

CHAPTER 4 — MEASUREMENT OF HUMIDITY

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MEASUREMENT OF HUMIDITY

4.1 General

The measurement of atmospheric humidity, and often also its continuous recording, is an important requirement of most areas of meteorological activity. This chapter deals with the measurement of humidity at or near the surface of the Earth. There are many different methods in use, and there is a vast literature on the subject. An old but still useful wide-ranging account of the techniques is given in Wexler (1965).

4.1.1 Definitions

Definitions of the terms used in this chapter follow those given in the WMO *Technical Regulations* (WMO 1988, Appendix B), the full text of which is reproduced in Annex 4.A.

The simple definitions of the most frequently used quantities in humidity measurements are:

Mixing ratio, r : The ratio between the mass of water vapour and the mass of dry air.

Specific humidity, q : The ratio between the mass of water vapour and the mass of moist air.

Dew-point temperature, T_d : The temperature at which moist air saturated with respect to water at a given pressure has a saturation mixing ratio equal to the given mixing ratio.

Relative humidity, U : The ratio in per cent of the observed vapour pressure to the saturation vapour pressure with respect to water at the same temperature and pressure.

Vapour pressure, e' : The partial pressure of water vapour in air.

Saturation vapour pressures, e'_w and e'_i : Vapour pressures in air in equilibrium with surface of water and ice, respectively.

Annex 4.B provides the formulae for the computation of various measures of humidity. These versions of the formulae and coefficients were adopted by WMO in 1989. They are convenient for computation and are of sufficient accuracy for all normal meteorological applications.

More accurate and detailed formulations of these and other quantities may be found in Sonntag (1990). Older formulations such as those of the Smithsonian Institution (1951) and WMO (1988, Appendix A) are widely used and are still sufficient for most applications.

4.1.2 Units and scales

The following units and symbols are normally used for expressing the most commonly used quantities associated with water vapour in the atmosphere:

- (a) Mixing ratio r , and specific humidity q (in kg kg^{-1});
- (b) Vapour pressure in air e' , e'_w , e'_i and pressure p (in hPa);

- (c) Temperature T , wet-bulb temperature T_w , dew-point temperature T_d , and frost-point temperature T_f (in K);
- (d) Temperature t , wet-bulb temperature t_w , dew-point temperature t_d , and frost-point temperature t_f (in $^{\circ}\text{C}$);
- (e) Relative humidity U (in per cent).

4.1.3 Meteorological requirements

Humidity measurements at the Earth's surface are required for meteorological analysis and forecasting, for climate studies, and for many special applications in hydrology, agriculture, aeronautical services and environmental studies, in general. They are particularly important for their relevance to the changes of state of water in the atmosphere.

General requirements for the range, resolution, and accuracy of humidity measurements are given in Chapter 1, Part I and in Table 4.1. The achievable accuracies listed in the table refer to good quality instruments which are well operated and maintained. In practice, these are not easy to achieve. In particular, the psychrometer in a thermometer shelter without forced ventilation, still in widespread use, may have significantly lower performance.

TABLE 4.1
Summary of performance requirements for surface humidity

Requirement	Wet-bulb temperature	Relative humidity	Dew-point temperature
Range	-10 to 35 $^{\circ}\text{C}$	5-100%	At least 50 K in the range -60 to 35 $^{\circ}\text{C}$
Target accuracy (1)	± 0.1 K high RH ± 0.2 K mid RH	$\pm 1\%$ high RH $\pm 5\%$ mid RH	± 0.1 K high RH ± 0.5 K mid RH
Achievable observing accuracy (2)	± 0.2 K	$\pm 3-5\%$ (3)	± 0.5 K (3)
Reporting code resolution	± 0.1 K	$\pm 1\%$	± 0.1 K
Sensor time constant (4)	20 s	40 s	20 s
Output averaging time (5)	60 s	60 s	60 s

NOTES:

- (1) Accuracy is the given uncertainty stated as two standard deviations.
- (2) At mid-range relative humidity for well designed and operated instruments; difficult to achieve in practice.
- (3) If measured directly.
- (4) For climatological use, a time constant of 60 seconds is required (for 63 per cent of a step change).
- (5) For climatological use, an averaging time of three minutes is required.

For most purposes, time constants of the order of one minute are appropriate for humidity measurements. The response times readily available with operational instruments are discussed in section 4.1.4.9.

4.1.4 *Methods of measurement*

4.1.4.1 **HYGROMETERS**

Any instrument for measuring humidity is known as a hygrometer. The physical principles most widely employed for hygrometry are given in sections 4.1.4.4 to 4.1.4.8. More information on the different methods is found in Wexler (1965). The report of a WMO international comparison of various hygrometers is given WMO (1989b).

4.1.4.2 **EXPOSURE: GENERAL COMMENTS**

The general requirements for the exposure of humidity sensors are similar to those for temperature sensors, and a suitably positioned thermometer screen may be used for that purpose. Particular requirements include:

- (a) Protection from direct solar radiation, atmospheric contaminants, rain, and wind;
- (b) Avoidance of the creation of a local microclimate within the sensor housing structure or sampling device. Note that wood and many synthetic materials will sorb or desorb water vapour according to the atmospheric humidity.

Exposures appropriate to particular instruments are described in sections 4.2 to 4.7.

4.1.4.3 **SOURCES OF ERROR: GENERAL COMMENTS**

Errors in the measurement of humidity may be caused by:

- (a) Modification of the air sample, e.g. by heat or water-vapour source or sink;
- (b) Contamination of the sensor, e.g. dirt, sea spray;
- (c) Calibration error, including pressure correction, temperature coefficient of sensor, and electrical interface;
- (d) Inappropriate treatment of water/ice phase;
- (e) Poor instrument design, e.g. stem heat conduction in the wet-bulb thermometer;
- (f) Incorrect operation, e.g. failure to achieve stable equilibrium;
- (g) Inappropriate sampling and/or averaging intervals.

The time constant of the sensor, the time-averaging of the output, and the data requirement should be consistent.

The different types of humidity sensors vary in their susceptibility to, and significance of, each of the above; further discussion will be found in the appropriate sections of this chapter.

4.1.4.4 **GRAVIMETRIC HYGROMETRY**

This method uses absorption of water vapour by a desiccant from a known volume of air (gravimetric hygrometer — used for primary standards only). Some details are given in section 4.9.

The gravimetric method yields an absolute measure of the water vapour content of an air sample in terms of its humidity mixing ratio. This is obtained by first removing the water vapour from the sample. The mass of the water vapour is determined through the weighing of the drying agent before and after absorbing the vapour. The mass of the dry sample is determined either by weighing or by measuring its volume.

The method is restricted to providing an absolute calibration reference standard and such apparatus is found mostly in national calibration standards laboratories.

4.1.4.5 **CONDENSATION METHODS**

4.1.4.5.1 **CHILLED-MIRROR METHOD (DEW- OR FROST-POINT HYGROMETER)**

When moist air at temperature T , pressure p and mixing ratio r_w (or r_i) is cooled, it eventually reaches its saturation point with respect to water (or to ice at lower temperatures) and a deposit of dew (or frost) can be detected on a solid non-hygroscopic surface. The temperature of this saturation point is the dew-point temperature T_d (or the frost-point T_f).

The chilled-mirror hygrometer is used to measure T_d or T_f . The most widely used systems employ a small polished-metal reflecting surface, cooled electrically by using a peltier-effect device, and sense condensation with an optical detector.

The condensation method is used for observational purposes, and might also be used as working standards and/or reference standards (see section 4.4).

4.1.4.5.2 **HEATED SALT-SOLUTION METHOD (VAPOUR EQUILIBRIUM HYGROMETER, KNOWN AS THE DEW CELL)**

The equilibrium vapour pressure at the surface of a saturated salt solution is less than that for a similar surface of pure water at the same temperature. This effect is exhibited by all salt solutions but particularly so by lithium chloride, which has an exceptionally low-equilibrium vapour pressure.

An aqueous salt solution (whose equilibrium vapour pressure is below the ambient vapour pressure) may be heated until a temperature is reached at which its equilibrium vapour pressure exceeds the ambient vapour pressure. At this point, the balance will shift from condensation to evaporation and eventually there will be a phase transition from the liquid solution to a solid hydrate (crystalline) form. The transition point may be detected through a characteristic decrease in the electrical conductivity of the solution as it crystallizes. The temperature of the solution at which the ambient vapour pressure is reached provides a measure of the ambient vapour pressure. For this purpose, a thermometer is placed in good thermal contact with the solution. The ambient dew-point (i.e. with respect to a plane surface of pure water) may be determined by using empirical data relating vapour pressure to temperature

for pure water and for salt solutions. The most frequently used salt solution for this type of sensor is lithium chloride.

This method is used for observational purposes, especially for automatic weather stations (see section 4.5).

4.1.4.6 THE PSYCHROMETRIC METHOD

A psychrometer consists essentially of two thermometers exposed side by side, the surface of the sensing element of one being covered by a thin film of water or ice and termed the wet or ice bulb, as appropriate. The sensing element of the second thermometer is simply exposed to the air and is termed the dry bulb. This is the most widely used method, and is described in detail in section 4.2.

The temperature measured by the wet-bulb thermometer is generally lower, due to evaporation of water from the wet bulb, than that measured by the dry bulb. The difference in the temperatures measured by the pair of thermometers is a measure of the humidity of the air; the lower the ambient humidity, the greater the rate of evaporation and, consequently, the greater the depression of the wet-bulb temperature below the dry-bulb temperature. The size of the wet-bulb depression is related to the ambient humidity by a psychrometer formula.

This method is in widespread use for observational purposes. Instruments using the psychrometric method are also commonly used as working standards.

4.1.4.7 SORPTION METHODS

Certain materials interact with water vapour and undergo a change in a chemical or physical property that is sufficiently reversible for use as a sensor of ambient humidity. Water vapour may be adsorbed or absorbed by the material, adsorption being the taking up of one substance at the surface of another and absorption being the penetration of a substance into the body of another. A hygroscopic substance is one which characteristically absorbs water vapour from the surrounding atmosphere, by virtue of having a saturation vapour pressure which is lower than that of the surrounding atmosphere. For absorption to take place, a necessary condition requires that the ambient vapour pressure of the atmosphere exceeds the saturation vapour pressure of the substance. The following are two properties of sorption:

- (a) Changes in the dimension of hygroscopic materials: Certain materials vary dimensionally with humidity. Natural fibres tend to exhibit the greatest proportional change, and when coupled to a mechanical lever system, can be incorporated into an analogue linear displacement transducer. Such a transducer may be designed to move a pointer over a scale to provide a visual display, or be an electromechanical device which provides an electrical output.

Human hair is the most widely used material for this type of humidity sensor. Synthetic fibres may be used in place of human hair. Because of the very long lag time for synthetic fibres such sensors

should never be used below 10°C. The hair hygrometer is described in section 4.3.

Goldbeater's skin (an organic membrane obtained from the gut of domestic animals) has properties similar to those of human hair and has been used for humidity measurements, though most commonly in devices for making upper-air measurements;

- (b) Changes in electrical properties of hygroscopic materials: Certain hygroscopic materials exhibit changes in their electrical properties in response to a change in the ambient relative humidity with only a small temperature dependence. Commonly used methods making use of these properties are described in section 4.6.

Electrical relative humidity sensors are increasingly used for distant reading applications, particularly where a direct display of relative humidity is required.

Properties commonly exploited in the measurement of relative humidity include sensors made from chemically-treated plastic material having an electrically-conductive surface layer (electrical resistance) and sensors based upon the variation of the dielectric properties of a solid, hygroscopic, material in relation to the ambient relative humidity (electrical capacitance).

4.1.4.8 ABSORPTION OF ELECTROMAGNETIC RADIATION BY WATER VAPOUR (ULTRAVIOLET AND INFRARED ABSORPTION HYGROMETERS)

The water molecule absorbs electromagnetic radiation in a range of wavebands and discrete wavelengths; this property can be exploited to obtain a measure of the molecular concentration of water vapour in a gas. The most useful regions of the electromagnetic spectrum for this purpose lie in the ultraviolet and infrared regions, and the principle of the method is to determine the attenuation of radiation in a waveband which is specific to water vapour absorption, along the path between a source of the radiation and a receiving device. There are two principal methods for determining the degree of attenuation of the radiation:

- (a) Transmission of narrow band radiation at a fixed intensity to a calibrated receiver;
- (b) Transmission of radiation at two wavelengths, one of which is strongly absorbed by water vapour and the other of which is either not absorbed or only very weakly absorbed.

