NYAD, INC.

PRINCIPLES OF MOISTURE

MEASUREMENT

BY

E.J. ROSA, Ph.D.

INTRODUCTION

The term moisture refers to the water content of any material; solid, liquid or gas. However, in this discussion, the word "moisture" will refer to the water content of solids or liquids, reserving the term "humidity" for the water content of gases. This discussion of the principles of moisture measurement will cover basic concepts, definitions and units followed by descriptions of the commonly used instrumental methods including their strengths and weaknesses.

After considering some moisture calibration techniques, the discussion will conclude with a series of review questions.

HUMIDITY AND MOISTURE

"Humidity" as a technical term, refers to the amount of water contained in a gas. Here, water is in the form of water vapor, a fact which is easily forgotten in view of the virtual synonymy of water vapor and liquid in everyday usage. Water vapor is, in fact, the third largest component of the atmosphere after nitrogen and oxygen. At room temperature, as much as 2.5% by volume of the air may be water vapor.

Humidity terminology used here follows, for the most part, that given by "Definitions and Specifications of Water Vapor in the Atmosphere", which was adopted by the international meteorological Organization in 1947.

"Moisture" as a technical term, refers to the amount of water contained in a solid or liquid by adsorption or absorption. Such water can be removed from the substance without altering its chemical properties. This qualification is important. While water can, for example, be extracted from sugar with sulfuric acid, the remaining substance is no longer sugar. Moisture is customarily reported as mass of water per unit total mass. Thus 1.2% moisture in a solid indicates 1.2 Kg of water and 98.9 Kg of dry material per 100 Kg total mass. Moisture in solution with immiscible liquids is expressed as the ratio of the weight of dissolved water per unit weight of solvent, or more commonly as parts per million by weight.

BASIC CONCEPTS

1. *PARTIAL PRESSURE*

Dalton's Law of Partial Pressure states that the pressure in a given volume is proportional to the number of molecules in that volume. Extended to gaseous mixtures this law results in the idea that the total pressure of such a system is equal to the sum of the pressures that each individual gas would exert if it occupied the entire volume by itself. The pressure which each component of a gas mixture exerts is called its partial pressure. Thus, if a gas mixture consists of gases, A, B, and C, the total pressure of the mixture is the sum of the partial pressures of each of the three gases:

$$Pt = Pa + Pb + Pc$$

In the case of a gas mixture containing water vapor, the total pressure is equal to the sum of the partial pressure of the dry gas (Pd and the partial pressure of the water vapor (Pv).

$$Pt = Pd + Pv$$

This concept of the partial vapor pressure of water is <u>fundamental</u> and forms the foundation of all the ways in which we shall express humidity.

2. *SATURATION VAPOR PRESSURE (Ps)*

When liquid water at constant temperature is in contact with a gas mixture, two processes occur simultaneously: molecules of water evaporate from the liquid into the gas phase, and molecules of water condense from the gas phase into the liquid. At equilibrium, these two processes occur at the same rate. This is the saturation point and the vapor pressure of water is known as the saturation vapor pressure. If the partial pressure of water vapor is less than this saturation pressure, more water evaporates into the gas phase than is trapped from the gas phase by the liquid surface; the vapor pressure rises until evaporation and capture proceed at the same rate. On the other hand, if the partial pressure is above the saturation pressure, capture removes more water molecules from the gas phase

3

than enter it by evaporation, until capture and evaporation are again in balance. Thus when equilibrium is reached, the partial pressure of water vapor in the gas is the same as the vapor pressure of the water with which it is in contact.

The vapor pressure of water depends on the temperature of the water as shown in Figure 1. Figure 1 can be used to find the vapor pressure of liquid water at a given temperature or the saturation vapor pressure of a gas in contact with the liquid water. The two vapor pressures are the same when equilibrium has been reached.

To measure the amount of water vapor in a gas (its humidity) one could measure the partial pressure of the water vapor in the gas, then find the humidity from Dalton's Law. It is easy to measure the total pressure, however, it is difficult to measure partial pressures.

