

Gert J.W. Visscher. "Humidity and Moisture Measurement."

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Humidity and Moisture Measurement

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Whether one likes it or not, water and water vapor can be found everywhere. Because of the asymmetrical distribution of their electric charge, water molecules are easily adsorbed on almost any surface, where they are present as a mono- or multimolecular layer of molecules. Water vapor in the air or any other gas is generally called *humidity*; in liquids and solids, it is usually designated as *moisture*. The determination of humidity and moisture, as in prediction of floods, fog, conditions for the appearance of plant diseases, etc., is of great economic importance. Stored foodstuffs or raw materials may dry up at low humidity or get moldy at high humidity. In many industrial processes, the measurement of moisture and humidity is important for the maintenance of the optimum conditions in manufacturing. Humidity and moisture content can be expressed in a number of ways, and the number of methods for measuring them is even greater. An engineer whose main concern is to avoid condensation no matter where in his system will be interested in the *dewpoint* of the gas flow. A chemist may be interested in the mere *quantity* of water vapor, whereas in a printing-office or a storage-room, the *relative humidity* is of more importance.

Water vapor is one of the constituent gases of the Earth's atmosphere, the total pressure P of which is, according to Dalton's law, the sum of the partial pressures. This means that:

$$P = P_{N_2} + P_{O_2} + P_{H_2O} + P_{\text{other gases}} \quad (72.1)$$

Like other gases, water vapor can be considered to behave as an ideal gas, except near saturation. In average environmental conditions, water can also be present in the liquid and solid phase, the reason to

speak of water vapor rather than of water gas. An empty space in equilibrium with a flat water (or ice) surface can, at a given temperature, hold a well-defined maximum quantity of water vapor [1,2,3]. When this *saturation vapor pressure* is reached, any further addition of water vapor results in condensation. In the presence of air molecules at atmospheric pressure, the saturation vapor pressure is about 0.4% higher (expressed by the so-called enhancement factor [4]). The saturation vapor pressure for water is about 611 Pa at 0°C, 2339 Pa at 20°C, and 7383 Pa at 40°C. So, one can say that the average water vapor pressure in the Earth's atmosphere around us ranges from about a half to a few percent of the barometric pressure.

There are several ways to express humidity:

1. The *vapor pressure* is that part of the total pressure contributed by the water vapor.
2. The *absolute humidity* (or vapor concentration or vapor density) is the mass of water vapor per unit of volume. Effects of temperature and pressure are, except near saturation, according to gas laws.
3. The *relative humidity* is the ratio of the actual vapor pressure and the saturation vapor pressure at the prevailing temperature. It is usually expressed as a percentage. Since the maximum water vapor pressure depends on temperature, the relative humidity (r.h.) also depends, at a given water content, on temperature. At constant temperature and a given water content, the r.h. is, according to the equation for P mentioned above, dependent on total pressure.
4. The *dewpoint temperature* is the temperature to which a gas must be cooled, at constant pressure, to achieve saturation. When the condensate is ice, it is called *frost-point*. It is, with unchanging composition of the gas, independent of temperature. It changes with pressure since $P_{\text{H}_2\text{O}}$ is proportional to P . Of course, condensation will occur if saturation vapor pressure is reached.
5. The *mixing ratio* is the mass of water vapor per unit mass of dry gas, usually expressed in grams per kilogram. If the ratio is related to a unit mass of humid air, it is called the *specific humidity*.
6. The *mole fraction* is the ratio of the number of moles of a component to the total number of moles present.

Conversions between the different parameters used to be cumbersome. They are now becoming standard since the introduction of the microprocessor.

Concentrations of water in a *liquid* or a *solid* are normally given in kg/kg. Except in soil physics, volumetric units are rarely used. The expression *equilibrium relative humidity* (e.r.h.) refers to a condition where there is no net exchange of water vapor between a moisture-containing material (paper, medicines, foodstuffs, tobacco, seeds, etc.) and its environment. It is the equivalent for *water activity*, a_w , used in the fields of biology or food technology, generally expressed as a ratio rather than a percentage (i.e., 0.6 instead of 60%).

It is probably difficult to find a material that is inert to water molecules and with which it would be impossible, with some physical method, to measure the presence of water. Water molecules change the length of organic materials, the conductivity and weight of hygroscopic materials and chemical absorbers, and in general the impedance of almost any material. Water absorbs infrared as well as ultraviolet radiation. It changes the color of chemicals, the refractive index of air and liquids, the velocity of sound in air or electromagnetic radiation in solids, and the thermal conductivity of gases as well as that of liquids and solids. More fundamentally, the water content can be measured by removing the water (vapor) from the sample and measuring the change of weight (or the change of pressure in a gas). Other fundamental principles are the evaporation from a water surface into the stream of sample gas (*psychrometer*) and the cooling of the gas sample until condensation is detected. Microwave absorbance, the measurement of capacitance and nuclear magnetic resonance have found application in the measurement of moisture in liquids and solids.

