NBS CIRCULAR 512

Methods of Measuring Humidity and Testing Hygrometers

UNITED STATES DEPARTMENT OF COMMERCE

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Arnold Wexler and W. G. Brombacher

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Methods of Measuring Humidity and Testing Hygrometers

A Review and Bibliography

Arnold Wexler and W. G. Brombacher

This paper is a review of methods for the measurement of the water-vapor content of air and other gases and for the production and control of atmospheres of known humidity for hygrometer testing and calibration and for general research. Among the hygrometric techniques discussed are psychrometry, mechanical hygrometry, dewpoint measurement, electric hygrometry, gravimetric hygrometry, thermal conductivity, index of refraction, pressure and volume measurements, and dielectric constant. Descriptions are given of suitable equipment for establishing desired humidities over a wide range of temperature. A list of 157 selected references pertaining to hygrometry is included.

1. Introduction

The conditions under which the relative or absolute humidity of gases are measured, recorded, or controlled vary greatly, and as a result, many methods of humidity measurement have been developed or proposed. However, for some applications there is at present no satisfactory method available for such measurements, and the available information on methods and instruments for measuring humidity is quite scattered. This Circular, with the appended references, is intended to answer inquiries on humidity measurement in a more comprehensive manner than may be done by correspondence.

Knowledge of the moisture content of solid materials, particularly paper, wood, and grain, is often required during some stage of processing or storage. The equipment, known as moisture meters, used for this purpose is not discussed in this Circular.

In many cases a substantial gaseous equilibrium exists between the solid and the surrounding atmosphere. A satisfactory determination of the moisture content of the solid can be made by the relatively easy measurement of the humidity of the atmosphere, once the relation between the two has been established. The same is true, of course, for liquids of definite composition, except that the water content may vary.

2. Definitions

Relative humidity is the ratio, usually expressed in percent, of the pressure of water vapor in the gas to saturation pressure of water vapor at the temperature of the gas. In engineering, relative humidity is sometimes defined as the ratio of the weights per unit volume of the water vapor in the gas mixture and the saturated vapor at the temperature of the gas mixture. The two definitions are equivalent for all practical purposes.

Absolute humidity of a gas mixture may be defined as the pressure of water vapor, or as the weight per unit volume of water vapor.

Specific humidity, a term of use in air conditioning, is the weight of water vapor in air per unit weight of the dry air.

Dewpoint is the temperature to which water vapor must be reduced in order to obtain a relative humidity of 100 percent that is, to obtain saturation vapor pressure.

Instruments from which the relative humidity is determined are called either psychrometers or hygrometers. Generally, the dry- and wet-bulb instrument (described later) is called a psychrometer, and direct indicators of relative humidity are called hygrometers.

Hygrographs are recorders of relative humidity.

3. Classification of Instruments

Humidity-measuring instruments and methods may be divided into the following classes for convenience. No exhaustive search of the literature was made to insure a complete listing of all proposed instruments, so that it is anticipated that some omissions exist.

Dry- and wet-bulb. Measurements depending on the change in temperature due to rate of evaporation from wet surfaces, an example of which is the dry- and wet-bulb or sling psychrometer.

Mechanical hygrometers. Measurement of a change in a dimension of an absorbing material, such as human hair or goldbeater's skin.

Dewpoint indicators and recorders. Instruments which indicate or record the temperature at which dew from the gas (air and water vapor) mixture under test will just form. A common type employs a mirror for observing the formation of the dew.

Electrical hygrometer. Measurement of the electrical resistance of a film of moisture absorbing material exposed to the gas under test.

Gravimetric hygrometer. Measurement of weight of moisture absorbed by a moisture absorbing material.

(a) Increase in weight of a drying agent as gas with a constant moisture content is passed through it.

(b) Change in weight of an absorbing material with change in moisture content of the gas under test.

Thermal conductivity method. Measurement of the variation in thermal conductivity of a gas sample with water vapor.

Spectroscopic method. Measurement of the change in intensity of selected absorbing spectral lines with change in humidity of the gas under test.

Index of refraction. Measurement of change in index of refraction of a moisture absorbing liquid with change in ambient humidity.

