror at the declared dew/frost point.

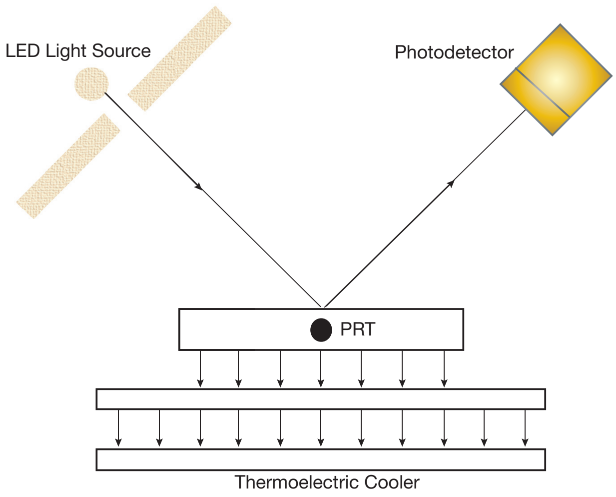

Figure 1. A CMH system shown diagrammatically; the temperature of the mirror is measured by a highly accurate and precise PRT; the mirror is cooled by a thermoelectric cooler (TEC), and the dew or frost layer thickness is controlled by an opto-electrical servo-controller. The control unit, not shown, provides all necessary algorithms.

Figure 2. An example of a chilled mirror hygrometer configured in an insertion probe for O-ring sealed duct mounting; the unit, the model D Series Probe with a Dew Master control unit, provides several output signals e.g. RS232, 4-20 ma, 0 to 10 Volt, offers unit interconversions like ppmv, dew/frost point, gr/lb, etc., and comes equipped with alarm settings.

Applications of CMH

There are two types of applications in which CMH is useful. In the first, the carrier gas or vapor and the water vapor are immiscible in the liquid or solid phase. When the boiling and melting points of the carrier gas or vapor are lower than the dew/frost point of water, the measurement is straight forward. Such is the case in many pharmaceutical applications, fuel cells, metal treatment, industrial drying, meteorology, food processing, and petroleum chemistry.

When the dew/frost point of the carrier gas is higher than the water vapor dew/frost point, the sample must be expanded to 1 atm (atmosphere) of pressure, at which point an inversion of the dew/frost points occur. Examples of this include SF_6 in switch gear and circuit breaker applications. The presence of excessive amounts of water vapor in SF_6 leads to the formation

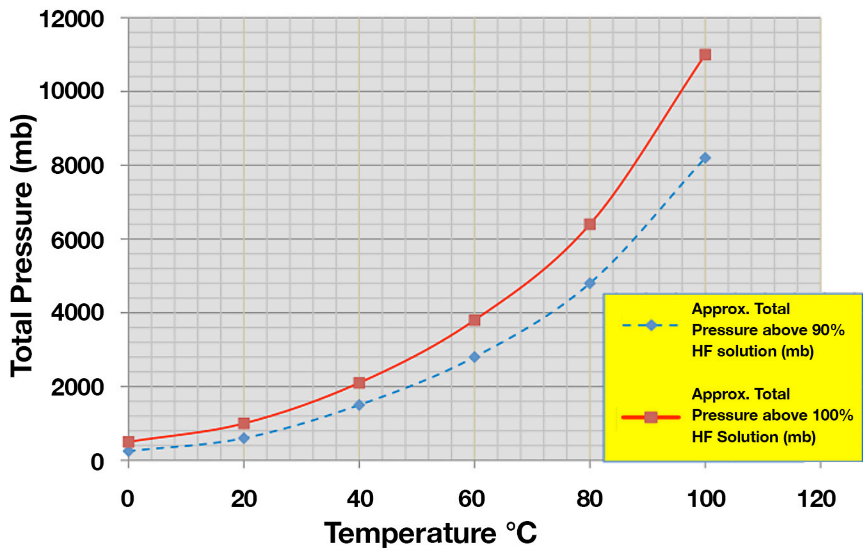

Figure 3. Total approximate pressure above aqueous solution of HF; the graph indicates that the addition of water to anhydrous HF lowers the total pressure i.e. partial pressures of HF, and water vapor above aqueous solutions of HF thus lowering the dew point of the system. In the 90% to 100% HF solution range, alterations in dew point are well within the precision and accuracy of a corrosion resistant chilled mirror system. The data is from Solvay.

Figure 4a: A portable humidity calibrator traceable to NIST used to calibrate several humidity transmitter probes at once; this highly accurate, +/-0.5%RH, +/-0.2°C air temp, precision instrument can be used in the field or in the lab.

Figure 4b: A high capacity precision humidity and temperature environmental chamber, ELH Environmental Chamber, fitted with a traceable Dew Master and chilled mirror hygrometer; accuracy of the CMH is +/-0.2°C or better, and precision at 50%RH is 0.5°C, nominal.

of hydrofluoric and sulfurous acids, which cause dielectric breakdown and corrosion of metal components.

The second type of application of CMH has to do with systems in which water and the carrier gas are miscible or somewhat soluble. Here the thermodynamic dew point of pure water vapor is not measured; rather, the total vapor pressure of the soluble or miscible system is measured. That in turn can be highly repeatable, and therefore provides useful measurement and control information to the process engineer. Examples of this are the processing of anhydrous and hydrous hydrogen fluoride and hydrogen chloride, essential chemical agents in much modern technology. Small amounts of water vapor in hydrogen fluoride can also cause extreme corrosion in industrial processes like semiconductor fabrication, petrochemical, glass etching, and polymer and chemical synthesis. A typical commercial specification for anhydrous hydrogen fluoride is 30 – 100 ppmv. Figure 3 indicates that below 100% of the weight of hydrogen fluoride, small additions of water can be detected by lowering the total partial pressure of the system.

CMH as the Basis of a Humidity Calibration System

Because CMH is a fundamental method of measurement, it can be made traceable to national standards. When CMH systems are married to precision humidity generators, they constitute a calibration system in which secondary humidity measuring devices e.g. polymer and inorganic oxide transmitters can be calibrated. The precision of the humidity generator sets the overall precision of the system. Such generators are shown in Figures

4a and 4b.

For instance, if the humidity generator has a precision of 0.5ºC dew point, and the accuracy of the CMH is 0.1ºC, the overall precision of the system at 50%RH at 20ºC temperature is 0.5ºC dew point (+/- 2%RH), with an overall average accuracy of 0.1ºC.

Two examples of such calibration systems are seen in Figure 4; one is portable (4a) with the ability to test several probes, while the other (4b)is stationery with a large calibration capacity allowing many secondary devices to be calibrated, or materials to be conditioned at desired relative humidities.

Conclusion

The operating principles of chilled mirror hygrometry are based on a fundamental measurement of water, specifically the dew/frost point. With its wide dynamic range and high accuracy and precision, it is a versatile means of measuring humidity in many process applications where ease of use and maintenance are desirable. This technology can also be made traceable to NIST. G&I

Dr. Gerald Schultz *is Principal Scientist at Edgetech Instruments, 399 River Road Hudson, MA. He holds a PhD in Polymer Chemistry, and has spent his career, primarily in the field of sensor development, specifically with regards to humidity, gas, and temperature sensors. His foci of interests at Edgetech Instruments include the research and development of chilled mirror hygrometers of new format for challenging industrial and lab environments. Examples would include petrochemical, refinery, natural gas, and power Industry to include* SF_6*, and pollution control in coal fired power plants. Gerald can be reached at gerald.schultz@edgetechinstruments.com.*