Both types of instruments require frequent calibration and are more suitable for measuring changes in vapour concentration rather than absolute levels. Their use remains restricted to research activities; a brief account of these instruments is given in section 4.7.

4.1.4.9 TIME CONSTANTS OF HUMIDITY SENSORS

The specification of the time constant for a humidity sensor implies that the response of the sensor to a step

change in humidity is consistent with a known function. In general usage, the term refers to time taken for the sensor to indicate 63.2 per cent ($1/e$) of a step change in the measurand (in this case humidity), and assumes that the sensor has a first-order response to changes in the measurand (i.e. the rate of change of the measurement is proportional to the difference between the measurement and the measurand). It is then possible to predict that 99.3 per cent of the change will take place after a period five time constants in duration.

Table 4.2 gives $1/e$ time-constant values typical for various types of humidity sensor.

TABLE 4.2
Time constants for humidity sensors

85 per cent relative humidity	$1/e$ time constant (s)		
	20°C	0°C	-20°C
Sensor type			
Ordinary human hair	32	75	440
Rolled hair	10	10	12
Goldbeater's skin	10	16	140
Electrical capacitance	1-10	1-10	1-10
Electrical resistance	1-10	—	—
Assmann psychrometer	30-50	30-50	30-50
Condensation hygrometers			
Electrolytic hygrometers			
Optical hygrometer	<0.01	<0.01	<0.01

NOTE: The first-order relation does not hold particularly well for sorption sensors since the forcing agent for vapour equilibrium, the local gradient of vapour pressure, is dependent upon the local migration of water vapour molecules within the body of a solid humidity element. In general, a first-order response will be most closely exhibited by those sensors having a thin active element.

4.1.4.10 MAINTENANCE: GENERAL COMMENTS

The following maintenance procedures should be considered:

- (a) Cleanliness: Sensors and housings should be kept clean. Some sensors, e.g. chilled-mirror and hair hygrometers, may be cleaned with distilled water and this should be carried out regularly. Others, notably those having some form of electrolyte coating but also some with a polymeric substrate, may on no account be treated in this way. The provision of clear instructions for observers and maintenance staff is vital;
- (b) Checking and calibration of field instruments: Regular calibration is required for all humidity sensors in the field. For psychrometers, chilled-mirror, and heated 'dew-point' hygrometers which use a temperature detector the calibration of that item can be checked whenever the regular maintenance routine is performed. A comparison with a working reference hygrometer, such as an Assmann psychrometer, should also be performed at least once a month.

Saturated salt solutions have applications with sensors which require only a small sample volume. A very stable ambient temperature is required and it is difficult to be confident about their use in the field.

The use of a standard type of aspirated psychrometer, such as the Assmann, as a field reference, has the advantage that its own integrity can be verified through the facility to compare the dry- and wet-bulb thermometers, and that adequate aspiration may be expected from a healthy sounding fan. The reference instrument should itself be calibrated at intervals which are appropriate to its type.

It is important to check the calibration of electrical interfaces regularly and throughout their operational range. A simulator may be used in place of the sensor for this purpose. However, it will still remain necessary to calibrate the ensemble at selected points, since the combination of calibration errors for sensor and interface which are individually within specification may be outside the specification for the ensemble.

Detailed requirements for maintenance which are specific to each class of hygrometer described in this chapter are included in the appropriate section.

4.1.4.11 PROTECTIVE FILTERS

A protective filter is commonly used to protect a humidity sensor from contaminants which may adversely affect its performance. Where a sensor is not artificially aspirated, the use of a filter tends to slow the response rate of the sensor by preventing the bulk movement of air and by relying upon molecular diffusion through the filter material. Although the diffusion of water vapour through some materials, such as some cellulosic products, is theoretically more rapid than for still air, porous hydrophobic membranes achieve better diffusion rates in practice. The pore size should be sufficiently small to trap harmful aerosol particles — in a maritime environment sea salt particles may be present in significant quantity down to a diameter of $0.1 \mu\text{m}$ — and the porosity should be sufficient to allow an adequate diffusion rate.

The size of the filter, as well as its porosity, affects the overall diffusion rate. Diffusion will be enhanced by aspiration, but it must be remembered that this technique relies upon maintaining low air pressure on the sensing side of the filter and that this can have a significant effect on the measurement.

Non-aspirated sensors should, in general, be protected using a hydrophobic, inert material. High-porosity polymeric membranes made from an expanded form of polytetrafluoroethylene have been used successfully for this purpose in a variety of situations and are fairly robust.

Sintered metal filters may be used, but they should be heated to avoid problems with condensation within the material. This is not normally appropriate for a relative humidity sensor, but is quite acceptable for a dew-point sensor. Sintered metal filters are robust and

well suited for aspirated applications, which allow the use of a filter having a large surface area and, consequently, an acceptably small pressure differential.

Where diffusion is not enhanced by artificial aspiration the relation of the surface area of the filter to the volume of the air that is being sampled by the sensor must be considered. In the case of a typical sorption sensor composed of a flat substrate, a flat membrane positioned close to the sensor surface will provide the optimum configuration. In the case of a cylindrical sensing surface, a cylindrical filter is appropriate.

4.2 The psychrometer

4.2.1 General considerations

4.2.1.1 PSYCHROMETRIC FORMULAE AND TABLES

The following paragraphs summarize the existing practice in drawing up psychrometric tables.

The usual practice is to derive the vapour pressure e' under the conditions of observation from the semi-empirical psychrometric formulae:

$$e' = e'_w(p, T_w) - Ap(T - T_w) \quad (4.1)$$

and:

$$e' = e'_i(p, T_i) - Ap(T - T_i) \quad (4.2)$$

where e'_w is the saturation vapour pressure with respect to water at temperature T_w and pressure p of the wet bulb, e'_i is the saturation vapour pressure with respect to ice at temperature T_i and pressure p of the ice bulb, p is the pressure of the air, T the temperature of the dry bulb, and A is the psychrometer coefficient. (The latter is preferred to the term "psychrometer constant", which is a misnomer.)

The wet-bulb thermometer temperature T_w for most instruments is not identical with the thermodynamic wet-bulb temperature defined in Annex 4.A, which depends only upon p , T and r (the humidity mixing ratio). The temperature measured by a practical wet-bulb thermometer depends also upon a number of variables which are influenced by the dynamics of heat transfer across a liquid/gas interface (in which the gas must be characterized in terms of its component laminar and turbulent layers). The description of a satisfactory thermodynamic model is beyond the scope of this publication. The inequality of the thermodynamic and measured wet-bulb temperatures is resolved in practice through the empirical determination of the psychrometer coefficient A (see section 4.2.6).

In general, the coefficient A depends upon the design of the psychrometer (in particular the wet-bulb system), the rate of airflow past the wet bulb (termed the ventilation rate), and the air temperature and its humidity. At low rates of ventilation, A depends markedly upon the ventilation rate. However, at ventilation rates of 3 to 5 m s⁻¹ (for thermometers of conventional dimensions) or higher, the value of A becomes substantially independent of the ventilation rate and is practically the same for well-designed psychrometers. The value of A does not, then, depend very much on temperature or humidity and

its dependence on these variables is usually considered unimportant. A is smaller when the wet bulb is coated with ice than when it is covered with water.

The formulae and coefficients appropriate for the various forms of psychrometer are discussed in the following sections.

4.2.1.2 THE SPECIFICATION OF A PSYCHROMETER

The equipment used for psychrometric observations should, as far as practicable, conform with the following recommendations (see sections 4.2.3 and 4.2.6):

- (a) At sea level, and in the case where the thermometers are of the types ordinarily used at meteorological stations, air should be drawn past the thermometer bulbs at a rate not less than 2.2 m s⁻¹ and not greater than 10 m s⁻¹. For appreciably different altitudes, these air speed limits should be adjusted in inverse proportion to the density of the atmosphere;
- (b) The wet and dry bulbs must be protected from radiation, preferably by a minimum of two shields. In a psychrometer with forced ventilation, such as the Assmann, the shields may be of polished, unpainted metal, separated from the rest of the apparatus by insulating material. Thermally-insulating material is preferable in principle, and must be used in psychrometers which rely on natural ventilation;
- (c) If the psychrometer is exposed in a louvred screen with forced ventilation, then separate ventilation ducts should be provided for the two thermometers. The entrance to the ducts should be located so as to yield a measurement of the true ambient temperature, and the air should be exhausted above the screen in such a way as to prevent recirculation;
- (d) The greatest care should be taken to prevent the transfer of significant amounts of heat from an aspirating motor to the thermometers;
- (e) The water reservoir and wick should be arranged in such a way that the water will reach the bulb with sensibly the wet-bulb temperature, so as not to affect the temperature of the dry bulb.

4.2.1.3 THE WET-BULB SLEEVE

The wet bulb usually has a cotton wick, or similar fabric, fitting closely around the sensing element in order to maintain an even covering of water, which is either applied directly or by some form of capillary feed from a reservoir. The wick commonly takes the form of a sleeve which has a good fit around the bulb, and extends at least 2 cm up the stem of the thermometer.

The fabric used to cover the wet bulb should be thin but closely woven. Before installation, it should be washed thoroughly in an aqueous solution of sodium bicarbonate (NaHCO₃), at a dilution of 5 g per litre, and rinsed several times in distilled water. Alternatively, a solution of pure detergent in water may be used. If a wick is to be employed, it should be similarly treated.

Any visible contamination of the wick or the wet-bulb sleeve should be considered an absolute indication of the necessity for its replacement. Great care should be exercised in handling the sleeve and wick to prevent contamination through the hands. Distilled water should be used for the wet bulb.

The proper management of the wet bulb is particularly important. Observers should be encouraged to change the wet-bulb sleeve and wick regularly. The replacement should be made at least once a week for all psychrometers which are continuously exposed. At places near the sea and in dusty or industrialized districts it may be necessary to replace these items more frequently. The water supply should be checked frequently and replaced or replenished as required.

Under hot dry conditions, it can be an advantage to wet the covering with water from a porous vessel. This will cause the water to be pre-cooled by evaporation from the porous surface. The vessel should be kept in the shade, but not in the immediate vicinity of the psychrometer.

4.2.1.4 OPERATION OF THE WET BULB BELOW FREEZING

The psychrometer is difficult to operate at temperatures below freezing, but it is used in climates where such temperatures occur. A wick cannot be used to convey water from a reservoir to the wet-bulb sleeve by capillary action when the wet-bulb temperature is below 0°C. Under these conditions, care should be taken to form only a thin layer of ice on the sleeve. It is an absolute necessity that the thermometers be artificially ventilated; if they are not, the management of the wet bulb will be extremely difficult.

The water should, as far as possible, have a temperature near the freezing point. If a button of ice forms at the lowest part of the bulb, it should be immersed in water long enough to melt the ice.

The amount of time required for the wet bulb to reach a steady reading after the sleeve is wetted depends on the ventilation rate and on the actual wet-bulb temperature. An unventilated thermometer usually requires from a quarter to three-quarters of an hour, while an aspirated thermometer will require a much shorter period. It is essential that the formation of a new ice film on the bulb be made at an appropriate time. If hourly observations are being made with a simple psychrometer, it will usually be preferable to form a new coating of ice just after each observation. If the observations follow longer intervals, then the observer should visit the screen sufficiently in advance of each observation to form a new ice film on the bulb. The wet bulb of the aspirated and sling psychrometers should be moistened immediately before use.

The evaporation of an ice film may be prevented or slowed by enclosing the wet bulb in a small glass tube, or by stopping the ventilation inlet of the wet bulb between intervals. (Note that the latter course should not

be taken if the circumstances are such that the ventilating fan would overheat.)

The effect of supercooled water on the wet bulb may be dealt with in two ways:

- (a) By using different tables when the wet bulb is coated with ice and with supercooled water, respectively. To find out which table should be used, the wet bulb should be touched with a snow crystal, a pencil or other object, just after each observation is completed. If the temperature rises towards 0°C, and then commences to fall again, it can be assumed that the water on the wet bulb was supercooled at the time of the observation;
- (b) By using a table appropriate for an ice-covered wet bulb and inducing the freezing of supercooled water in the same way as for method (a). In order to save time and to ensure that the wet bulb is ice-covered, the observer should make a point of initiating the freezing of the water at each observation as early as possible after moistening the bulb. From the behaviour of the wetted thermometer at the freezing point it may usually be determined whether the bulb is covered by ice or by supercooled water. The recommended procedure, however, is to initiate the freezing of the water at each observation when the wet-bulb temperature is assumed to be below 0°C, regardless of whether the behaviour of the thermometer after moistening has been observed or not.