A more convenient way to measure the partial pressure of water vapor in a gas can be illustrated by the following example:

We have a gas which is not saturated and is known to contain some water vapor. The temperature of the gas is known. We also know the saturation vapor pressure of water at any temperature (Figure 1). We can now either add water vapor to the gas until saturation occurs, at which point we would know the total vapor pressure from (Figure 1). Subtracting the amount of water added from the total would give the vapor pressure in the original gas or we could cool the gas until saturation occurs. By measuring the temperature at which saturation occurred, we would know the vapor pressure of water in the gas, again from (Figure 1).

In practice, the entire gas need not be cooled – only a small sample is cooled to saturation. The temperature at which a gas becomes saturated is called its "Dew Point".

DEFINITION OF UNITS

1. *DEWPOINT*

The partial vapor pressure of water in a gas mixture can be expressed in millimeters of mercury (mmHg), millibars, or inches of water, etc., the usual practice is to express it as Dew Point, the temperature at which the water vapor would be in 3quilibrium with liquid water or Frost Point, the temperature at which the water vapor would be in equilibrium with ice.

4

Since saturation vapor pressure is a unique function of temperature, specifying the temperature at which water vapor begins to condense on a cooled surface is equivalent to giving its partial vapor pressure. Mathematically:

$$D.P. = Pv$$

2. *CONCENTRATION*

The proportion of water vapor in a gas mixture can be expressed in the usual concentration terms; mass of water vapor per unit volume or mass of water vapor per unit mass of dry gas. The former is called "absolute humidity" and the latter "mixing ratio".

Mass per unit volume is meaningful only when the temperature and pressure of the gas mixture are specified, due to the dependence of volume on these factors.   The necessity of reducing actual data to reference conditions limits the usefulness of this method of expressing humidity. The natural gas industry commonly expresses the humidity of natural gas in units of lbs/MMSCF or pounds of water per million standard cubic feet of gas.

Mass per unit mass is independent of temperature and pressure as neither factor affects the mass of either the water vapor or the gas involved. On a mass per unit-mass basis, concentration is expressed in percent or parts per million.

Customarily mixing ratio is expressed in terms of ratio of mass or volume of water vapor to mass or volume of dry gas (excluding the water vapor), rather than to the mass or volume of the total gas mixture (including the water vapor),; the latter is termed "specific humidity".

In industrial applications the most commonly used units 6o express humidity as a concentration are parts per million on a volume basis (ppmv) or the ratio of the volume of water vapor to the volume of dry gas. Assuming ideal gas behavior ($Pv = nRT$) and low humidity, concentration can be expressed as:

$$Ppmv = \frac{Pv \ \ x \ \ 10}{Pt}$$

where Pv is the partial vapor pressure of water and Pt is the total gas pressure.

3. *__RELATIVE HUMIDITY__*

Relative humidity (RH) is the ratio of the partial pressure of water vapor in a gas mixture to the saturation water vapor pressure with respect to water at the prevailing temperature, or the fraction of the water carrying capacity of the gas represented by the amount of water vapor actually present. Relative humidity is usually expressed as a percent and varies with both the temperature and pressure of a gas.

$$\% \ RH = \frac{Pv \ x \ 100}{Ps}$$

where Pv is partial vapor pressure and Ps is saturation vapor pressure.

The choice of humidity units depends on the application; no single unit is appropriate for all uses. Generally, dew and frost points are used when dryness of the gas is important; as where condensation of moisture from the gas at low temperatures is to be avoided. For a given volume of gas, Dew/Frost temperature is independent of gas temperature (above saturation) but varies with total gas pressure. Concentration units are usually given where water vapor is viewed as a chemical impurity, as in the case of a gas mixture intended for use as a component in a manufacturing process. For a fixed gas volume, concentration on a volume basis is i8ndependent of both temperature and pressure.