Pressure or volume. Measurement of the pressure or volume of the water vapor in a gas sample.

Thermal rise. Measurement of the temperature rise of a material exposed to water vapor.

Mobility of ions. Measurement of the change in mobility of ions due to the presence of water vapor.

Dielectric constant. Measurement of the dielectric constant of a gas with change in water-vapor content.

Critical flow. Measurement of the variation of pressure drop across two combinations of nozzles, operating at critical flow, with a desiccant between one pair of nozzles.

Diffusion hygrometer. Measurement of effects due to diffusion of gases with and without water vapor.

Chemical methods. Procedures involving chemical reactions or phenomena.

For sources of supply for the instruments indicated as commercially available, consult *Thomas Register of American Manufacturers* or *The Instruments Index.*

4. Description of Instruments

4.1. Dry- and Wet-Bulb Psychrometer

The psychrometric method of determining humidity is of importance in the fields of meteorology, air conditioning, refrigeration, and the drying of foods, lumber, etc. Its basic simplicity and fundamental calibration have made it the dominant means for measuring the moisture content of air. The elemental form of the psychrometer comprises two thermometers. The bulb of one thermometer is covered with a moistened cotton or linen wick and is called the wet-bulb, whereas the bulb of the other thermometer is left bare and is referred to as the dry-bulb. The evaporation of water from the moistened wick of the wet-bulb thermometer produces a lowering in temperature and from the readings of the two thermometers and the air or gas pressure, the humidity, absolute or relative, may be determined. It is current standard practice to ventilate the thermometers by slinging, whirling, or forced-air circulation.

To obtain the relative or absolute humidity, the relation between the wet- and dry-bulb readings and the actual pressure of the water vapor must be known. This correlation was obtained by Ferrel (26)[1] in 1886, based on the data of Marvin and Hazen, who made numerous observations of wet- and dry-bulb readings with sling and whirled psychrometers and simultaneous determinations of dewpoints with Regnault and Alluard dewpoint apparatus. Ferrel, after reducing these data, fitted them into the expression

$$e=e'-AP(t-t')$$

where, in metric units,

$A=6.60\times10^{-4}\ (1+0.00115t')$
e=partial pressure of water vapor in mm Hg at the dry-bulb temperature t°C
e'=saturation pressure of water vapor in mm Hg at the wet-bulb temperature t'°C
P=total pressure (which, in the case of meteorological observations, is atmospheric pressure) in mm Hg

---

[1] Figures in parentheses indicate the literature references at the end of this paper.

and where, in English units,

$A = 3.67 \times 10^{-4} [1 + 0.00064 (t' - 32)]$
e = partial pressure of water vapor in. Hg at the dry-bulb temperature t°F
e' = saturation pressure of water vapor in in. Hg at the wet-bulb temperature t'°F
P = total pressure in in. Hg.

Starting from fundamental concepts, several theories have been developed that attempt to explain the phenomena that occur at the wet-bulb and which, at the same time, yield expressions of the form used by Ferrel. The first equations for use in psychrometry were developed by Ivory (21) in 1822 and extended by August (22) in 1825 and Apjohn (23) in 1837. The so-called convection theory is the result of their work. In 1911, Carrier (28, 42) and in 1922, Lewis (40) reestablished the basis of this theory and renamed it the adiabatic saturation theory. This theory, which depends on a heat balance at the wet-bulb, found wide acceptance in the air-conditioning and refrigerating industries and has been used extensively in the construction of phychrometric charts. The agreement between theory and experimental data was investigated by Carrier (28) and Dropkin (87). Their results indicate that for most work of engineering accuracy, the adiabatic saturation theory is adequate for predicting the vapor pressure of water vapor from wet- and dry-bulb readings. Maxwell (11) in 1877 deduced an equation based on the diffusion of heat and vapor through a surface gas film on the wet-bulb. In recent years, further work has been done experimentally (71) and theoretically (73) on psychometric theory, and in reviewing the subject (93).

As the psychrometric formula gives the partial pressure of the water vapor of the gas under test, a computation is necessary to convert to humidity in other terms. The relative humidity, for example, is obtained from the equation

$$RH = \frac{e}{e_s} \times 100,$$

where
e = the partial pressure of water vapor as determined by the psychrometric formula
e_s = the saturation pressure of water vapor at the dry-bulb temperature
RH = the relative humidity, in percent.