The first method is usually the quickest, but it involves the need for two tables and this may cause some confusion.

4.2.1.5 GENERAL PROCEDURE FOR MAKING OBSERVATIONS

The procedures given in Chapter 2, Part I for the measurement of temperature should be followed, in addition to the following procedures:

- (a) If the wet-bulb sleeve, wick, or water have to be changed, this should be done sufficiently in advance of the observation. The period required for the correct wet-bulb temperature to be attained will depend upon the type of psychrometer;
- (b) The thermometers should be read to the nearest tenth of a degree;
- (c) When making an observation, the readings of the two thermometers should, as far as possible, be taken simultaneously, and it should be ascertained that the wet bulb is receiving a sufficient water supply.

4.2.1.6 USE OF ELECTRICAL RESISTANCE THERMOMETERS

Precision platinum electrical resistance thermometers are widely used in place of mercury-in-glass thermometers, in particular where distant reading and continuous measurements are required. It is necessary to ensure that the devices, and the interfacing electrical circuits

selected, meet the performance requirements. These are detailed in the Chapter 2, Part I. Particular care should always be taken with regard to self-heating effects in electrical thermometers.

The psychrometric formulae in Annex 4.B used for Assmann aspiration psychrometers are also valid if platinum resistance thermometers are used in place of the mercury-in-glass instruments, with different configurations of elements and thermometers. The formula for water on the wet bulb is also valid for some transversely ventilated psychrometers (WMO, 1989a).

4.2.1.7 SOURCES OF ERROR IN PSYCHROMETRY

The following main sources of error have to be considered:

(a) Index errors of the thermometers: It is very important in psychrometric measurements that the index errors of the thermometers be known over the actual temperature range and that corrections for these errors be applied to the readings before the humidity tables are used.

Any other errors in the wet-bulb or ice-bulb temperature caused by other influences will appear in the same way as index errors.

Table 4.3 shows the error in relative humidity $\varepsilon(U)$, derived from wet- and ice-bulb measurements having errors $\varepsilon(t_x)$ where x is water for $t > 0^\circ\text{C}$ and ice for $t < 0^\circ\text{C}$, respectively of 0.5 and 0.1 K, for a relative humidity U of 50 per cent and a range of true air temperatures (where the dry-bulb reading is assumed to give the true air temperature);

TABLE 4.3
Error in derived relative humidity resulting from wet- and ice-bulb index errors $\varepsilon(t_x)$ for $U = 50$ per cent

Air temperature in $^\circ\text{C}$	Error in relative humidity, $\varepsilon(U)$ in per cent due to an error in wet- or ice-bulb temperature	
	$\varepsilon(t_x) = 0.5 \text{ K}$	$\varepsilon(t_x) = 0.1 \text{ K}$
-30	60	12
-20	27	5
-10	14	3
0	8	2
10	5	1
20	4	0.5
30	3	0.5
40	2	0.5
50	2	0

(b) Thermometer lag coefficients: To obtain the highest accuracy with a psychrometer it is desirable to arrange for the wet and dry bulbs to have approximately the same lag coefficient; with thermometers having the same bulb size the wet bulb has an appreciably smaller lag than the dry bulb;

(c) Errors connected with ventilation: Errors due to insufficient ventilation become much more serious through the use of inappropriate humidity

tables (see sections covering individual psychrometer types);

(d) Errors due to excessive covering of ice on the wet bulb: Since a thick coating of ice will increase the lag of the thermometer, it should be removed immediately by dipping the bulb into distilled water;

(e) Errors due to contamination of the wet-bulb sleeve or to impure water: Large errors may be caused by the presence of substances that alter the vapour pressure of water. The wet bulb with its covering sleeve should be washed at regular intervals in distilled water to remove soluble impurities. This procedure is more frequently necessary in some regions than in others, e.g. at or near the sea or in areas subject to air pollution;

(f) Errors due to heat conduction from the thermometer stem to the wet-bulb system: Conduction of heat from the thermometer stem to the wet bulb will reduce the wet-bulb depression and lead to determinations of humidity that are too high. The effect is most pronounced at low relative humidity but can be effectively eliminated by extending the wet-bulb sleeve at least 2 cm beyond the bulb up the stem of the thermometer.

4.2.2 The Assmann aspirated psychrometer

4.2.2.1 DESCRIPTION

Two mercury-in-glass thermometers, mounted vertically side by side in a chromium- or nickel-plated polished metal frame, are connected by ducts to an aspirator. The aspirator may be driven by a spring or an electric motor. One thermometer bulb has a well-fitted muslin wick which, before use, is moistened with distilled water. Each thermometer is located inside a pair of coaxial metal tubes, highly polished inside and out, which screen the bulbs from external thermal radiation. The tubes are all thermally insulated from each other.

A WMO international intercomparison of Assmann-type psychrometers from 10 countries (WMO, 1989a) showed that there is good agreement between dry- and wet-bulb temperatures of psychrometers with the dimensional specifications close to the original specification, and with aspiration rates above 2.2 m s^{-1} . Not all commercially available instruments fully comply. A more detailed discussion is found in WMO (1989a). The performance of the Assmann psychrometer in the field may be as good as the achievable accuracy stated in Table 4.1, and with great care it can be significantly better.

Annex 4.B lists standard formulae for the computation of measures of humidity using an Assmann psychrometer¹, which are the bases of some of the other artificially ventilated psychrometers, in the absence of well-established alternatives.

¹ Recommended by the Commission for Instruments and Methods of Observation at its tenth session, 1989.

4.2.2.2 OBSERVATION PROCEDURE

The wick, which must be free of grease, is moistened with distilled water. Dirty or crusty wicks should be replaced. Care should be taken not to introduce a water bridge between the wick and the radiation shield.

The mercury columns of the thermometers should be inspected for breaks, which should be closed up or the thermometer replaced.

The instrument is normally operated with the thermometers held vertically. The thermometer stems should be protected from solar radiation by turning the instrument so that the lateral shields are in line with the Sun. The instrument should be tilted so that the inlet ducts open into the wind, but care should be taken that solar radiation does not fall on the thermometer bulbs. A wind screen is necessary in very windy conditions when the rotation of the aspirator is otherwise affected.

The psychrometer should be in thermal equilibrium with the surrounding air. At air temperatures above 0°C, reading of at least three minutes should be made following an aspiration period. Below 0°C it is necessary to wait until the freezing process has finished, and observe whether there is water or ice on the wick. During the freezing and thawing processes the wet-bulb temperature remains constant at 0°C. In the case of outdoor measurements, several measurements should be made and the average taken. Thermometer readings should be made with a resolution of 0.1 K or better.

A summary of the observation procedure is as follows:

- (a) Moisten the wet bulb;
- (b) Wind the clockwork motor (or start the electric motor);
- (c) Wait two or three minutes or until the wet-bulb reading has become steady;
- (d) Read the dry bulb;
- (e) Read the wet bulb;
- (f) Check the reading of the dry bulb.

4.2.2.3 EXPOSURE AND SITING

Observations should be made in an open situation with the instrument either suspended from a clamp or bracket attached to a thin post, or held with one hand at arm's length with the inlets slightly inclined into the wind. The inlets should be at a height from 1.2 to 2 m above ground when making normal measurements of air temperature and humidity.

Great care should be taken to avoid any influence on the readings by the presence of the observer or any other nearby sources of heat and water vapour, such as the exhaust pipe of a motor vehicle.

4.2.2.4 CALIBRATION

The ventilation system should be regularly checked, at least once per month.

The calibration of the thermometers should also be regularly checked. The two may be compared together,

both measuring the dry-bulb temperature. Comparison with a certificated reference thermometer should be performed at least once a year.

4.2.2.5 MAINTENANCE

Between readings, the instrument should be stored in an unheated room or otherwise protected from precipitation and strong insolation. When not in use, the instrument should be stored indoors in a sturdy packing case such as that supplied by the manufacturer.

4.2.3 *Screen psychrometer*

4.2.3.1 DESCRIPTION

Two mercury-in-glass thermometers are mounted vertically in a thermometer screen. The diameter of the sensing bulbs should be about 10 mm. One of the bulbs is fitted with a wet-bulb sleeve, which should fit closely to the bulb and extend at least 20 mm up the stem beyond it. If a wick and water reservoir are used to keep the wet-bulb sleeve in a moist condition, then the reservoir should preferably be placed to the side of the thermometer and with the mouth at the same level as, or slightly lower than, the top of the thermometer bulb. The wick should be kept as straight as possible and its length should be such that water reaches the bulb with sensibly the wet-bulb temperature and in sufficient (but not excessive) quantity. If no wick is used, then the wet bulb should be protected from dirt by enclosing the bulb in a small glass tube between the readings.

It is recommended that screen psychrometers be artificially aspirated. Both thermometers should be aspirated at an air speed of about 3 m s⁻¹. Both spring-wound and electrically-driven aspirators are in common use. The air should be drawn in horizontally across the bulbs, rather than vertically, and exhausted in such a way as to avoid recirculation.

The performance of the screen psychrometer may be much worse than that shown in Table 4.1, especially in light winds if the screen is not artificially ventilated.

The psychrometric formulae given in section 4.2.1.1 apply to screen psychrometers, but the coefficients are quite uncertain. A summary of some of the formulae in use is given by Bindon (1965). If there is artificial ventilation at 3 m s⁻¹ or more across the wet bulb the values given in Annex 4.B may be applied, with a psychrometer coefficient of $6.53 \cdot 10^{-4} \text{ K}^{-1}$ for water. However, values from 6.50 to $6.78 \cdot 10^{-4}$ are in use for wet bulbs above 0°C and 5.70 to $6.53 \cdot 10^{-4}$ for below 0°C. For a naturally ventilated screen psychrometer, coefficients in use range from 7.7 to $8.0 \cdot 10^{-4}$ above freezing and 6.8 to $7.2 \cdot 10^{-4}$ for below freezing when there is some air movement in the screen, which is probably nearly always the case. However, coefficients up to $12 \cdot 10^{-4}$ for water and $10.6 \cdot 10^{-4}$ for ice have been advocated for the case of no air movement.

The psychrometer coefficient appropriate for a particular configuration of screen, shape of wet bulb,

and degree of ventilation may be determined by comparison with a suitable working or reference standard, but there will be a wide scatter in the data, and a very large experiment would be necessary to obtain a stable result. Even when a coefficient has been obtained by such an experiment, the confidence limits for any single observation will be wide, and there would be little justification for departing from established national practices.

4.2.3.2 SPECIAL OBSERVATION PROCEDURES

The procedures described in section 4.2.1.5 apply to the screen psychrometer. In the case of a naturally-aspirated wet bulb, provided the water reservoir has about the same temperature as the air, the correct wet-bulb temperature will be attained approximately 15 minutes after fitting a new sleeve; if the water temperature differs substantially from that of the air, it may be necessary to wait for 30 minutes.

4.2.3.3 EXPOSURE AND SITING

Exposure and siting of the screen is described in Chapter 2, Part I.

4.2.4 *Sling or whirling psychrometers*

4.2.4.1 DESCRIPTION

A small portable type of whirling or sling psychrometer consists of two mercury-in-glass thermometers mounted on a sturdy frame; it is provided with a handle and spindle and located at the furthest end from the thermometer bulbs, by means of which the frame and thermometers may be rotated rapidly about a horizontal axis.

The wet-bulb arrangement varies according to individual design. Some designs shield the thermometer bulbs from direct insolation, and these are to be preferred for meteorological measurements.

The psychrometric formulae in Annex 4.B may be used.

4.2.4.2 OBSERVATION PROCEDURE

The following guidelines should be applied:

- (a) All instructions with regard to the handling of Assmann aspirated psychrometers apply also to sling psychrometers;
- (b) Sling psychrometers lacking radiation shields for the thermometer bulbs should be shielded from direct insolation in some other way;
- (c) Thermometers should be read at once after aspiration ceases because the wet-bulb temperature will begin to rise immediately, and the thermometers are likely to be subject to insolation effects.

4.2.5 *Heated psychrometer*

The principle of the heated psychrometer is that the water vapour content of an air mass does not change if it is heated. This property may be exploited to the advantage of the psychrometer by avoiding the need to maintain an ice bulb under freezing conditions.