Relative Humidity is the unit of greatest interest when the influence or the environment on product quality is of primary concern. For example, low RH can cause brittleness and static electricity problems, while high RH can cause swelling and clumping. RH in a given volume is dependent on both gas temperature and pressure.

In all the expressions of humidity, one physical property is seen to be basic and unifying:

__Pv,__ the partial vapor pressure of water.

HUMIDITY MEASURMENT

Measurement of moisture in gases, liquids or solids uses one of three instrumentation principles listed in Table I.

A discussion of the instrumental methods using some of these principles will be given in order of their decreasing accuracy and/or range.

1. *STANDARD HYGROMTER – NBS GRAVIMETRIC*

The current state-of-the-art in a precision humidity instrument is the gravimetric hygrometer developed and maintained by the National Bureau of Standards. The gravimetric hygrometer yields a determination of absolute water vapor content, since the weight of the water absorbed and the precise measurement of the gas volume associated with the water vapor determine the absolute humidity of the incoming gas.

In this system, a test gas is pumped from a humidity generator through a drying train and a precision gas volume measuring system contained within a temperature-controlled bath. The precise measurements of the weight of water absorbed from the test gas and the associated volume of gas as measured at closely controlled temperature and pressure, accurately define the absolute humidity of the test gas in units of weight per unit volume. When used as a calibration instrument the same test gas is also supplied to an instrument under calibration. This system has been chosen as the primary standard because the required measurements of weight, temperature, pressure and volume can be made with extreme precision. The gravimetric hygrometer is a rather unwieldy instrument to use, and in the low humidity ranges may require up to 30 hours per calibration point. For this reason, the gravimetric hygrometer is not used for normal measurement purposes and would not be useful for industrial measurement of control. NBS has also developed a two-pressure humidity generator which is commonly used as the NBS transfer standard.

2. *TWO PRESSURE GENERATOR*

The two pressure system used by the NBS, first saturates a gas sample at a constant temperature and then expands the sample to a lower pressure, at the same or a different temperature.

The principle of operation is based on Dalton's Law, in that the ratio of partial pressures varies directly with the total pressure.

In this instrument, gas is saturated with water vapor at a given pressure and temperature. The percent relative humidity at the final pressure may be expressed as the ratio of the two absolute pressures.

Relative humidity produced in this type of generator does not depend o measuring the amount of water vapor in the test chamber, but is dependent on the measurement of pressure only, and on the maintenance of constant temperature conditions.

The two pressure humidity generator is more convenient for normal calibration purposes than the gravimetric standard, but is still not a practical system for industrial applications.

3. *DEW POINT TECHNIQUES*

The direct observation of dew point via a chilled surface, using either visual observation or instrumental detection of dew formation with automatic maintenance of the surface at its dew point temperature, is a popular measurement technique because of its accuracy and wide range. Dew Point temperatures from –100 degrees F to +200 degrees F can be measured, and accuracy of better than 0.5 degrees F are possible.

Historically, the cooling of a condensing surface has been accomplished with acetone and dry ice, liquid gases, mechanical refrigeration and, more recently, by thermoelectric heat pumps. Detection of the condensation can be observed visually, and the equilibrium cooling controlled manually. Automatic versions utilize solid state optical detection methods to automatically control the condensation process.

The temperature instrumentation used to measure the surface or Dew Point temperature include glass bulb thermometers and all types of electrical temperature elements. The most accurate being the platinum resistance detector.

Instruments utilizing the dew point technique range from the manually cooled, visually observed optical hygrometer known as a dew cup to the sophisticated automatic models using thermoelectric heat pumps and solid state optical detectors for the observing the dew formation and servo control of detector temperature.

Optical dew point hygrometers are best applied to clean gas streams because their detection method is not specific to water and can be confused by the presence of other condensables or particulates. Manual versions suffer from operator error resulting in a tendency to "overshoot" the dew point and give measured values that are significantly below actual values.

The more sophisticated automatic versions are relatively expensive.