After an engineer has decided which parameter has to be measured, he has to realize a few things [5].

First, what is the minimum range of operation required? Over-specification can be expensive. Besides, instruments suitable for drying processes at high temperatures and, at the same time, trace detection of water vapor in dry gases do not exist.

TABLE 72.1 Methods for Measuring Humidity and Moisture

Method	g, l, s ^a	Range	Manufacturer ^b	Approx. Price \$
Mechanical (hair)	g	0–100% rh	Lambrecht, Thies, Haenni, Jumo, Sato, Casella, Pékly et Richard	0.3–1 k
Condens.dewpoint	g	–80/+100°C dp	General Eastern, Michell Instr., EG&G, E+H ³ , MBW, Protimeter, Panametrics	2–20 k
Dry and wet bulb	g	10–100% rh	Lambrecht, Thies, Haenni, ASL, Jenway, Casella, Ultrakust, IMAG-DLO	0.5–3 k
Lithium chloride	g	–45/+95°C dp	Honeywell, Jumo, Lee Engineering, Siemens, Philips, Weiss	0.7–2 k
Polymer (capac.)	g, s	0–100% rh	Vaisala, Rotronic, Testo, Hycal, Panametrics, Novasina, EE Elektronik, Chino, Lee Integer	0.5–2.5 k
Electrical (others)	g, s	0–100% rh	PCRC, General Eastern, Rotronic, Chino, Elmwood, Shinyei Kaisha	0.5–2.5 k
Thermal conductivity	g	0–130 g/m ³	Shibaura Electronics Co. Ltd	0.1–1 k
Al ₂ O ₃ /silicon	g, l	–80/+20°C dp	E+H, Gen. Eastern, Panametrics, Michell Instr., MCM, Shaw	1.5–3 k
Phosphorous pentoxide	g	0.5–10000 ppm	Anacon, Beckman, Dupont	2–6 k
Crystal oscillator	g	0.02–1000 ppm	Dupont	25–30 k
Infrared absorbance	g, l	0–50 ppm up to 65 °C dp	Siemens, H&B, ADC, Anacon, Kent, Horiba, Sieger, Beckman, Li-Cor	5–15 k
Infrared reflectance	s	0.02–100%	Anacon, Infrared Engin., Moisture Systems Corp., Pier Electronic, Zeltex, Bran & Luebbe, Bühler	5–15 k
NMR	l, s	0.05–100%	Oxford Anal. Instr., Bruker	10–30 k
Neutron moderation	s	>0.5%	Kay Ray, Berthold, Nuclear Ent.	8–25 k
Microwave attenuation	s	0–85%	Mütec, Scanpro, Kay Ray Inc., BFMRA	12–35 k
TDR	s	0–100%	IMKO GmbH, Campbell Sci. Inc., Soil Moisture, Tektronix	5–20 k
FD	s	0–100%	ΔT Devices, IMAG-DLO, VITEL, Troxler	0.1–10 k

^a g, l, s: gas/liquid/solid.

^b The table is inevitably incomplete; a manufacturer not mentioned may deliver a high-quality instrument (see also Reference 9).

^c Abbreviations used: E+H: Endress+Hauser; MBW: MBW Elektronik AG; ASL: Automatic Systems Laboratories Ltd; PCRC: Physical and Chemical Research Corporation; MCM: Moisture Control and Measurement Ltd; H&B: Elsag Bailey Hartmann & Braun; ADC: Analytical Development Company; IMAG-DLO: Institute for Agricultural and Environmental Engineering.

Second, unlike a temperature sensor, a humidity sensor can, at least in air, essentially not be shielded from its direct environment. The question of how to measure humidity cannot be separated from the measuring problem in question (contamination, condensation, etc.). A question might be: is there a danger of condensation before or after the period of real measurement?

Third, the accuracy that may be expected in the field of hygrometry is considerably lower than that in other fields of measurement. One should be careful not to ask or to expect accuracies better than 2% or 3% r.h. or 0.5°C in dewpoint. Before deciding to use a certain method or to buy a particular instrument, it is very useful to go once more through things like humidity as well as temperature and pressure range, possible contaminants in the process, and accuracy and response time really needed. After this a consideration of frequency of service and calibration, cost of sensor replacement, etc. has to be made. At the end, it is sensible to find a supplier or manufacturer that is willing to think along with the customer. Table 72.1 provides a selective listing of the methods, ranges, and manufacturers for measuring humidity and moisture. The methods are discussed below.

72.1 Gases

There are several methods of measuring humidity, the most important of which are described here. The scope of the present survey is limited. More can be found in the literature [6,7,8,9,10]. Reference 9 covers measurement in liquids and solids as well.