4.2.5.1 DESCRIPTION

Air is drawn into a duct where it passes over an electrical heating element and then into a measuring chamber containing both dry- and wet-bulb thermometers and a water reservoir. The heating element control circuit ensures that the air temperature does not fall below a certain level, which might typically be 10°C. The temperature of the water reservoir is maintained in a similar way. Thus, neither the water in the reservoir nor the water at the wick should freeze, certainly provided that the wet-bulb depression is less than 10 K, and that the continuous operation of the psychrometer is secured even if the air temperature is below 0°C. At temperatures above 10°C the heater may be automatically switched off, when the instrument reverts to normal psychrometric operation.

Electrical thermometers are used so that they may be entirely enclosed within the measuring chamber and without the need for visual readings.

A second dry-bulb thermometer is located at the inlet of the duct to provide a measurement of the ambient air temperature. Thus, the ambient relative humidity may be determined.

The psychrometric thermometer bulbs are axially aspirated at an air velocity in the region of 3 m s⁻¹.

4.2.5.2 OBSERVATION PROCEDURE

A heated psychrometer would be suitable for automatic weather stations.

4.2.5.3 EXPOSURE AND SITING

The instrument itself should be mounted outside a thermometer screen. The air inlet, where ambient air temperature is measured, should be inside the screen.

4.2.6 *The WMO reference psychrometer*

The reference psychrometer and procedures for its operation are described in WMO (1992). The wet- and dry-bulb elements are enclosed in an aspirated shield, for use as a free-standing instrument. Its significant characteristic is that the psychrometer coefficient is calculable from the theory of heat and mass exchanges at the wet bulb, and is different from the coefficient for other psychrometers, with a value of $6.53 \cdot 10^{-4} \text{ K}^{-1}$ at 50 per cent relative humidity, 20°C and 1 000 hPa. Its wet-bulb temperature is very close to the theoretical value (see Annex 4.A, paragraphs 18 and 19). This is achieved by ensuring that the evaporation at the wet bulb is very efficient and that extraneous heating is minimized. The nature of the airflow over the wet bulb is controlled by careful shaping of the duct and the bulb, and by controlling the ventilation rate. The double shield is highly reflective externally, and blackened inside, and the thermometer elements are insulated and separated by a shield. The shields and the wet-bulb element (which contains the thermometer) are of stainless steel to minimize thermal conduction.

The procedures for the use of the reference psychrometer ensure that the wet bulb is completely free of grease, even in the monomolecular layers that always arise from handling any part of the apparatus with the fingers. This is probably the main reason for the close relation of the coefficient to the theoretical value, and its difference from the psychrometer coefficients of other instruments.

The reference psychrometer is capable of great accuracy, ± 0.38 per cent in relative humidity at 50 per cent relative humidity and 20°C. It has also been adopted as the WMO reference thermometer. It is designed for use in the field but it is not suitable for routine use. It should be operated only by staff who are accustomed to very sensitive laboratory work. Its use as a reference instrument is discussed in section 4.9.7.

4.3 The hair hygrometer

4.3.1 General considerations

Any absorbing material tends to equilibrium with its environment in both temperature and humidity. The water vapour pressure at the surface of the material is determined by the temperature and the amount of water bound by the material. Any difference between this pressure and the water-vapour pressure of the surrounding air will be equalized by the exchange of water molecules.

The change in length of hair has been found to be a function primarily of the change in relative humidity with respect to liquid water (both above and below an air temperature of 0°C), and an increase by about 2 to 2.5 per cent when the humidity changes from zero to 100 per cent. By rolling the hairs to produce an elliptical cross-section and by dissolving out the fatty substances with alcohol, the ratio of the surface area to the enclosed volume increases and yields a decreased lag coefficient which is particularly relevant for use at low air temperatures. This procedure also results in a more linear response function although the tensile strength is reduced. For accurate measurements, a single hair element is to be preferred, but a bundle of hairs is commonly used to provide a degree of ruggedness. Chemical treatment with barium (BaS) or sodium (Na₂S) sulfide yields further linearity of response.

The hair hygrograph or hygrometer is considered to be a satisfactory instrument for use in situations or during periods where extreme and very low humidities are seldom or never found. The mechanism of the instrument should be as simple as possible, even if this makes it necessary to have a non-linear scale; this is especially important in industrial regions, since air pollutants may act on the surface of the moving parts of the mechanism and increase friction between them.

The rate of response of the hair hygrometer is very dependent on air temperature. At -10°C the lag of the instrument is approximately three times greater than the lag at 10°C. For air temperatures between 0 and 30°C and relative humidities between 20 and 80 per cent a

good hygrograph should indicate 90 per cent of a sudden change in humidity within about three minutes.

A good hygrograph in perfect condition should be capable of recording relative humidity at moderate temperatures with an uncertainty of ± 3 per cent. At low temperatures, the uncertainty will be greater.

Hair pre-treated by rolling (as described above) is a requirement if useful information is to be obtained at low temperatures.

4.3.2 Description

The detailed mechanism of hair hygrometers varies according to the manufacturer. Some instruments incorporate a transducer to provide an electrical signal and these may also provide a linearizing function so that the overall response of the instrument is linear with respect to changes in relative humidity.

The most commonly used hair hygrometer is the hygrograph. This employs a bundle of hairs held under slight tension by a small spring and connected to a pen arm in such a way as to magnify a change in the length of the bundle. A pen at the end of the pen arm is in contact with a paper chart fitted around a metal cylinder and registers the angular displacement of the arm. The cylinder rotates about its axis at a constant rate determined by a mechanical clock movement. The rate of rotation is usually one revolution either per week or per day. The chart has a scaled time axis which extends round the circumference of the cylinder and a scaled humidity axis parallel to the axis of the cylinder. The cylinder normally stands vertically.

The mechanism connecting the pen arm to the hair bundle may incorporate specially designed cams which translate the non-linear extension of the hair in response to humidity changes into a linear angular displacement of the arm.

The hair used in hygrometers may be of synthetic fibre. Where human hair is used it is normally first treated as described in section 4.3.1 to improve both the linearity of its response and the response lag, although this does result in a lower tensile strength.

The pen arm and clock assembly are normally housed in a box with glass panels which allow the registered humidity to be observed without disturbing the instrument, and one end open to allow the hair element to be exposed in free space outside the limits of the box. The sides of the box are separate from the solid base, but the end opposite the hair element is attached to it by a hinge. This arrangement allows free access to the clock cylinder and hair element. The element may be protected by an open mesh cage.

4.3.3 Observation procedure

The hair hygrometer should always be tapped lightly before reading in order to free any tension in the mechanical system. The hygrograph should, as far as possible, not be touched between changes of the charts except for the making of time marks.

Both the hygrometer and the hygrograph can normally be read to the nearest one per cent relative humidity. Attention is drawn to the fact that the hair hygrometer measures relative humidity with respect to saturation over liquid water even at air temperatures below 0°C.

The humidity of the air may change very rapidly and, therefore, accurate setting of time marks on a hygrograph is very important. In making the marks, the pen arm should be moved only in the direction of decreasing humidity on the chart. This is done so that the hairs are slackened by the displacement and, to bring the pen back to its correct position, the restoring force is applied by the tensioning spring. However, the effect of hysteresis may be evidenced in the failure of the pen to return to its original position.

4.3.4 *Exposure and siting*

The hygrograph or hygrometer should be exposed in a thermometer screen. Ammonia is very destructive to natural hair. Exposure in the immediate vicinity of stables and industrial plants using ammonia should be avoided.

When used in polar regions, the hygrograph should preferably be exposed in a special thermometer screen which provides the instrument with sufficient protection against precipitation and drifting snow. For example, a cover for the thermometer screen can be made of fine-meshed net (Mullergas) as a precautionary measure to prevent the accumulation of snow crystals on the hairs and bearing surfaces of the mechanical linkage. This method can be used only if there is no hazard of wetting the net by melting snow crystals.

4.3.5 *Sources of error*

4.3.5.1 **CHANGES IN ZERO OFFSET**

For various reasons which are poorly understood, the hygrograph is liable to change its zero. The most likely cause is that excess tension has been induced in the hairs. For instance, the hairs may be stretched if time marks are made in the direction of increasing humidity on the chart or if the hygrograph mechanism sticks during decreasing humidity. The zero may also change if the hygrograph is kept in very dry air for a long time, but the change may be reversed by placing the instrument in a saturated atmosphere for a sufficient length of time.

4.3.5.2 **ERRORS DUE TO CONTAMINATION OF THE HAIR**

Most kinds of dust will cause appreciable errors in observations (perhaps as much as 15 per cent relative humidity). In most cases this may be eliminated, or at least reduced, by cleaning and washing the hairs. However, the harmful substances found in dust may also be destructive to hair (see section 4.3.4).

4.3.5.3 **HYSTERESIS**

Hysteresis is exhibited both in the response of the hair element and in the recording mechanism of the hair

hygrometer. Hysteresis in the recording mechanism is reduced through the use of a hair bundle, which allows a greater loading force to overcome friction. It should be remembered that the displacement magnification of the pen arm lever applies also to the frictional force between the pen and paper, and requires a proportionately higher tension in the hair to overcome it. The correct setting of the tensioning spring is also required to minimize hysteresis, as is the correct operation of all parts of the transducing linkage. The main fulcrum and any linearizing mechanism in the linkage introduce much of the total friction.

Hysteresis in the hair element is normally a short-term effect related to the absorption-desorption processes and is not a large source of error once vapour pressure equilibrium is established (see section 4.3.5.1 in respect of prolonged exposure at low humidity).

4.3.6 *Calibration and comparisons*

The readings of a hygrograph should be checked as frequently as is practical. In the case where wet- and dry-bulb thermometers are housed in the same thermometer screen these may be used to provide a comparison whenever suitable steady conditions prevail, but otherwise field comparisons have limited value due to the difference in response rate of the instruments.

Accurate calibration can only be obtained through the use of an environmental chamber and by comparison with reference instruments.

The 100 per cent humidity point may be checked, preferably indoors with a steady air temperature, by surrounding the instrument with a saturated cloth (though the correct reading will not be obtained if a significant mass of liquid water droplets form on the hairs).

The ambient indoor humidity may provide a low relative humidity check point for comparison against a reference aspirated psychrometer. A series of readings should be obtained.

Long-term stability and bias may be appraised by presentation of comparisons with a reference aspirated psychrometer in terms of a correlation function.

4.3.7 *Maintenance*

Observers should be encouraged to maintain the hygrometer in a clean condition.

The hair should be washed down at frequent intervals with distilled water on a soft brush to remove accumulated dust or soluble contaminants. The hair should at no time be touched with the fingers. The bearings of the mechanism should be kept clean and a little clock oil should occasionally be applied. The bearing surfaces of any linearizing mechanism will contribute largely to the total friction in the linkage, which may be minimized by polishing the surfaces with graphite. This procedure may be carried out by using a piece of blotting paper rubbed with a lead pencil.

With proper attention, the hairs may last for several years in a temperate climate and when not subject to severe atmospheric pollution. Recalibration and adjustment will be required following replacement of the hairs.

4.4 The chilled-mirror dew-point hygrometer

4.4.1 General considerations

4.4.1.1 THEORY

The dew-point (or frost-point) hygrometer is used to measure the temperature at which moist air, when cooled, reaches saturation and a deposit of dew (or ice) can be detected on a solid surface, which usually is a mirror. The deposit is normally detected optically. The principle of the measurement is described in section 4.1.4.5 and below.

The thermodynamic dew point is defined for a plane surface of pure water. In practice, water droplets have curved surfaces, over which the saturation vapour pressure is higher than for the plane surface (known as the Kelvin effect). Hydrophobic contaminants will exaggerate the effect, whilst soluble ones will have the opposite effect and lower the saturation vapour pressure (the Raoult effect). The Kelvin and Raoult effects (which, respectively, raise and lower the apparent dew point) are minimized if the critical droplet size adopted is large rather than small; this reduces the curvature effect directly and reduces the Raoult effect by lowering the concentration of a soluble contaminant.

4.4.1.2 PRINCIPLES

When moist air at temperature T , pressure p and mixing ratio r_w (or r_i) is cooled, it eventually reaches its saturation point with respect to a free water surface (or to a free ice surface at lower temperatures) and a deposit of dew (or frost) can be detected on a solid non-hygroscopic surface. The temperature of this saturation point is called the thermodynamic dew-point temperature T_d (or the thermodynamic frost-point temperature T_f). The corresponding saturation vapour pressure with respect to water, e'_w , (or ice e'_i) is a function of T_d (or T_f), as shown in the following equations:

$$e'_w(p, T_d) = f(p) \cdot e_w(T_d) = \frac{r \cdot p}{0.62198 + r} \quad (4.3)$$

$$e'_i(p, T_f) = f(p) \cdot e_i(T_f) = \frac{r \cdot p}{0.62198 + r} \quad (4.4)$$

The hygrometer measures T_d or T_f . Despite the great dynamic range of moisture in the troposphere, this instrument is capable of detecting both very high and very low concentrations of water vapour by means of a thermal sensor alone.