4. *PYSYCHROMETRY*

The thermodynamic wet bulb temperature of moist air at constant pressure, temperature and humidity is the temperature produced when pure water evaporates into the air to saturate it adiabatically.   The wet bulb temperature is obtained by covering an electrical or mechanical temperature sensor with a moistened wick, aspirating the sensor at a constant flow rate and then noting the temperature.

This process is dependent on water purity, wick cleanliness, ventilation rate, radiation affects, size and accuracy of the temperature sensor and the density, viscosity and thermal conductivity of the gas. When properly used at atmospheric pressures and gases, it can serve as a calibration standard. In normal process applications it is very susceptible to operator error and contamination. To convert the measured wet and dry bulb temperatures to units of RH or dew point, psychrometric tables must be used.

5. *SATURATED SALT (LITHIUM CHLORIDE)*

The heated lithium chloride sensor consists of a thin wall tube, generally metal, with a conventional temperature-measuring element within it. The tube is covered with a woven glass or other inert fabric sleeve which is impregnated with a lithium chloride solution. The entire bobbin is then wound with a bifilar winding which is used for heating the entire sensor assembly.

The sensor is heated to its equilibrium temperature as measured by a minimum in the electrical resistance of the salt solution. Lithium chloride is the only salt widely used for this method because it reaches its natural equilibrium humidity at approximately 11% RH. The temperature of the bobbin is measured and related to the water vapor pressure or dew point. Lithium chloride sensors are widely used in meteorological applications. However, they have their limitations. The most severe problem is that the salt solution can be washed off in the event of exposure to liquid water.

6. *SPECTROSCOPIC*

The spectroscopic hygrometers are optical instruments that measure the humidity of gases by detecting the energy absorption by the presence of water vapor.

The basic unit consists of an energy source, detector, and optical systems for isolating specific wavelengths, and a measurement system for determining the attenuation of radiant energy caused by the water vapor in the optical path.

Commercial infrared analyzers have been used for detecting water vapor in special applications. These analyzers are expensive and require continual maintenance to care for the optical system. Absorption by gases can also cause severe interference to this method.

7. *ELECTROLYTIC*

The Keidel electrolytic sensor uses a bifilar winding coated with a thin film of phosphorous pentoxide. As incoming water vapor is absorbed by the desiccant, an electrical potential is applied to the windings which electrolyzes the water to hydrogen and oxygen. The currant, consumed by the electrolysis, determines the mass of water vapor entering the sensor.

The flow rate and pressure of the incoming sample must be controlled precisely to maintain a standard sample mass flow rate into the sensor. Because the mechanism within the cell is complex, several additional phenomena affect its operation. Perhaps the most troublesome of these is recombination.

This is a term applied to the reverting to water of the electrolysis products in either hydrogen-rich or oxygen-rich samples. This is another method, which requires the use of clean sample free of liquids or other contamination impurities.

8. *PIEZOELECTRIC SORPTION*

This instrument compares the changes in frequency of two hygroscopically coated quartz crystal oscillators. As the mass of the crystal changes due to the adsorption of water vapor, the frequency changes. Commercial versions use an integral system to produce dry reference gas. Since it is inherently a mass measuring device, the frequency change is corrected for flow and type of carrier gas.

This type of instrument is relatively expensive in commercial versions. In addition its flow sensitivity, susceptibility to damage by contact with water, and calibration dependence on an internal reference gas, make it a difficult instrument to apply in general industrial applications.

9. *ALUMINUM OXIDE*

The Aluminum Oxide sensor consists of an aluminum base, which is anodized to produce a thin layer of active aluminum oxide. A thin coating of noble metal is evaporated over this structure. The two metal layers form the electrodes of a capacitor, which contains an aluminum oxide dielectric.

Water vapor is rapidly transported through the noble metal layer and adsorbs onto the oxide to a degree related to the vapor pressure of water surrounding the sensor. The number of water molecules adsorbed on the oxide will cause a change in the dielectric constant of the sensor. A measure of the sensor impedance is a measure of the sample water vapor pressure. This sensor can be placed directly in many process streams wi5hout the necessity of controlling sample pressure or flow. Contact with liquid water does not damage the sensor and it is the only electric sensor that can be immersed directly in hydrocarbon liquids to determine the concentration of dissolved moisture.