In practice, calculations directly involving the use of the psychrometric formula are rarely made. The customary procedure is to employ tables (1, 4, 5, 7, 13, 14, 15, 16, 18, 44, 67, 81, and 96) or charts or curves (1, 9, 18, 77, 82, 100, 107, 115) that conveniently and rapidly yield the relative humidity, vapor pressure, or dewpoint from the dry- and wet-bulb thermometer readings and the air pressure.

The sling psychrometer (1, 8, 12, 15, 60), using two mercury thermometers, is the common form of this instrument. It is relied upon principally by meteorologists and is widely used by other scientists and by engineers for measuring relative humidity. Ventilation is obtained by swinging the thermometers to produce a minimum air velocity of 900 ft/min at sea level (higher at altitude). It is supplied by firms manufacturing meteorological instruments and by many laboratory apparatus supply houses. Stationary thermometers, with ventilation produced by a motor-driven fan or blower integral with the instrument, are known as Assmann or aspiration psychrometers (1, 8, 12, 60). These are also commercially available from a smaller number of firms. Unventilated psychrometers are unreliable and hence rarely used.

In addition to the mercury-in-glass thermometer, other temperature measuring devices may be adapted for psychrometric use. Resistance thermometers (47, 64, 70) thermocouples (68, 69, 72, 89, 90, 108), and bimetal thermometers (148) can be used for both indicating, recording, and control. Thermocouples are of special interest where low lag is important, where there is little or no ventilation (72, 89, 90) or where very low relative humidities (91) are to be measured.

Instead of direct temperature measurements, the temperature of the thermometers may be equalized (140). In this method the temperature of the wet-bulb is raised to that of the dry-bulb and the heat measured which is required to maintain equilibrium. This is accomplished by winding a manganin wire heater around the wet-bulb and under the wick and measuring the current when the wet- and dry-bulb thermometers read alike. A convenient arrangement utilizes a differential thermocouple psychrometer whose output is read on a galvanometer. The current to the wet-bulb heater is adjusted until the galvanometer no longer deflects.

The psychrometric method often may be applied in specialized or unconventional conditions. At temperatures below freezing, the psychrometer continues to function, but the magnitude of the depression is greatly reduced and proper precautions must be taken to obtain reliable data (121). At elevated temperatures or low relative humidities, special instruments (56), tables (67) and techniques (74) must be used. Most tables and charts are designed for use at atmospheric pressures. When low or high pressures are encountered, either special tables (15, 44) or charts (82) must be used or the relative humidity must be computed.

Where the moisture content of gases other than air is to be determined, the psychrometric constant A must be modified, to account for the physical properties of the particular gas. Values of A for several mono-, di- and triatomic gases are given by Brauckhoff (143).

Among the factors influencing the performance and accuracy of the psychrometric method are (a) the sensitivity, accuracy and agreement in reading of the thermometers, (b) the speed of air past the wet-bulb thermometer, (c) radiation, (d), the size, shape, material and wetting of the wick, (e) the relative position of the dry- and wet-bulb thermometers, and (f) the temperature and purity of the water used to wet the wick. A discussion of these factors will be found in (1, 8, 12, 15, 35, 37, 46, 60, 74, 78, 90, 98, 121, 151).

The thermometers used in psychrometry should be high-grade matched instruments, else appreciable error may be introduced. While a calibration of the thermometers is desirable, an intercomparison at several temperatures to determine whether they read alike usually suffices. In addition, when high accuracy is desired and low relative humidities are measured, corrections for the emergent stem of the wet-bulb thermometer should be applied.