Cooling using a low-boiling point liquid has been used but is now largely superseded except for very low water vapour concentrations.

It follows from the above that it must also be possible to determine whether the deposit is super-cooled

liquid or ice when the surface temperature is at or below the freezing point.

The chilled-mirror hygrometer is used for meteorological measurements and as a reference instrument both in the field and in the laboratory.

4.4.2 Description

4.4.2.1 SENSOR ASSEMBLY

The most widely used systems employ a small polished-metal reflecting surface, cooled electrically by using a Peltier-effect device. The sensor consists of a thin metallic mirror of small (2–5 mm) diameter which is thermally regulated by using a cooling assembly (and possibly a heater), with a temperature sensor (thermocouple or platinum resistance thermometer) embedded on the underside of the mirror. The mirror should have a high thermal conductance, optical reflectivity, and corrosion resistance combined with a low permeability to water vapour. Suitable materials used include gold, rhodium-plated silver, chromium-plated copper, and stainless steel.

The mirror should be equipped with a device (preferably automatic) for detecting contaminants which may raise or lower the apparent dew point (see section 4.4.2.2) so that they may be removed.

4.4.2.2 OPTICAL DETECTION ASSEMBLY

An electro-optical system is usually employed to detect the formation of condensate and to provide the input to the servo-control system to regulate the temperature of the mirror. A narrow beam of light is directed at the mirror at an angle of incidence of about 55°. The light source may be incandescent but is now commonly a light-emitting-diode. In simple systems, the intensity of the directly reflected light is detected by a photodetector which regulates the cooling and heating assembly through a servo-control. The specular reflectivity of the surface decreases as the thickness of the deposit increases; cooling should cease whilst the deposit is thin, with a reduction in reflectance in the range of five to 40 per cent. More elaborate systems use an auxiliary photodetector which detects the light scattered by the deposit; the two detectors are capable of very precise control. A second, uncooled, mirror may be used to improve the control system.

Greatest precision is obtained by controlling the mirror to a temperature at which condensate neither accumulates nor dissipates, though, in practice, the servo-system will oscillate around this temperature. The response time of the mirror to heating and cooling is critical in respect of the amplitude of the oscillation, and should be of the order of one to two seconds. The airflow rate is also important for maintaining a stable deposit on the mirror. It is possible to determine the temperature at which condensation occurs with a precision of 0.05 K.

It is feasible, but a time-consuming and skilled task, to observe the formation of droplets by using a microscope and to regulate the mirror temperature under manual control.

4.4.2.3 THERMAL CONTROL ASSEMBLY

A Peltier-effect thermojunction device provides a simple reversible heat pump; the polarity of direct current energization determines whether heat is pumped to, or from, the mirror. The device is bonded to, and in good thermal contact with, the underside of the mirror. For very low dew points, a multi-stage Peltier device may be required.

Thermal control is achieved by using an electrical servo-system which takes as input the signal from the optical detector subsystem. Modern systems operate under microprocessor control.

A low-boiling-point fluid, such as liquid nitrogen, may be used to provide cooling, but this technique is no longer widely used. Similarly, electrical resistance-wire may be used for heating but is now superseded with the advent of small Peltier devices.

4.4.2.4 TEMPERATURE DISPLAY SYSTEM

The mirror temperature, as measured by the electrical thermometer embedded beneath the mirror surface, is presented to the observer as the dew point of the air sample. Commercial instruments normally include an electrical interface for the mirror thermometer and a digital display, but may also provide digital and analogue electrical outputs for use with data-logging equipment. A chart recorder is particularly useful for monitoring the performance of the instrument in the case where the analogue output provides a continuous registration of the mirror thermometer signal but the digital display does not.

4.4.2.5 AUXILIARY SYSTEMS

A microscope may be incorporated to provide a visual method to discriminate between supercooled water droplets and ice crystals for mirror temperatures below 0°C. Some instruments have a detector mounted on the mirror surface to provide an automatic procedure for this purpose (e.g. capacitive sensor), whilst others employ a method based on reflectance.

A microprocessor-based system may incorporate algorithms to calculate and display relative humidity. In this case, it is important that the instrument correctly discriminates between a water and an ice deposit.

Many instruments provide an automatic procedure for minimizing the effects of contamination. This may be a regular heating cycle in which volatile contaminants are evaporated and removed in the air stream. Systems including automatic cleaning of the mirror by means of a wiper are also in use.

For meteorological measurements, and in most laboratory applications, a small pump is required to draw the sampled air through the measuring chamber. A regulating device is also required to set the flow at a rate which is consistent with the stable operation of the mirror temperature servo-control system and at an acceptable rate of response to changes in humidity. The

optimum flow rate is dependent upon the moisture content of the air sample and is normally within the range of 0.25 to 1 l min⁻¹.

4.4.3 Observation procedure

The correct operation of a dew-point hygrometer depends upon achieving an appropriate volume airflow rate through the measuring chamber. The setting of a regulator for this purpose, usually a throttling device located downstream of the measuring chamber, is likely to require adjustment to accommodate diurnal variations in air temperature. Adjustment of the airflow will disturb the operation of the hygrometer and it may even be advisable to initiate a heating cycle. Both measures should be taken with sufficient time in order for a stable operation to be achieved before a reading is taken. The amount of time required will depend upon the control cycle of the individual instrument. The manufacturer's instructions should be consulted to provide appropriate guidance on the airflow rate to be set and on details of the instrument's control cycle.

The condition of the mirror should be checked frequently; the mirror should be cleaned as necessary. The stable operation of the instrument does not necessarily imply that the mirror is clean. It should be washed with distilled water and dried carefully by wiping with a soft cloth or cotton dabstick to remove any soluble contaminant. Care must be taken not to scratch the surface of the mirror, most particularly where the surface has a thin plating to protect the substrate or where an ice/liquid detector is incorporated. If an air filter is not in use, then cleaning should be performed at least daily. If an air filter is in use then its condition should be inspected at each observation. The observer should take care not to stand next to the air inlet nor to allow the outlet to become blocked.

For readings at or below 0°C the observer should determine whether the mirror condensate is supercooled water or ice. If no automatic indication is given then the mirror must be observed. From time to time the operation of any automatic system should be verified.

An uncertainty of ± 0.3 K over a wide dew-point range (-60 to 50°C) is specified for the best instruments.

4.4.4 Exposure and siting

The criteria for siting of the sensor unit are similar to those for any aspirated hygrometer, although less stringent than for either a psychrometer or a relative humidity sensor, considering the fact that the dew or frost point of an air sample is unaffected by changes to the ambient temperature provided that it remains above the dew point at all times. For this reason, a temperature screen is not required. The sensor should be exposed in an open space and may be mounted on a post, within a protective housing structure, with an air inlet at the required level.

An air-sampling system is required. This is normally a small pump which must draw air from the

outlet port of the measuring chamber and eject it away from the inlet duct. Recirculation of the airflow should be avoided as this represents a poor sampling technique, although under stable operation the water vapour content at the outlet should be effectively identical with that at the inlet. Recirculation may be avoided by fixing the outlet at a level above the inlet, although this may not be effective under radiative atmospheric conditions when a negative air temperature lapse rate exists.

An air filter should be provided for continuous outdoor operations. It must be capable of allowing an adequate through-flow of air without a large blocking factor, as this may result in a significant drop in air pressure and affect the condensation temperature in the measuring chamber. A sintered metal filter may be used in this application to capture all but the smallest aerosol particles. A metal filter has the advantage that it may be heated easily by an electrical element in order to keep it dry under all conditions. It is more robust than the membrane-type and more suited to passing the relatively high airflow rates required by the chilled-mirror method as compared with the sorption method. On the other hand, a metallic filter may be more susceptible to corrosion by atmospheric pollutants than some membrane filters.

4.4.5 Calibration

Regular comparisons against a reference instrument, such as an Assmann psychrometer or another chilled mirror hygrometer, should be made as the operation of a field chilled mirror is subject to a number of influences which may degrade its performance. An instrument continuously in the field should be the subject of weekly check measurements. As the opportunity arises, its operation at both dew and frost points should be verified. When the mirror temperature is below 0°C the deposit should be inspected visually, if this is possible, to determine whether it is of super-cooled water or ice.

A useful check is to compare the mirror temperature measurement with the air temperature while the thermal control system of the hygrometer is inactive. The instrument should be aspirated, and the air temperature measured at the mouth of the hygrometer air intake. This check is best performed under stable, non-condensing conditions. In bright sunshine, the sensor and duct should be shaded and allowed to come to equilibrium. The aspiration rate may be increased for this test.

An independent field calibration of the mirror thermometer interface may be performed by simulating the thermometer signal. In the case of a platinum resistance thermometer, a standard platinum resistance simulation box, or a decade resistance box and a set of appropriate tables, may be used. A special simulator interface for the hygrometer control unit may also be required.

4.5 The lithium chloride heated condensation hygrometer (dew cell)

4.5.1 General considerations

4.5.1.1 PRINCIPLES

The physical principles of the heated salt-solution method are discussed in section 4.1.4.5.2. The equilibrium vapour pressure at the surface of a saturated lithium chloride solution is exceptionally low. As a consequence, a solution of lithium chloride is extremely hygroscopic under typical conditions of surface atmospheric humidity; if the ambient vapour pressure exceeds the equilibrium vapour pressure of the solution, then water vapour will condense over it (e.g. at 0°C water vapour condenses over a plane surface of a saturated solution of lithium chloride to only 15 per cent relative humidity).

A thermodynamically self-regulating device may be achieved if the solution is heated directly by passing an electrical current through it from a constant voltage device. An alternating current should be used to prevent polarization of the solution. As the electrical conductivity decreases, so will the heating current, and an equilibrium point will be reached whereby a constant temperature is maintained; any cooling of the solution will result in the condensation of water vapour, thus causing an increase in conductivity and an increase in heating current, which will reverse the cooling trend. Heating beyond the balance point will evaporate water vapour until the consequent fall in conductivity reduces the electrical heating to the point where it is exceeded by heat losses and cooling ensues.

It follows from the above that there is a lower limit to the ambient vapour pressure that may be measured in this way at any given temperature. Below this value, the salt solution would have to be cooled in order for water vapour to condense and would be equivalent to the chilled-mirror method except that, in the latter case, condensation takes place at a lower temperature when saturation is achieved with respect to a pure water surface, i.e. at the ambient dew point.

A degree of uncertainty is inherent in the method due to the existence of four different hydrates of lithium chloride. At certain critical temperatures, two of the hydrates may be in equilibrium with the aqueous phase, and the equilibrium temperature achieved by heating is affected according to the hydrate transition that follows. The most serious ambiguity for meteorological purposes occurs for ambient dew-point temperatures below -12°C; for an ambient dew point of -23°C the potential difference in equilibrium temperature, according to which of the two hydrate-solution transitions takes place, results in an uncertainty of ± 3.5 K in the derived dew-point value.

4.5.1.2 DESCRIPTION

The dew-cell hygrometer measures the temperature at which the equilibrium vapour pressure for a saturated

solution of lithium chloride is equal to the ambient water vapour pressure. Empirical transformation equations, based on saturation vapour pressure data for lithium chloride solution and for pure water, provide for the derivation of the ambient water vapour and dew point with respect to a plane surface of pure water. The dew-point temperature range from -12 to 25°C results in dew-cell temperatures in the range 17 to 71°C .

4.5.1.3 SENSORS WITH DIRECT HEATING

The sensor consists of a tube, or bobbin, with a resistance thermometer fitted axially within. The external surface of the tube is covered with a glass fibre material (usually as tape wound around and along the tube) that is soaked with an aqueous solution of lithium chloride, sometimes combined with potassium chloride. Bifilar silver or gold wire is wound over the covering of the bobbin with equal spacing between the turns. An alternating electrical current source is connected to the two ends of the bifilar winding; this is commonly derived from the normal electrical supply (50 or 60 Hz). The lithium chloride solution is electrically conductive to a degree determined by the concentration of solute. A current passes between adjacent bifilar windings, which act as electrodes, and through the solution. The current causes heating of the solution, and an increase in its temperature.