The Gravimetric Method

The gravimetric method is the most fundamental way of accessing the amount of water vapor in a moist gas. In a gravimetric hygrometer, the water vapor is frozen out by a cold trap or absorbed by a chemical desiccant and weighed, while the volume or the mass of dry gas is measured directly. Since the result of a measurement gives the average value over an extended time, the instrument is used in combination with a humidity generator, capable of producing a gas of constant humidity. The method is used for primary standards of, among others, NIST in the U.S., NPL in the U.K., and NRLM in Japan. Achievable accuracies are approximately 0.1% to 0.2% in mixing ratio, or 0.04°C in the range of -35°C to +50°C dewpoint, increasing to 0.08°C at +80°C and 0.15°C at -75°C. The operation of such a standard requires high skill and sophisticated hardware.

Precision Humidity Generators

For less elaborate calibration work, a precision humidity generator is preferred. The best ones are reported to have an accuracy comparable to that of a gravimetric standard [11]. Therefore, such a generator may be considered as a primary standard as well. Three practical methods to produce an atmosphere of known humidity are described by Hasegawa [12]: the two-flow, the two-temperature, and the two-pressure method. Briefly, in the first method, a test chamber is fed by two streams of air, one being dry, the second one saturated with water at a known temperature. The resulting humidity can be calculated from the two flow rates. The two-temperature method uses air that has been saturated with water vapor at a well-known temperature, after which the air is heated to a higher temperature. In the two-pressure method, air is saturated with water vapor at an elevated pressure, and expanded isothermally to a lower, normally atmospheric pressure. Both temperature and pressure of the saturator and the test chamber are measured accurately. In general, precision generators are not transportable, so intercomparisons have to be made with a transfer standard of high accuracy. A good, if not the only, choice is a standard mirror dewpoint meter.

The Condensation Dewpoint Hygrometer

The saturation vapor pressure in air increases with temperature (Figure 72.1). This means that the air under test can be cooled to a temperature where it is just saturated with water vapor. If this is done at constant pressure and specific humidity, the true dewpoint temperature is obtained. In practice, a sample of the gas is usually drawn over a thermoelectrically cooled metal mirror. The mirror is cooled until dew or frost is detected, by optical means. In some cases, where the mirror is replaced by an inert substrate, the formation of dew is detected by electrical means or the use of surface acoustic waves. The temperature is maintained such that the thickness of the deposit is neither increasing nor decreasing. The highest accuracy of a transfer standard can be expected to be 0.03°C to 0.05°C in the range of -20°C to +40°C dewpoint. Industrial optical condensation dewpoint hygrometers claim accuracies up to 0.2°C, which may be true in case of a clean mirror; in practice 0.5°C is often more realistic. Advantages of this principle are its fundamental nature and the wide range: dewpoints to 90°C under ambient temperature can be measured. One of the disadvantages is the susceptibility of the mirror to contaminants, especially soluble salts. The sensor may measure the dewpoint of another condensable vapor if its dewpoint is above that of the water. A good control of the mirror temperature requires a temperature difference between dewpoint and ambient temperature of the sensing head. This means that at high relative humidities, the gas must be heated and measured outside the process stream. At temperatures below 0°C, there may be