Thermometer errors may combine in several ways to influence the accuracy of the relative humidity. Thus either the dry-bulb thermometer or the wet-bulb thermometer or both may be in error. The magnitude of the error in relative humidity will depend not only on the magnitude of the thermometer errors, but also on their particular combination, since both the dry-bulb temperature and the wet-bulb depression are required for a determination. Occasionally, in psychrometric work, instead of measuring both the dry- and wet-bulb temperatures separately, the dry-bulb temperature and the wet-bulb depression are measured, from which the wet-bulb temperature can be computed for use in entering commonly available tables. The latter is obtained by measuring the temperature difference with, say, a differential thermocouple, one end of which is maintained dry and the other wet. Here the errors may occur either in the dry-bulb measurement or in the depression measurement or in both. Errors in the depression, however, may be considered as equivalent to errors in the wet-bulb reading, so that essentially the combinations of errors are the same as those first listed.

In order to obtain an estimate of the errors in relative humidity arising from thermometer errors, it will be assumed that psychrometric measurements are made at atmospheric pressure (29.92 in. Hg), at dry-bulb temperatures of 150°, 100°, 75°, 50°, and 32° F, and at wet-bulb depressions of 0.1, 1.0, and 10° F. For these given conditions, the errors in relative humidity, due to (a) a negative error of 1° F in wet-bulb temperature with the dry-bulb temperature correct, (b) a positive error of 1° F in dry-bulb temperature with the wet-bulb temperature correct, (c) an error of 1° F in dry-bulb temperature and an error of 1° F in wet-bulb temperature, both errors being negative, and (d) a positive error of 1° F in dry-bulb temperature and a negative error of 1° F in wet-bulb temperature, have been determined and are given, correspondingly, in table 1. It is seen in (c), table 1, that the errors are greatly reduced if the thermometers are matched.

TABLE 1. *Error in relative humidity due to uncorrected errors in the thermometers*

(a) Dry-bulb thermometer reads correctly; wet bulb thermometer reads 1 deg F low

Dry bulb temperature	Error in relative humidity at a wet bulb depression of—		
	0.1 deg F	1.0 deg F	10 deg F
°*F*	%	%	%
150	2.6	2.6	2.1
100	3.6	3.5	2.9
75	4.6	4.5	3.7
50	6.7	6.6	5.6
32	10.5	10.3	------------

(b) Dry bulb thermometer reads 1 deg F high; wet bulb thermometer reads correctly

Dry bulb temperature	Error in relative humidity at a wet bulb depression of—		
	0.1 deg F	1.0 deg F	10 deg F
°*F*	%	%	%
150	2.6	2.5	2.0
100	3.5	3.4	2.6
75	4.5	4.4	3.1
50	6.6	6.4	4.3
32	9.8	9.4	------------

(c) Dry bulb thermometer reads 1 deg F low; wet bulb thermometer reads 1 deg F low

Dry bulb temperature	Error in relative humidity at a wet bulb depression of—		
	0.1 deg F	1.0 deg F	10 deg F
°*F*	%	%	%
150	0.00	0.02	0.11
100	.00	.03	.32
75	.00	.05	.51
50	.00	.11	1.24
32	.02	.26	------------

(d) Dry bulb thermometer reads 1 deg F high; wet bulb thermometer reads 1 deg F low

Dry bulb temperature	Error in relative humidity at a wet bulb depression of—		
	0.1 deg F	1.0 deg F	10 deg F
°*F*	%	%	%
150	5.1	5.0	4.1
100	7.0	6.8	5.4
75	8.9	8.7	6.7
50	13.0	12.7	9.8
32	19.8	19.3	------------

The psychrometric constant, A, in the Ferrel formula is not invariant but is a function of the velocity of ventilation across the wet-bulb thermometer, and reaches a minimum value as the velocity is increased. This is reflected as a maximum wet-bulb depression. Any further increase in velocity will have negligible effect. When the velocity is sufficiently high so that A, is constant, then the magnitude of the velocity need not be measured or estimated. For most mercury-in-glass thermometers with bulbs 1/4-inch diameter or less, the acceptable minimum rate of ventilation is

900 ft/min. If this velocity is not achieved, then the measured wet-bulb depression will not be a maximum, and the use of the psychrometric formula, tables or charts will yield values of relative humidity that are too high.