Except under conditions of extremely low humidity, the ambient vapour pressure will be higher than the equilibrium vapour pressure over the solution of lithium chloride at ambient air temperature, and water vapour will condense onto the solution. As the solution is heated by the electrical current, a temperature will eventually be reached above which the equilibrium vapour pressure exceeds the ambient vapour pressure, evaporation will begin, and the concentration of the solution will increase.

An operational equilibrium temperature exists for the instrument, depending upon the ambient water-vapour pressure. Above the equilibrium temperature, evaporation will increase the concentration of the solution, and the electrical current and the heating will decrease and allow heat losses to cause the temperature of the solution to fall. Below the equilibrium temperature, condensation will decrease the concentration of the solution, and the electrical current and the heating will increase and cause the temperature of the solution to rise. At the equilibrium temperature, neither evaporation nor condensation occur because the equilibrium vapour pressure and the ambient vapour pressure are equal.

In practice, the equilibrium temperature measured is influenced by individual characteristics of sensor construction and has a tendency to be higher than that predicted from equilibrium vapour-pressure data for a saturated solution of lithium chloride. However, reproducibility is sufficiently good to allow the use of a standard transfer function for all sensors constructed to a given specification.

Strong ventilation affects the heat transfer characteristics of the sensor and fluctuations in ventilation lead to unstable operation.

In order to minimize the risk of excessive current when switching on the hygrometer (as the resistance of the solution at ambient temperature is rather low), a current limiting device, in the form of a small lamp, is normally connected to the heater element. The lamp is chosen so that at normal bobbin operating currents the filament resistance will be low enough for the hygrometer to function properly, while the operating current for the incandescent lamp (even allowing for a bobbin offering no electrical resistance) is below a value that might damage the heating element.

The equilibrium vapour pressure for saturated lithium chloride depends upon the hydrate being in equilibrium with the aqueous solution. In the range of solution temperatures corresponding to dew points of -12 to 41°C monohydrate normally occurs. Below -12°C , dihydrate forms, and above 41°C , anhydrous lithium chloride forms. Close to the transition points, the operation of the hygrometer is unstable and the readings are ambiguous. However, the -12°C lower dew point limit may be extended to -30°C by the addition of a small amount of potassium chloride (KCl).

4.5.1.4 SENSORS WITH INDIRECT HEATING

Improved accuracy, compared with the arrangement described in section 4.5.1.2, may be obtained when a solution of lithium chloride is heated indirectly. The conductance of the solution is measured between two platinum electrodes and provides control of a heating coil.

4.5.2 Operational procedure

Readings of the equilibrium temperature of the bobbin are taken and a transfer function is applied to obtain the dew-point temperature.

Disturbing the sensor should be avoided as the equilibrium temperature is sensitive to changes in heat losses at the bobbin surface.

The instrument should be energized continuously. If allowed to cool below the equilibrium temperature for any length of time, condensation will occur and the electrolyte will drip off.

Check measurements with a working reference hygrometer must be made at regular intervals and the instrument must be cleaned and retreated with a lithium chloride solution, as necessary.

A current-limiting device should be installed if not provided by the manufacturer, otherwise the high current may damage the sensor when the instrument is powered-up.

4.5.3 Exposure and siting

The hygrometer should be located in an open area in a housing structure which protects it from the effects of wind and rain. A system for providing a steady aspiration rate is required.

The heat from the hygrometer may affect other instruments and this should be taken into account when choosing its location.

The operation of the instrument will be affected by atmospheric pollutants, particularly substances which dissociate in solutions and produce a significant ion concentration.

4.5.4 Sources of error

An electrical resistance thermometer is required for measuring the equilibrium temperature; the usual sources of error for thermometry are present.

The equilibrium temperature achieved is determined by the properties of the solute, and significant amounts of contaminant will have an unpredictable effect.

Variations in aspiration affect the heat exchange mechanisms and, thus, the stability of operation of the instrument. A steady aspiration rate is required for a stable operation.

4.5.5 Calibration

A field calibration should be performed at least once a month, by comparing with a working standard instrument. Calibration of the bobbin thermometer and the temperature display should be performed regularly as for other operational thermometers and display systems.

4.5.6 Maintenance

The lithium chloride should be renewed regularly. This may be required once a month, but will depend upon the level of atmospheric pollution. When renewing the solution, the bobbin should be washed with distilled water and then fresh solution should be applied. The housing structure should be cleaned at the same time.

Fresh solution may be prepared by mixing five parts by weight of anhydrous lithium chloride with 100 parts by weight of distilled water. This is equivalent to 1 g of anhydrous lithium chloride to 20 ml of water.

The temperature-sensing apparatus should be maintained in accordance with the recommendations for electrical instruments used for making air-temperature measurements, but bearing in mind the difference in the range of temperatures measured.

4.6 Electrical resistive and capacitive hygrometers

4.6.1 General considerations

Certain hygroscopic materials exhibit changes in their electrical properties in response to a change in the ambient relative humidity with only a small temperature-dependence.

Electrical relative humidity sensors are increasingly used for distant reading applications, particularly where a direct display of relative humidity is required. Many of them have very non-linear responses to changes of humidity, so the manufacturers often supply them with special data-processing and display systems.

4.6.2 Electrical resistance

Sensors made from chemically-treated plastic material having an electrically-conductive surface layer on the non-conductive substrate may be used for meteorological purposes. The surface resistivity varies according to the ambient relative humidity. The process of adsorption, rather than absorption, is dominant because the humidity-sensitive part of such a sensor is restricted to the surface layer. As a result, this type of sensor is capable of responding rapidly to a change in ambient humidity.

This class of sensor includes various electrolytic types in which the availability of conductive ions in a hygroscopic electrolyte is a function of the amount of sorbed water vapour. The electrolyte may take various physical forms, such as liquid or gel solutions, or an ion-exchange resin. The change in impedance to an alternating current, rather than to a direct current, is measured in order to avoid polarization of the electrolyte. Low-frequency supply can be used, as it is the DC resistance that is to be measured, and so it is possible to employ quite long leads between the sensor and its electrical interface.

4.6.3 Electrical capacitance

The method is based upon the variation of the dielectric properties of a solid, hygroscopic, material in relation to the ambient relative humidity. Polymeric materials are most widely used for this purpose. The water bound in the polymer alters its dielectric properties due to the large dipole moment of the water molecule.

The active part of the humidity sensor consists of a polymer foil sandwiched between two electrodes to form a capacitor. The electrical impedance of this capacitor provides a measure of relative humidity. The nominal value of capacitance may be only a few or several hundred picofarads, depending upon the size of the electrodes and the thickness of the dielectric. This will, in turn, influence the range of excitation frequency used to measure the impedance of the device, which is normally at least several kHz and, thus, requires that short connections be made between the sensor and the electrical interface to minimize the effect of stray capacitance. Therefore, capacitance sensors normally have the electrical interface built into the probe and it is necessary to consider the effect of environmental temperature on the performance of the circuit components.

4.6.4 Observation procedure

Sensors based on changes in electronic properties of hygroscopic materials are frequently used for distant reading of relative humidity and also for automatic weather stations.

4.6.5 Exposure and siting

The sensors should be mounted inside a thermometer screen. The manufacturers' advice regarding mounting of the actual sensor should be followed. The use of

protective filters is mandatory. Direct contact with liquid water will seriously harm sensors using hygroscopic electrolyte as a sensor element. Great care should be taken to prevent liquid water from reaching the sensitive element of such sensors.

4.6.6 Calibration

Field and laboratory calibrations should be carried out as for hair hygrometers. Suitable auxiliary equipment to enable checks by means of salt solutions are available for most sensors of this type.

4.6.7 Maintenance

Observers should be encouraged to maintain the hygrometer in clean conditions (see section 4.1.4.11).

4.7 Hygrometers using absorption of electromagnetic radiation

The water molecule absorbs electromagnetic radiation (EMR) in a range of wavebands and discrete wavelengths; this property can be exploited to obtain a measure of the molecular concentration of water vapour in a gas. The most useful regions of the electromagnetic spectrum, for this purpose, lie in the ultraviolet and infrared regions. Therefore, the techniques are often classified as optical hygrometry or, more correctly, EMR absorption hygrometry.

The method makes use of measurements of the attenuation of radiation in a waveband specific to water vapour absorption, along the path between a source of the radiation and a receiving device. There are two principal methods for determining the degree of attenuation of the radiation:

- (a) Transmission of narrow-band radiation at a fixed intensity to a calibrated receiver: The most commonly used source of radiation is hydrogen gas; the emission spectrum of hydrogen includes the Lyman-Alpha line at 121.6 nm, which coincides with a water vapour absorption band in the ultraviolet region where there is little absorption by other common atmospheric gases. The measuring path is typically a few centimetres in length;
- (b) Transmission of radiation at two wavelengths, one of which is strongly absorbed by water vapour and the other either not absorbed or only very weakly absorbed: If a single source is used to generate the radiation at both wavelengths, then the ratio of their emitted intensities may be accurately known, so that the attenuation at the absorbed wavelength can be determined by measuring the ratio of their intensities at the receiver. The most widely used source for this technique is a tungsten lamp, filtered to isolate a pair of wavelengths in the infrared region. The measuring path is normally greater than 1 m.

Both types of EMR absorption hygrometer require frequent calibration and are more suitable for measuring changes in vapour concentration rather than absolute levels. The most widespread application of the EMR

absorption hygrometer is in the monitoring of very high-frequency variations in humidity, since the method does not require the detector to achieve vapour pressure equilibrium with the sample. The time constant of an optical hygrometer is typically just a few milliseconds. The use of optical hygrometers remains restricted to research activities.

4.8 Safety

Chemical agents are widely used in the measurement of humidity. The properties of such agents should always be made known to the personnel handling them. All chemicals should be kept in secure and clearly labelled containers and should be stored in an appropriate environment. Instructions concerning the use of toxic materials may be prescribed by local authorities.

Saturated salt solutions are widely used in the measurement of humidity. The notes that follow give some guidance for the safe use of some commonly used salts:

- (a) Barium chloride (BaCl_2): Colourless crystals; very soluble in water; stable, but may give off toxic fumes in fire; no hazardous reaction with water, acids, bases, oxidizers, or with combustible materials; ingestion causes nausea, vomiting, stomach pains, and diarrhoea; harmful by inhalation as dust, by contact with skin, irritating to eyes; treat with copious water and obtain medical attention if ingested;
- (b) Calcium chloride (CaCl_2): Colourless crystals; deliquescent; very soluble in water, dissolves with increase in heat; will initiate exothermic polymerization of methyl vinyl ether; can react with zinc to liberate hydrogen; no hazardous reactions with acids, bases, oxidizers, or combustibles; irritating to skin, eyes and respiratory system; ingestion causes gastric irritation; ingestion of large amounts can lead to hypercalcaemia, dehydration, and renal damage; treat with copious water and obtain medical attention;
- (c) Lithium chloride (LiCl): Colourless crystals; stable if kept dry; very soluble in water; may give off toxic fumes in fire; ingestion may affect ionic balance of blood leading to anorexia, diarrhoea, vomiting, dizziness and central nervous system disturbances; kidney damage may result if sodium intake is low (give plenty of water and obtain medical attention); no hazardous reactions with water, acids, bases, oxidizers, or combustibles;
- (d) Magnesium nitrate ($\text{Mg}(\text{NO}_3)_2$): Colourless crystals; deliquescent; very soluble in water; may ignite combustible material; can react vigorously with deoxidizers, can decompose spontaneously in dimethylformamide; may give off toxic fumes in fire (fire-fight with water spray); ingestion of large quantities can have fatal effects (give plenty of water and obtain medical attention); may irritate skin and eyes (wash with water);

- (e) Potassium nitrate (KNO_3): White crystals or crystalline powder; very soluble in water; stable but may give off toxic fumes in fire (fire-fight with water spray); ingestion of large quantities causes vomiting, but is rapidly excreted in urine (give plenty of water); may irritate eyes (wash with water); no hazardous reaction with water, acids, bases, oxidizers, or combustibles;
- (f) Sodium chloride (NaCl): Colourless crystals or white powder; very soluble in water; stable; no hazardous reaction with water, acids, bases, oxidizers, or combustibles; ingestion of large amounts may cause diarrhoea, nausea, vomiting hyperpnea, and convulsions (in severe cases obtain medical attention).

Advice concerning the safe use of mercury is given in Chapter 3, Part I.