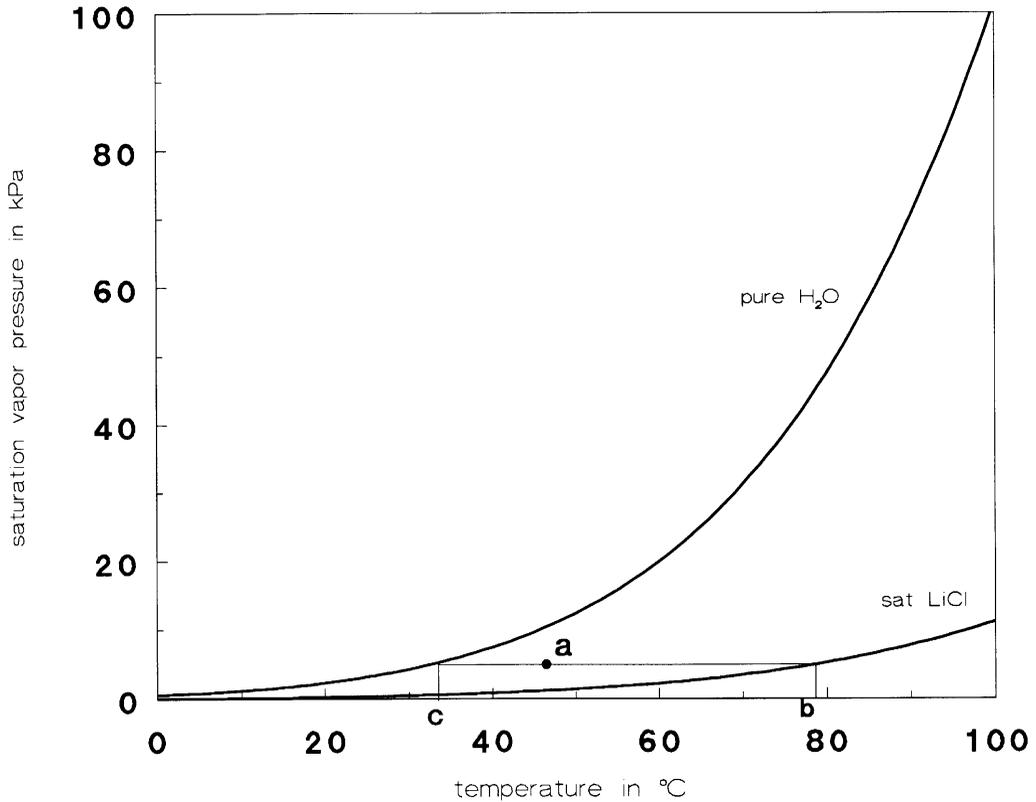


FIGURE 72.1 Saturation water vapor pressure above pure water and above a saturated solution of lithium chloride. In order to be in equilibrium with a gas sample at condition **a**, a saturated solution of LiCl has to be heated to temperature **b**. A free water surface must be cooled to a temperature **b**, as is the case in a mirror dewpoint hygrometer.

supercooled water instead of ice on the mirror. Observations have shown that below -25°C , the deposit will usually be ice. As the saturation vapor pressures over water and ice differ, one has to know the nature of the condensed layer; thus, for accurate measurements, a microscope is required. A rule of thumb is that the difference between water and ice on the mirror means a difference in dewpoint of one tenth of the temperature in degrees Celsius below zero, the dewpoint above water being the lower. Where low water content has to be measured, special attention should be given to the material and cleanliness of the pipes used. Stainless steel, polished at the internal surface, is to be preferred. The lower the moisture content, the more significant the effects are (Figure 72.2).

The Psychrometer

Two thermometers are ventilated with the gas of unknown humidity. One sensor, the dry bulb, measures the gas temperature t . The other sensor, the wet bulb, is surrounded by a wick saturated with pure water. The energy required to evaporate water into the air stream cools the wet bulb to a temperature t_w . The vapor pressure e in the sampled gas is calculated with the psychrometer equation:

$$e = e_w - A \cdot P \cdot (t - t_w) \tag{72.2}$$

where e_w is the saturated vapor pressure at temperature t_w , P is the total atmospheric pressure, and A is the psychrometer coefficient. A depends on ventilation speed, dimensions of the wet bulb, and radiative

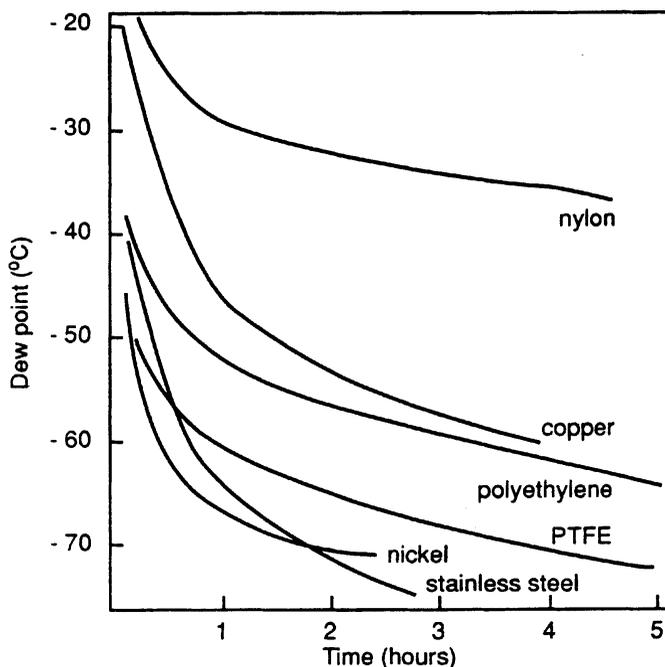


FIGURE 72.2 Illustration of the moisture given off by different tubing materials when flushed with very dry gas after being at ambient humidity. (From Reference 8.)

heat exchange between both dry and wet bulbs and their surroundings. The attractiveness of the psychrometric method lies in the fact that it is a direct and relatively simple method, with a theoretically strong basis. The accuracy of the method is determined by the accuracy of both dry and wet bulb sensors, the maintenance of a minimum ventilation speed, and a clean wick. With a ventilation speed of more than 3 m s^{-1} and a bulb diameter of 3 mm to 5 mm, *A* can, according to recent investigations, be assumed to be $(6.35 \pm 0.15) \times 10^{-4} \text{ }^{\circ}\text{C}^{-1}$, for Assmann-type psychrometers with a polished internal screen as well as sensors in a transverse air stream in a “black” radiation environment [13,14]. The radiation environment for axially ventilated psychrometers is of crucial importance. Especially when $t-t_w$ is measured directly the psychrometer is the preeminent instrument to measure near or at 100% r.h. The principle can be used up to a wet bulb temperature of 100°C at atmospheric pressure; dry bulb temperature may exceed 100°C (up to 165°C , Ultrakust, Germany). Depending on the dry bulb temperature, the wick may have problems with water supply at strong evaporation. Frozen wet bulbs, already possible at ambient temperatures below 9°C , can also lead to problems. Generally, this method adds water vapor to the atmosphere, which might be undesirable in specific applications.