The biggest limitation of the Aluminum Oxide sensor is its need for periodic calibration against standard to determine if changes have occurred in its calibration due to contact with corrosive substances such as strong acids or bases.

10. *SAMPLING*

Of al the factors considered in humidity measurement, one of the most important, and that which is often given the least attention, is the sampling system. Considerations of leakage, pressure and temperature gradients, and moisture absorption/desorption characteristics are often overlooked. The problem of leakage is relative, i.e., if the humidity being measure is close to that in the gas surrounding the sample system a leak will have very little effect compared to measurements which have large differences between the sample and surroundings.

The temperature stability of the sample system components is also quite important. At a given equilibrium condition of temperature the system will adsorb a specific amount of moisture. Any factor, which upsets this equilibrium, whether it is a change in sample, concentration or a change in ambient temperature will require new equilibrium conditions to be established before the true humidity can be measure. Large changes on sample line temperatures should be avoided as much a s possible.

Of equal importance is the effect of material adsorption/desorbtion on overall system response. Although not true for all applications, stainless steel, glass and nickel alloy tubing are the best possible non-hygroscopic materials and should be used for low humidity applications. Most plastic and rubber tubing is unacceptable in all ranges. For example, nylon cannot be used at low dew points because the equilibrium condition may actually take days to stabilize.

The last factor to be considered is the effect of absolute pressure on the humidity measurement. With analyzers that measure system dew point the measurement will vary as the gas mixture is subjected to changes in pressure. Dalton's Law indicates that the partial pressure of water vapor will change in the same ratio as total pressure. This results n a direct change in dew point for any change in total pressure. It is important therefore, for one to know both the process pressure and the pressure in the sensor, for a complete evaluation of the measurement.

TABLE I – INSTRUMENTATION PRINCIPLES

EXTRACTION OF WATER PRINCIPLES

Desiccation

Electrolytic

Gas Chromatography

Karl-Fischer Titration

PROPERTY OF WATER (DEPENDENT ON MOISTURE)

Conductivity

Dew Point

Dielectric Constant

Infrared Absorption

Microwave Absorption

Neutron Scattering

Ultraviolet Absorption

CHANGE IN PROPERTIES OF A MATERIAL (DUE TO WATER CONTENT)

Cobalt Chloride

Dunmore Sensor

Brady Array

Hair Hygrometer

Lithium Chloride Dewpoint

Wet-Dry Bulb

REVIEW QUESTIONS

1. A gas mixture of 78% N2, 20% O2 and 2% water vapor exerts a total pressure of 750 mmHg. The partial pressure of oxygen in this mixture is?

    _____

2. A caisson is maintained a pressure of 2700 mmHg (3.4 atm.) A percolator in caisson is boiling water for coffee. The temperature of the boiling water is?

    _____

3. A bottle of air at 50% RH is sealed and heated form its original temperature of 20 degrees C to 30 degrees C. Its RH is now? _____

4. 6000 ppmv of water in air is equivalent to about_____ppmw?

5. If the relative humidity is 80% and the dry bulb temperature is 80 degrees F, the dew point is?

    _____

6. It is known that the dew point of a sample of gas is 40 degrees F and the temperature of the gas is 65 degrees F. The RH is? _____

7. The saturation vapor pressure of water at 100 degrees C is? _____

8. A bottle half full of water at 20 degrees C is first flushed with totally dry nitrogen (20 degrees C, 760 mmHg) and then sealed. After equilibrium, what should the pressure composition and relatively humidity of the air in the bottle be if the temperature is maintained at 20 degrees C?

    _____

9. The saturation vapor pressure of water at 0 degrees C is 0mmHg. True or False?

    _____

10. Relative humidity is defined as the ration of _____to _____.