4.9 Standard instruments and calibration

4.9.1 Principles involved in the calibration of hygrometers

Precision in the calibration of humidity sensors entails special problems, to a great extent owing to the relatively small quantity of water vapour which can exist in

an air sample at normal temperatures, but also due to the general difficulty of isolating and containing gases and, more particularly, vapour. An ordered hierarchy of international traceability in humidity standards is only presently emerging.

An absolute standard for humidity (i.e. a realization of the physical definition for the quantity of humidity) can be achieved by gravimetric hygrometry. The reference psychrometer (within its limited range) is also a form of primary standard, in that its performance is calculable. The calibration of secondary, reference, and working standards involves several steps. Table 4.4 shows a summary of humidity standard instruments and their performances.

A practical field calibration is most frequently done by means of well designed aspirated psychrometers and dew-point sensors as working standards. These specific types of standards must be traceable to the higher levels of standards by careful comparisons. Any instrument used as a standard must be individually calibrated for all variables involved in calculating humidity (air temperature, wet-bulb temperature, dew-point temperature, etc.). Other factors affecting performance, such as airflow, must also be checked.

TABLE 4.4
Standard instruments for the measurement of humidity

Standard instrument	Dew-point temperature		Relative humidity (%)	
	Range ($^{\circ}\text{C}$)	Uncertainty (K)	Range	Uncertainty
<i>Primary standard</i>				
Requirement	-60 to -15 -15 to 40	± 0.3 ± 0.1	5 to 100 5 to 100	± 0.2 ± 0.2
Gravimetric hygrometer	-60 to -35 -35 to 35 35 to 60	± 0.25 ± 0.03 ± 0.25		
Standard two-temperature humidity generator	-75 to -15 -15 to 30 30 to 80	± 0.25 ± 0.1 ± 0.2		
Standard two-pressure humidity generator	-75 to 30	± 0.2		
<i>Secondary standard</i>				
Requirement	-80 to -15 -15 to 40	± 0.75 ± 0.25	5 to 100	± 0.5
Chilled-mirror hygrometer Reference psychrometer	-60 to 40	± 0.15	5 to 100	± 0.6
<i>Reference standard</i>				
Requirement	-80 to -15 -15 to 40	± 1.0 ± 0.3	5 to 100	± 1.5
Reference psychrometer Chilled-mirror hygrometer	-60 to 40	± 0.3	5 to 100	± 0.6
<i>Working standard</i>				
Requirement	-15 to 40	± 0.5	5 to 100	± 2
Assmann psychrometer Chilled-mirror hygrometer	-10 to 25 -10 to 30	± 0.5 ± 0.5	40 to 90	± 1

4.9.2 Calibration intervals and methods

Regular calibration is required for all humidity sensors in the field. For psychrometers, chilled-mirror, and heated dew-point hygrometers which use a temperature detector, their calibration can be checked whenever a regular maintenance routine is performed. A comparison with a working standard, such as an Assmann psychrometer, should be performed at least once a month.

The use of a standard type of aspirated psychrometer, such as the Assmann, as a working standard has the advantage that its integrity can be verified by comparing the dry- and wet-bulb thermometers, and that adequate aspiration may be expected from a healthy sounding fan. The reference instrument should itself be calibrated at an interval appropriate to its type.

Saturated salt solutions can be applied with sensors which require only a small-volume sample. A very stable ambient temperature is required and it is difficult to be confident about their use in the field. When using salt solutions for control purposes one should bear in mind that the nominal humidity value given for the salt solution itself is not traceable to any primary standard.

4.9.3 Laboratory calibration

Laboratory calibration is essential for maintaining accuracy in the following ways:

(a) Field and working standard instruments: Laboratory calibration of field and working standard instruments should be carried out on the same regular basis as for other operational thermometers. For this purpose, the chilled-mirror sensor device may be considered separately from the control unit. The mirror thermometer should be calibrated independently and the control unit should be calibrated on the same regular basis as other items of precision electronic equipment. The calibration of a field instrument in a humidity generator is not strictly necessary if the components have been calibrated separately, as described previously.

The correct operation of an instrument may be verified under stable room conditions by comparison with a reference instrument, such as an Assmann psychrometer or a standard chilled-mirror hygrometer. If the field instrument incorporates an ice detector, then the correct operation of this system should be verified;

(b) Reference and standard instruments: Laboratory calibration of reference and standard instruments requires a precision humidity generator and a suitable transfer standard hygrometer. Two-pressure and two-temperature humidity generators are able to deliver a suitable controlled flow of air at a predetermined temperature and dew point. The calibration should be performed at least every 12 months and over the full range of the reference application for the instrument. The calibration of

the mirror thermometer and the temperature display system should be performed independently at least once every 12 months.

4.9.4 Primary standards

4.9.4.1 GRAVIMETRIC HYGROMETRY

The gravimetric method yields an absolute measure of the water vapour content of an air sample in terms of its humidity mixing ratio. This is obtained by first removing the water vapour from the sample using a known mass of a drying agent — such as anhydrous phosphorous pentoxide (P_2O_5) or magnesium perchlorate ($Mg(ClO_4)_2$). The mass of the water vapour is determined through the weighing of the drying agent before and after absorbing the vapour. The mass of the dry sample is determined either by weighing (after liquefaction to render the volume of the sample manageable) or by measuring its volume (and having knowledge of its density).

The complexity of the apparatus required to carry out accurately the procedure described limits the application of this method to the laboratory environment. In addition, a substantial volume sample of air is required for accurate measurements to be made and a practical apparatus requires a steady flow of the humid gas for a number of hours, depending upon the humidity, in order to remove a sufficient mass of water vapour for an accurate weighing measurement. As a consequence, the method is restricted to providing an absolute calibration reference standard. Such an apparatus is found mostly in national calibration standards laboratories.

4.9.4.2 DYNAMIC TWO-PRESSURE STANDARD HUMIDITY GENERATOR

This laboratory apparatus serves to provide a source of humid gas whose relative humidity is determined on an absolute basis. A stream of the carrier gas is passed through a saturating chamber at pressure P_1 and permitted to expand isothermally in a second chamber at a lower pressure P_2 . Both chambers are maintained at the same temperature in an oil bath. The relative humidity of the water vapour-gas mixture is straightforwardly related to the total pressures in each of the two chambers through Dalton's law of partial pressures; the partial pressure e' of the vapour in the low-pressure chamber will be in the same relation to the saturation vapour pressure e'_w as the total pressure in the high-pressure saturator is to the total pressure in the low-pressure chamber. Thus, the relative humidity U_w is given by:

$$U_w = 100 \cdot e'/e'_w = 100 \cdot P_1/P_2 \quad (4.5)$$

The relation also holds for the solid phase if the gas is saturated with respect to ice at pressure P_1 :

$$U_i = 100 \cdot e'/e'_i = 100 \cdot P_1/P_2 \quad (4.6)$$

4.9.4.3 DYNAMIC TWO-TEMPERATURE STANDARD HUMIDITY GENERATOR

This laboratory apparatus provides a stream of humid gas at temperature T_1 having a dew- or frost-point temperature T_2 . Two temperature-controlled baths, each equipped with heat exchangers and one with a saturator containing either water or ice, are used first to saturate the air stream at temperature T_1 and then to heat it isobarically to temperature T_2 . In practical designs, the air stream is continuously circulated to ensure saturation. Test instruments draw off air at temperature T_2 and a flow rate which is small in proportion to the main circulation.

4.9.5 Secondary standards

A secondary standard instrument should be carefully maintained and removed from the calibration laboratory only for the purpose of calibration with a primary standard or for intercomparison with other secondary standards. Secondary standards may be used as transfer standards from the primary standards.

A chilled-mirror hygrometer may be used as a secondary standard instrument under controlled conditions of air temperature, humidity, and pressure. For this purpose, it should be calibrated from a recognized accredited laboratory, giving uncertainty limits throughout the operational range of the instrument. This calibration must be directly traceable to a primary standard and should be renewed at an appropriate interval (usually once every 12 months).

General considerations for chilled-mirror hygrometers are discussed in section 4.4. This method presents a fundamental technique for determining atmospheric humidity. Provided that the instrument is maintained and operated correctly, following the manufacturer's instructions, it can provide a primary measurement of dew or frost point within limits of uncertainty determined by the correspondence between the mirror surface temperature at the appropriate point of the condensation/evaporation cycle and the temperature registered by the mirror thermometer at the observation time. The Kelvin and Raoult effects upon the condensation temperature must be taken into consideration, and any change of the air pressure resulting from the sampling technique must be taken into account by using the equations given in section 4.4.1.2.

4.9.6 Working standards (and field reference instruments)

A chilled-mirror hygrometer or an Assmann psychrometer may be used as a working standard for comparisons under ambient conditions in the field or the laboratory. For this purpose, it is necessary to have performed comparisons at least at the reference standard level. The comparisons should be performed at least once every 12 months under stable room conditions. The working standard will require a suitable aspiration device to sample the air.

4.9.7 The WMO reference psychrometer

This type of psychrometer is essentially a primary standard because its performance is calculable. However, its main use is as a highly accurate reference instrument, specifically for type-testing other instrument systems in the field. It is intended for use as a free-standing instrument, alongside the screen or other field instruments and must be made precisely to its general specification and must be operated by skilled staff experienced in precise laboratory work; careful attention should be given to aspiration and to avoiding the contamination of the wet bulb by contact with the fingers or other objects. There are, however, simple tests by which the readings may be validated at any time, and these should be used frequently during the operation. Its description and operating instructions are given in WMO (1992).

4.9.8 Saturated salt solutions

Vessels containing saturated solutions of appropriate salts may be used to calibrate relative humidity sensors. Commonly used salts, and their saturation relative humidities at 25°C are:

Barium chloride (BaCl_2):	90.3 per cent
Sodium chloride (NaCl):	75.3 per cent
Magnesium nitrate ($\text{Mg}(\text{NO}_3)_2$):	52.9 per cent
Calcium chloride (CaCl_2):	29.0 per cent
Lithium chloride (LiCl):	11.1 per cent

It is important that the surface area of the solution be large compared to that of the sensor element and the enclosed volume of air so that equilibrium may be achieved quickly; an airtight access port is required for the test sensor. The temperature of the vessel should be measured and maintained at a constant level as the saturation humidity for most salts has a significant temperature coefficient.

Care should be taken in the use of saturated salt solutions. The degree of toxicity and corrosivity of salt solutions should be known to personnel dealing with them. The salts listed above may all be used quite safely, but it is nevertheless important to avoid contact with the skin, and to avoid ingestion and splashing in the eyes. The salts should always be kept in secure and clearly labelled containers which detail any hazards involved. Care should be taken when dissolving calcium chloride crystals in water, as much heat is evolved. Section 4.8 deals with chemical hazards in greater detail.

Although use of saturated salt solutions provides a simple method to adjust some (relative) humidity sensors, such adjustment cannot be taken as a traceable calibration of the sensors. The (nominal) values of salt solutions have, at the moment, generally no traceability to reference standards. Measurements from sensors adjusted by means of the saturated salt solution method should always be checked by calibration standards after adjustment.

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ANNEX 4.A

DEFINITIONS AND SPECIFICATIONS OF WATER VAPOUR IN THE ATMOSPHERE

(1) **The mixing ratio r** of moist air is the ratio of the mass m_v of water vapour to the mass m_a of dry air with which the water vapour is associated:

$$r = \frac{m_v}{m_a} \quad (4.A.1)$$

(2) **The specific humidity, mass concentration or moisture content q** of moist air is the ratio of the mass m_v of water vapour to the mass $m_v + m_a$ of moist air in which the mass of water vapour m_v is contained:

$$q = \frac{m_v}{m_v + m_a} \quad (4.A.2)$$

(3) **Vapour concentration (density of water vapour in a mixture) or absolute humidity:** For a mixture of water vapour and dry air the vapour concentration ρ_v is defined as the ratio of the mass of vapour m_v to the volume V occupied by the mixture:

$$\rho_v = \frac{m_v}{V} \quad (4.A.3)$$

(4) **Mole fraction of the water vapour of a sample of moist air:** The mole fraction x_v of the water vapour of a sample of moist air, composed of a mass m_a of dry air and a mass m_v of water vapour, is defined by the ratio of the number of moles of water vapour ($n_v = m_v/M_v$) to the total number of moles of the sample $n_v + n_a$, where n_a indicates the number of moles of dry air ($n_a = m_a/M_a$) of the sample concerned. This gives us:

$$x_v = \frac{n_v}{n_a + n_v} \quad (4.A.4)$$

or:

$$x_v = \frac{r}{0.62198 + r} \quad (4.A.5)$$

where r is merely the mixing ratio ($r = m_v/m_a$) of the water vapour of the sample of moist air.