Mechanical Hygrometers

Although mechanical hygrometers are losing ground, they are still widely used, mainly in room conditions. The principle relies on the elongation with r.h. of mainly human hair, textiles, or plastic fibers, the effect of which can be amplified mechanically to move a pen on a recorder. The best accuracy is 2% to 3% r.h. (for hair, in the range between 35% and 95% r.h., if regenerated at regular intervals); in general, it is wise not to expect better than 5% r.h. In the case of hair, one must be aware of the fact that the hair may be in a state different from that during calibration. Hair exhibits a dry and a wet curve; the transition takes place below 35% r.h. Once at the dry curve, the instrument may read to 20% r.h. too high if it was calibrated at the wet curve as is usually done. If the instrument is kept overnight under a wet cloth, the wet curve calibration will be re-established. The response time strongly depends on temperature: it ranges from a few minutes at 20°C to 20 or 30 min at -10°C . Temperature limits are -60°C to $+90^{\circ}\text{C}$.

TABLE 72.2 Equilibrium Relative Humidities (%)
Over Some Saturated Salt Solutions

Salt	Temperature (°C)			
	10	20	30	40
LiCl	11.3	11.3	11.3	11.2
MgCl ₂	33.5	33.1	32.4	31.6
Mg(NO ₃) ₂	57.4	54.4	51.4	48.4
NaCl	75.7	75.5	75.1	74.7
KCl	86.8	85.1	83.6	82.3
K ₂ SO ₄	98.2	97.6	97.0	96.4

Although the initial costs of a mechanical hygrometer are low, the long range costs of calibration and maintenance are considerable.

The Lithium Chloride Dewpoint Meter

Addition of a hygroscopic soluble salt to pure water decreases the equilibrium saturation vapor pressure above the solution (*Raoult's law*). In Figure 72.1, this change is illustrated for a saturated lithium chloride solution, which has an equilibrium relative humidity of about 11% (see Table 72.2). A gas sample at condition *a* is in equilibrium with a saturated LiCl solution of a (higher) temperature *b*. (It is also in equilibrium with pure water at a lower temperature *c*; note the similarity with a mirror dewpoint meter.) The application of this principle led to a simple and effective sensor. A fabric sleeve over a bobbin with a bifilar winding of inert electrodes is coated with a dilute solution of lithium chloride. As the bobbin is heated by an alternating current, its resistance increases sharply at the point where the surface begins to dry out, the heating stops, the sensor begins to cool, attracts water vapor, etc., until an equilibrium temperature has been reached. This is measured by, for example, a resistance thermometer sensor in the bobbin. The sensor is simple, rugged, relatively cheap and, after some calamity, it can be reactivated by recoating it. The dewpoint range goes from -40 to $+90^{\circ}\text{C}$, with a claimed accuracy of about 0.5°C . This estimate is often too optimistic because the influence of ambient temperature cannot be neglected. Moreover, LiCl has hydrates with one, two, three, and five molecules of water per molecule of salt. In the dewpoint regions between 34°C and 41°C , the ambiguity leads to a possible error in that area of up to 1.5°C in dewpoint. Below -12°C , the error can rise to 3.5°C . Low flow rates can cause stratification around the sensing surface, high rates can cool it too much, resulting in too high and too low readings, respectively. Flow rates somewhere between 0.05 and 1 m s^{-1} are generally recommended. Response times of commercially available sensors are on the order of minutes. Disadvantages include: the lower limit lies at 11% relative humidity, the sensor is washed out by accidental immersion, and the power supply should not be turned off accidentally. From an ionic standpoint, the sensor can be considered precontaminated and therefore, according to the manufacturer [5], relatively insensitive to contamination. Another source [9] reports a number of gases, like sulfur vapors, ammonia, high concentrations of carbon dioxide, chlorine, hydrogen sulfide, and condensable hydrocarbons, that could attack the lithium chloride sensor.

Electric Relative Humidity Sensors

Talking about numbers, the category of electric r.h. sensors is certainly by far the greatest part. The sensors are generally small, fast responding, do not dissipate heat, and can be used in confined spaces. Until 1975, the rights in this field were almost exclusively claimed by two resistance types: the Dunmore and the Pope sensor. The Dunmore sensor uses a dilute lithium chloride solution in a polyvinylacetate binder on an insulating substrate, with the danger of washout at saturation. The resistance of the sensor, measured between a bifilar grid, is a function of the r.h. of the surrounding air. This also applies to the Pope sensor, where a polystyrene substrate itself is the sensitive part of the sensor, after treatment with sulfuric acid. This sensor is less sensitive to washout, and has a wider range (15% to 99% r.h.) than the

Dunmore type. Modern bulk sensors, based on the measurement of the change in resistance, are manufactured by, for example, Shinyei Kaisha and Elmwood Sensors. Since 1970 a lot of work has been done in the development of capacitive sensors, where the stability, the influence of temperature, the temperature range, and the susceptibility for condensation conditions could be greatly improved. Since the 1980s, this sensor type has surpassed the mentioned resistance types. Basically, this type of sensor consists of a thin polymer layer between two electrodes of various materials. The types differ mainly in polymer type and electrode material, resulting in sensors with different characteristics to withstand pollution and temperatures up to 190°C. A drawback that still seems not completely under control is the fact that a polymer swells at high humidities, causing an undesirable shift in capacitance of the sensor.

Aluminium Oxide Hygrometers

Briefly, a sheet or wire of aluminium is anodized, producing a thin layer of water-sensitive pores. Subsequently, a conductive, water-permeable gold film is deposited over it. The radius of the pores is such that the sensor is specific for water molecules, and the amount absorbed is directly related to the dewpoint of the gas. The dewpoint range goes from -110 to 20°C, measured as a change in capacitance between the aluminium base and the gold electrode. The sensor works up to high pressures (30 MPa). The response time depends on the dewpoint, ranging from seconds at 10°C to minutes below -40°C. Stated accuracies are $\pm 1^\circ\text{C}$ at higher dewpoints to $\pm 3^\circ\text{C}$ at -100°C. The sensors show slow drift, and recalibration at least twice a year is generally recommended. Where chemical attack of the aluminium can be expected, silicon capacitive type sensors may be an alternative. A commercially available type of MCM (Moisture Controls & Measurement Ltd., U.K.) is temperature controlled, and has a very short response time: less than 15 s to a level of 1 ppm. Both aluminium and silicon sensors can withstand immersion in water.

Coulometric Method

In an electrolytic hygrometer, water in a sample stream is quantitatively absorbed by a phosphorous pentoxide layer. At the moment water molecules are present, the probe becomes electrically conducting. With a dc voltage over the sensor, water is electrolyzed and, according to Faraday's law, a current with a well-defined magnitude occurs ($1 \text{ mA} \triangleq 0.0935 \mu\text{g H}_2\text{O/s}$). For the measurement of the mixing ratio, the flow through the cell must be measured accurately. Further calibration is, in principle, not necessary. At higher flow rates and moisture content (3000 ppm to 10,000 ppm by volume), the water vapor may not be absorbed quantitatively, so this method is especially suited for low water contents, beginning at 1 ppm. The response time is about 1 min. Typical measurement uncertainties are 10% at 1 ppm, decreasing to 5% at higher values.

Crystal Oscillator

Even lower concentrations (down to 0.02 ppm by volume) can be detected with a hygroscopic coating on the surface of a quartz crystal. The resonant frequency of the crystal is a function of the mass of the coating — in other words, the moisture content of the gas. The crystal is alternately exposed to dry and humid gas, and the shift in frequency is measured. The response time is 1 min. Typical measurement uncertainty is 1 ppm or 5%. The instrument is relatively expensive (Du Pont).

Infrared Methods

Like any heteroatomic gas, water vapor absorbs radiation in the infrared region. So, if the gas is led through the optical path between an infrared source and a detector, there is a reduction of the transmitted radiation. The source can be dispersive, that is, generated by a monochromator, or nondispersive, wide-band radiation, generated by a heated tungsten or nichrome wire. In the monochromatic mode, the transmittance ratio at two different wavelengths is measured. In the nondispersive (NDIR) method,

usually another path through a reference gas is taken. The detector can be gas-filled, solid-state, or pyroelectric, with adequate optical or gas filters in the right wave bands. A popular detector was and still is the Luft type. A Luft detector has two radiation-absorbing chambers containing the specific gas of interest, separated by a thin membrane. Since the detector is a dynamic device, the radiation paths are chopped, allowing the measurement of the change in capacitance. This method allows measurement over a wide range, from ppm level up to saturation. It can be used in corrosive gases, the concentration of which can be measured simultaneously by the use of another detector. The instrument must be calibrated at regular intervals; typical measurement uncertainty is 1%. Response times to less than 1 s are possible, depending on the attainable refreshment time in the measuring chamber. Since the absorption depends on the number of atoms, transmittance depends on pressure. The method used to be relatively expensive, even compared with a mirror dewpoint meter, but developments in the field of inexpensive semiconductor detectors and better optical filters have reduced prices. Further developments are going on in the direction of fiber-optic probes.