(5) **The vapour pressure e'** of water vapour in moist air at total pressure p and with mixing ratio r is defined by:

$$e' = \frac{r}{0.62198 + r} p = x_v p \quad (4.A.6)$$

(6) **Saturation:** Moist air at a given temperature and pressure is said to be saturated if its mixing ratio is such that the moist air can co-exist in neutral equilibrium with an associated condensed phase (liquid or solid) at the same temperature and pressure, the surface of separation being plane.

(7) **Saturation mixing ratio:** The symbol r_w denotes the saturation mixing ratio of moist air with respect to a plane surface of the associated liquid phase.

The symbol r_i denotes the saturation mixing ratio of moist air with respect to a plane surface of the associated solid phase. The associated liquid and solid phases referred to consist of almost pure water and almost pure ice, respectively, there being some dissolved air in each.

(8) **Saturation vapour pressure in the pure phase:** The saturation vapour pressure e_w of pure aqueous vapour with respect to water is the pressure of the vapour when in a state of neutral equilibrium with a plane surface of pure water at the same temperature and pressure; similarly for e_i with respect to ice. e_w and e_i are temperature-dependent functions only, i.e.:

$$e_w = e_w(T) \quad (4.A.7)$$

$$e_i = e_i(T) \quad (4.A.8)$$

(9) **Mole fraction of water vapour in moist air saturated with respect to water:** The mole fraction of water vapour in moist air saturated with respect to water, at pressure p and temperature T , is the mole fraction x_{vw} of the water vapour of a sample of moist air, at the same pressure p and the same temperature T , that is in stable equilibrium in the presence of a plane surface of water containing the amount of dissolved air corresponding to equilibrium. Similarly, x_{vi} will be used to indicate the saturation mole fraction with respect to a plane surface of ice containing the amount of dissolved air corresponding to equilibrium.

(10) **Saturation vapour pressure of moist air:** The saturation vapour pressure with respect to water e'_w of moist air at pressure p and temperature T is defined by:

$$e'_w = \frac{r_w}{0.62198 + r_w} p = x_{vw} p \quad (4.A.9)$$

Similarly, the saturation vapour pressure with respect to ice e'_i of moist air at pressure p and temperature T is defined by:

$$e'_i = \frac{r_i}{0.62198 + r_i} p = x_{vi} p \quad (4.A.10)$$

(11) **Relations between saturation vapour pressures of the pure phase and of moist air:** In the meteorological range of pressure and temperature the following relations hold with an error of 0.5 per cent or less:

$$e'_w = e_w \quad (4.A.11)$$

$$e'_i = e_i \quad (4.A.12)$$

(12) **The thermodynamic dew-point temperature T_d** of moist air at pressure p and with mixing ratio r is the temperature at which moist air, saturated with respect to water at the given pressure, has a saturation mixing ratio r_w equal to the given mixing ratio r .

(13) **The thermodynamic frost-point temperature** T_f of moist air at pressure p and mixing ratio r is the temperature at which moist air, saturated with respect to ice at the given pressure, has a saturation mixing ratio r_i equal to the given ratio r .

(14) **The dew- and frost-point temperatures** so defined are related to the mixing ratio r and pressure p by the respective equations:

$$e_w(p, T_d) = f(p) \cdot e_w(T_d) = x_v \cdot p = \frac{r \cdot p}{0.62198 + r} \quad (4.A.13)$$

$$e_i(p, T_f) = f(p) \cdot e_i(T_f) = x_v \cdot p = \frac{r \cdot p}{0.62198 + r} \quad (4.A.14)$$

(15)² **The relative humidity U_w with respect to water of moist air** at pressure p and temperature T is the ratio in per cent of the vapour mole fraction x_v to the vapour mole fraction x_{vw} which the air would have if it were saturated with respect to water at the same pressure p and temperature T . Accordingly:

$$\begin{aligned} U_w &= 100 \left(\frac{x_v}{x_{vw}} \right)_{p,T} = 100 \left(\frac{px_v}{px_{vw}} \right)_{p,T} \\ &= 100 \left(\frac{e'}{e'_w} \right)_{p,T} \end{aligned} \quad (4.A.15)$$

where subscripts p, T indicate that each term is subject to identical conditions of pressure and temperature. The last expression is formally similar to the classical definition based on the assumption of Dalton's law of partial pressures.

U_w is also related to the mixing ratio r by:

$$U_w = 100 \frac{r}{r_w} \cdot \frac{0.62198 + r_w}{0.62198 + r} \quad (4.A.16)$$

where r_w is the saturation mixing ratio at the pressure and temperature of the moist air.

(16)² **The relative humidity U_i with respect to ice of moist air** at pressure p and temperature T is the ratio in per cent of the vapour mole fraction x_v to the vapour mole fraction x_{vi} which the air would have if it were saturated with respect to ice at the same pressure p and temperature T .

Corresponding to the defining equation in paragraph 15:

$$U_i = 100 \left(\frac{x_v}{x_{vi}} \right)_{p,T} = 100 \left(\frac{px_v}{px_{vi}} \right)_{p,T} = \left(\frac{e'}{e'_i} \right)_{p,T} \quad (4.A.17)$$

(17) **Relative humidity at temperatures less than 0°C** is to be evaluated with respect to water. The advantages of this procedure are as follows:

(a) Most hygrometers which are essentially responsive to the relative humidity indicate relative humidity with respect to water at all temperatures;

(b) The majority of clouds at temperatures below 0°C consist of water, or mainly of water;

(c) Relative humidities greater than 100 per cent would in general not be observed. This is of particular importance in synoptic weather messages, since the atmosphere is often supersaturated with respect to ice at temperatures below 0°C;

(d) The majority of existing records of relative humidity at temperatures below 0°C are expressed on a basis of saturation with respect to water.

(18) **The thermodynamic wet-bulb temperature of moist air** at pressure p , temperature T , and mixing ratio r is the temperature T_w attained by the moist air when brought adiabatically to saturation at pressure p by the evaporation into the moist air of liquid water at pressure p and temperature T_w and containing the amount of dissolved air corresponding to equilibrium with saturated air of the same pressure and temperature. T_w is defined by the equation:

$$\begin{aligned} h(p, T, r) + [r_w(p, T_w) - r] h_w(p, T_w) \\ = h(p, T_w, r_w(p, T_w)) \end{aligned} \quad (4.A.18)$$

where $r_w(p, T_w)$ is the mixing ratio of saturated moist air at pressure p and temperature T_w , $h_w(p, T_w)$ is the enthalpy³ of 1 gram of pure water at pressure p and temperature T_w , $h(p, T, r)$ is the enthalpy of 1 + r grams of moist air, composed of 1 gram of dry air and r grams of water vapour, at pressure p and temperature T , and $h(p, T_w, r_w(p, T_w))$ is the enthalpy of 1 + r_w grams of saturated air, composed of 1 gram of dry air and r_w grams of water vapour, at pressure p and temperature T_w . (This is a function of p and T_w only and may appropriately be denoted by $h_{sw}(p, T_w)$).

If air and water vapour are regarded as ideal gases with constant specific heats, then the above equation becomes:

$$T - T_w = \frac{[r_w(p, T_w) - r] L_v(T_w)}{c_{pa} + r c_{pv}} \quad (4.A.19)$$

where $L_v(T_w)$ is the heat of vaporization of water at temperature T_w , c_{pa} is the specific heat of dry air at constant pressure, and c_{pv} is the specific heat of water vapour at constant pressure.

NOTE: Thermodynamic wet-bulb temperature as here defined has for some time been called "temperature of adiabatic saturation" by the air-conditioning engineers.

(19) **The thermodynamic ice-bulb temperature of moist air** at pressure p , temperature T , and mixing ratio r is the temperature T_i at which pure ice at pressure p must be evaporated into the moist air in order to saturate it adiabatically at pressure p and temperature T_i . The saturation is with respect to ice. T_i is defined by the equation:

³ The enthalpy of a system in equilibrium at pressure p and temperature T is defined as $E + pV$, where E is the internal energy of the system and V is its volume. The sum of the enthalpies of the phases of a closed system is conserved in adiabatic isobaric processes.

² Definitions (15) and (16) do not apply to moist air when pressure p is less than the saturation vapour pressure of pure water and ice, respectively, at temperature T .

$$h(p, T, r) + [r_i(p, T_i) - r]h_i(p, T_i) = h(p, T_i, r_i(p, T_i)) \quad (4.A.20)$$

where $r_i(p, T_i)$ is the mixing ratio of saturated moist air at pressure p and temperature T_i , $h_i(p, T_i)$ is the enthalpy of 1 gram of pure ice at pressure p and temperature T_i , $h(p, T, r)$ is the enthalpy of 1 + r grams of moist air, composed of 1 gram of dry air and r grams of water vapour, at pressure p and temperature T , and $h(p, T_i, r_i(p, T_i))$ is the enthalpy of 1 + r_i grams of saturated air, composed of 1 gram of dry air and r_i grams of water vapour, at pressure p and temperature T_i . (This is a function of p and T_i only, and may appropriately be denoted by $h_{si}(p, T_i)$).

If air and water vapour are regarded as ideal gases with constant specific heats, then the above equation becomes:

$$T - T_i = \frac{[r_i(p, T_i) - r]L_s(T_i)}{c_p + rc_{pv}} \quad (4.A.21)$$

where $L_s(T_i)$ is the heat of sublimation of ice at temperature T_i .

The relationship between T_w and T_i as defined and the wet-bulb or ice-bulb temperature as indicated by a particular psychrometer is a matter to be determined by carefully controlled experiment, taking into account the various variables concerned — for example, ventilation, size of thermometer bulb and radiation.

ANNEX 4.B

FORMULAE FOR THE COMPUTATION OF MEASURES OF HUMIDITY

(see also section 4.1.2)

Saturation vapour pressure:

$$e_w(t) = 6.112 \exp [17.62 t / (243.12 + t)]$$

Water (-45 to 60°C)
(pure phase)

$$e'_w(p, t) = f(p) \cdot e_w(t)$$

Moist air

$$e_i(t) = 6.112 \exp [22.46 t / (272.62 + t)]$$

Ice (-65 to 0°C)
(pure phase)

$$e'_i(p, t) = f(p) \cdot e_i(t)$$

Moist air

$$f(p) = 1.0016 + 3.15 \cdot 10^{-6} p - 0.074 p^{-1}$$

Dew point and frost point:

$$t_d = \frac{243.12 \cdot \ln [e' / 6.112 f(p)]}{17.62 - \ln [e' / 6.112 f(p)]}$$

Water (-45 to 60°C)

$$t_f = \frac{272.62 \cdot \ln [e' / 6.112 f(p)]}{22.46 - \ln [e' / 6.112 f(p)]}$$

Ice (-65 to 0°C)

Psychrometric formulae for the Assmann psychrometer:

$$e' = e'_w(p, t_w) - 6.53 \cdot 10^{-4} \cdot (1 + 0.000944 t_w) \cdot p \cdot (t - t_w)$$

Water

$$e' = e'_i(p, t_i) - 5.75 \cdot 10^{-4} \cdot p \cdot (t - t_i)$$

Ice

Relative humidity:

$$U = 100 e' / e'_w(p, t)$$

$$U = 100 e'_w(p, t_d) / e'_w(p, t)$$

Units applied:

t = air temperature (dry-bulb temperature);

t_w = wet-bulb temperature;

t_i = ice-bulb temperature;

t_d = dew-point temperature;

t_f = frost-point temperature;

p = pressure of moist air;

$e_w(t)$ = saturation vapour pressure in the pure phase with regard to water at the dry-bulb temperature;

$e_w(t_w)$ = saturation vapour pressure in the pure phase with regard to water at the wet-bulb temperature;

$e_i(t)$ = saturation vapour pressure in the pure phase with regard to ice at the dry-bulb temperature;

$e_i(t_i)$ = saturation vapour pressure in the pure phase with regard to ice at the ice-bulb temperature;

$e'_w(t)$ = saturation vapour pressure of moist air with regard to water at the dry-bulb temperature;

$e'_w(t_w)$ = saturation vapour pressure of moist air with regard to water at the wet-bulb temperature;

$e'_i(t)$ = saturation vapour pressure of moist air with regard to ice at the dry-bulb temperature;

$e'_i(t_i)$ = saturation vapour pressure of moist air with regard to ice at the ice-bulb temperature;

U = relative humidity.