Miscellaneous Methods in Air

- The zirconia cell, acting as a battery on the presence of oxygen ions, is generally used in a mixture of air and steam. The sensor can be mounted directly in a hot gas stream (600/1700°C). Acceptable accuracies are reached at dew points of 70°C or higher.
- The frequency of a signal, generated by an acoustic source, depends on the mixing ratio. Measurements in gases up to 250°C, to dewpoints of about 70°C (0 to 30 vol.%, in special cases to 100 vol.%, Mahlo).
- The Lyman alpha hygrometer uses the 121-nm emission line of hydrogen, which is strongly absorbed by water vapor. Extremely small response times (milliseconds) can be obtained. The instrument is relatively expensive.
- The difference in thermal conductivity of dry and wet air allows the measurement of absolute humidity with two sensitive temperature sensors in a Wheatstone bridge (Shibaura).

72.2 Liquids and Solids

Gravimetric

Drying of a material at a controlled temperature and taking the difference in weight before and after drying is the most fundamental method, greatly improved by microprocessor-based instruments. The assumption is that the loss in weight is caused by water only and that no other volatile components have been removed. Another problem can arise if water present by surface adsorption or crystal water is removed.

Karl Fischer Method

A chemical method for the determination of water in solids and organic solvents is the Karl Fischer method. The Karl Fischer reagent is composed of iodine, sulfur dioxide, pyridine, and methanol. Addition of this reagent to water causes a chemical reaction in which, in excess of the other components, one mole of iodine is used for each mole of water. The reagent is added in a controlled way to a mixture of reagent and sample, while a current between two electrodes is measured. If all the water has been used, a sudden change in the current through the mixture is observed.

Infrared Techniques

The infrared technique is applied to liquids and solids as well, in the wavelength bands of 1.45, 1.94, and 2.95 μm . For liquids, the transmission mode described is used, leading to particular problems because of the small optical path needed. Even smaller transmittance paths would be necessary for solids, one of

the reasons to choose reflectance from the surface as a measure for water content. The surface has to be representative for the material in question. The system needs to be calibrated for each material. Concentrations as low as 0.02% to 100% can be measured. In case of specular reflection, the method cannot be used. A relatively new development is the attenuated total reflectance crystal (ATR) method. The crystal is inserted in the liquid, which may be opaque or semiopaque, or a slurry. A beam with two wavelengths, for reference and measurement entering the crystal is reflected on the internal surface, penetrating the solution one-half wavelength at each reflection point. The amplitude of the reflected signal decreases at each reflection. The number of reflections is determined by the length of the crystal and the angle of incidence, so the sensitivity can be changed. The measuring range is claimed 0% to 100% water in solutions; measuring water in emulsions requires some precautions. The response time is negligible.

Microwave Absorbance

Microwave absorbance is generally used in materials with a more or less constant composition, apart from the moisture content. Microwave radiation from a low-power, solid-state generator is absorbed by the sample and detected by a solid-state detector. The commonly used frequencies where water strongly absorbs are 1 to 2 GHz and 9 to 10 GHz, the latter being less dependent on the composition of the material. Operating ranges from 1% to 70% of water are mentioned, with achievable accuracies of $\pm 0.5\%$ of water. The attenuation is influenced by bulk density, bulk material, and temperature. The path between source and detector should not contain any metallic material.

NMR

Hydrogen atoms in the field of a permanent magnet are allowed, according to quantum mechanics, to have some defined orientations in that field. To shift an atom from one orientation to another requires a defined amount of energy, dependent on the strength of the magnetic field. If electromagnetic radiation at the right frequency is applied, resonance of the hydrogen atoms occurs, and a loss in frequency power can be detected. It is specific for all hydrogen atoms, so interference with liquids other than water in the sample can be expected. Temperature and flow must be controlled. Magnetic materials must be avoided. Measuring ranges of 0.05% to 100% have been reported [9].

Neutron Moderation

This method is, like NMR, specific to hydrogen atoms. Neutrons of high energy are slowed by nuclei of hydrogen atoms. The main components are a detector of slow neutrons, next to a source of fast neutrons. The measuring range goes from 0.5%. The sensor can be made very rugged. The measured volume is a sphere of up to tens of centimeters in diameter. The method is dependent on the bulk density of the material, but largely independent of the properties of the material being analyzed [9]. The method is not suitable for foodstuffs. It suffers from necessarily severe government regulations and low acceptance by the public and the operator.

TDR

Time domain reflectometry (TDR) measures the propagation velocity of electrical pulses, mainly between 1 MHz and 1 GHz. This method is well established, especially for the measurement of water content in soil. With certain limitations, it is proven suitable for automatic installations. The main disadvantage is the complexity of the data analysis [15].

FD

The general features of the FD (frequency domain) technique are comparable to those of TDR; however, there are some important differences. The dielectric properties of the material (soil, concrete, grain, oil,

etc.) can be measured at a single frequency. The ability to choose a whole range of frequencies makes the frequency domain (FD) sensor suitable for spectroscopic measurements. A sensor of this type has recently been developed by IMAG-DLO, Wageningen (The Netherlands). It is simple and inexpensive, and available for many purposes. The sensor uses a single application-specific integrated circuit (ASIC) and is suitable for the measurement of other properties of materials as well [15].

Measurement of Thermal Conductivity

The thermal conductivity of a material is related to the amount of water it contains. Heat pulses are supplied by a needle probe, and the cooling of the needle after ending the pulse is measured. It is a simple and inexpensive method, that needs calibration for the material in which it is going to be used.

Water Activity or Equilibrium Relative Humidity

A material enclosed in a measuring chamber is, after some time, in equilibrium with its environment. The moisture content of the material can be derived from the so-called adsorption isotherms for that specific material, which must be determined experimentally. The method is used for many materials, such as foodstuffs, chemicals, grains, seeds, etc., with electric humidity sensors described earlier. In cases where the water potential of living material like potatoes and leaves must be measured, thus at very high relative humidities, the junction of a small thermocouple is cooled by an electric current and, after the current has been turned off, used as an unventilated wet bulb psychrometer. It is an excellent method that requires skill.

72.3 Formulae

A relatively simple equation for the calculation of the saturation vapor pressure $e_w(t)$ in the pure phase with respect to water is the *Magnus formula*:

$$\ln e_w(t) = \ln 611.2 + 17.62t / (243.12 + t) \quad (72.3)$$

where t is the temperature in °C (on ITS-90) and $e_w(t)$ is in pascals. Equation (72.3) covers the range between -45°C and +60°C, with a maximum standard deviation of 0.3%. Over ice Equation (72.3) changes to:

$$\ln e_i(t) = \ln 611.2 + 22.46t / (272.62 + t) \quad (72.4)$$

covering the range between -65°C and 0°C with a standard deviation of less than 0.5%.

Equation 72.3 can easily be converted for the calculation of the dewpoint t_d :

$$t_d = \left[243.12 \ln(e/6.112) \right] / \left[17.62 - \ln(e/6.112) \right] \quad (72.5)$$

where e is the saturation vapor pressure e_w at dewpoint temperature t_d . The standard deviation in the range mentioned is less than 0.02K. The *frost point* t_f can be calculated from Equation 72.6:

$$t_f = \left[272.62 \ln(e/6.112) \right] / \left[22.46 - \ln(e/6.112) \right] \quad (72.6)$$

where e is the saturation vapor pressure e_i at frostpoint temperature t_f , in the range mentioned within a standard deviation of 4 mK.

More accurate formulae, given by Hyland and Wexler, updated by Sonntag can be found in Reference 7. The uncertainties mentioned above, given by Sonntag [7], are valid for the pure water system. In the presence of air, the uncertainties can only be maintained if the water vapor enhancement factor is taken into account.

72.4 Calibration

A few words about calibration, a most important and too often forgotten subject in humidity and moisture measurement. The gravimetric method has already been described, as well as some principles of humidity generators, which could be used as standards. Another method is the humidity chamber, with both temperature and humidity control, where an instrument is compared with a calibrated standard instrument like a mirror dewpoint meter or a psychrometer. Saturated (or diluted) salt solutions can be used to create a constant relative humidity in a confined space. Some values are listed in Table 72.2 (from Reference 16). The user should have knowledge of some critical factors like temperature, etc. for the application of this method. Permeation tubes are used where a repeatable, accurate, and low concentration flow is required. Unlike with temperature or pressure sensors, it is, except at the highest national level, not realistic to expect a reference or standard for humidity with an accuracy a factor 5 or 10 times better than the required accuracy for a measuring instrument. A good calibration guarantees traceability to a higher standard. This means, in general, that the calibration should be performed by a national or accredited laboratory. A rule of thumb for the intervals of calibration of humidity meters is as follows: condensation dewpoint meters and psychrometers require calibration once every 1 to 2 years; electric relative humidity sensors need calibration every 6 to 12 months; and less stable types like aluminium oxide sensors must be calibrated every 6 months, or sooner if desired [8]. A comprehensive treatment of calibration of hygrometers and attainable accuracies has been given by Wiederhold [10].

72.5 Developments

- Fiber optics are beginning to find their way in hygrometry, resulting in explosion-proof models. Changes in refractive index by the use of micropores are used in an instrument recently developed by Ultrakust (Germany). Fiber lengths go to 1000 m. The measuring range is 0% to 20% r.h. in a dewpoint range of -90°C to 20°C .
- A rapidly developing field is that of the monolithic integrated circuit sensors. Hycal (U.S.) manufactured a capacitive relative humidity sensor, while a recent commercial development in Germany reports the use of a monolithic integrated sensor instead of a mirror in a miniature dewpoint meter, with an accuracy of better than 0.5°C . Since the use of porous silicon allows the development of smart sensors, developments in that area will undoubtedly continue [17].
- The progress in the theoretical background of many water-related processes, made possible by an advanced FD sensor mentioned earlier, is of great importance for future development of simple, cheap, stable, and reliable sensors that can be used for many purposes.

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