The heat absorbed by the wet-bulb due principally to radiation tends to raise the wet-bulb temperature so that a true depression is not attained. To minimize this effect, radiation shielding is commonly employed. One method of such shielding, successfully used in some ventilated psychrometers, is to surround the wet-bulb with an external primary metal shield and to insert an auxiliary shield between the primary external shield and the wet-bulb, this auxiliary shield being covered with a wick so that, upon moistening, the auxiliary shield may be brought close to the wet-bulb temperature thereby practically eliminating the source of radiation and conduction due to the difference between the dry- and wet-bulb temperatures.

The function of the wick is to retain a thin film of water on the wet-bulb so that evaporation may continue until the true wet-bulb temperature is reached. Cotton or linen tubing of a soft mesh weave serves well for this purpose because of its excellent water-absorbent properties. Sizing in the wick material, encrustations forming after use and lack of a snug fit interfere with the maintenance of a continuous film of water. Substances in solution in the wick water, due either to impurities on the wick or in the water used for moistening will change the saturation vapor pressure of water and hence affect the results. Wicks should therefore be cleaned and replaced frequently, and distilled water should be used for moistening. The wick should extend beyond the bulb and onto the stem of the thermometer, for an inch or so, in order to reduce heat conduction along the stem to the bulb.

Although the temperature of the water used to moisten the wick is often at dry-bulb temperature, it should be preferably that of the wet-bulb or slightly higher. The use of water that has been brought to the wet-bulb temperature is especially important when the ambient temperature is high and when the relative humidity is low.

If the temperature of the water used to wet the bulb is too high, it may take a long time for the bulb to cool to wet-bulb temperature, and before this point is reached the water may have evaporated sufficiently so that the thermometer never reaches the wet-bulb temperature. If the moistening water temperature is appreciably lower than the wet-bulb temperature, the thermometer temperature will climb throughout the period of ventilation, remaining constant at the wet-bulb temperature only as long as there is sufficient water to keep the bulb surrounded with a film of water. If the temperature of the water used for moistening is at, or slightly above or below, the wet-bulb temperature, then the wet-bulb will remain or quickly attain the wet-bulb temperature and remain at this value for an appreciable length of time so that it can be read easily and accurately.

A separation of the dry- and wet-bulbs is necessary in order to prevent the air that passes the wet-bulb, and is thereby cooled by the evaporating water, from contacting the dry-bulb and giving rise to an erroneous dry-bulb reading. To avoid this, the thermometers may be arranged so that the air flows across the dry-bulb before it reaches the wet-bulb or the air sample may be divided so that one part flows across the wet-bulb and the other part across the dry-bulb.

4.2. Mechanical Hygrometer

In hygrometers of this type, human hair is commonly used as the sensing element. In indicators the midpoint of a bundle of hairs under tension is connected by the simplest possible lever system to a pointer. In recorders a pen arm, which is substituted for the pointer, traces an ink record on a clock-driven drum.

The hair hygrometer indicates relative humidity directly over a wide range of temperature, but its reliability rapidly decreases as the ambient temperature decreases below freezing (0° C).

At temperatures below freezing (0° C) the hair hygrometers indicate relative humidity in terms of the vapor pressure of supercooled water, not that of ice (117).

The chief defect is the lack of stability of the calibration under usual conditions of use. However, tests recently completed at this Bureau on two good quality recorders indicated little average shift in calibration over a period of almost 1 year; the hysteresis (difference in indication, humidity increasing and decreasing) was of the order of 3-percent relative humidity. See (1, 8, 12, 38, 45, 83, 88, 117) for performance data.

Reliable data on the lag of the hair hygrometer are lacking, particularly at low temperatures. Suddenly subjecting hygrometers at about 25° C to a change in relative humidity requires of the order of 5 minutes to indicate 90 percent of the change in relative humidity; this time interval increases with decrease in temperature of the hairs, and is of the order of 10 times greater at $-10°$ C. The effect of temperature on the calibration of hygrometers commercially available is not well established for temperatures below 0° C.

At the best, indications of the hair hygrometer have a reliability of about 3 percent in relative humidity at room temperature when exposed to a constant relative humidity long enough to obtain equilibrium. The large time lag of the hair hygrometer is a serious barrier to accuracy if changing humidity is being measured.

The hair hygrometer is made by a large number of industrial instrument companies, including meteorological instrument firms; the hair hygrograph (recorder) is made by a smaller but still large number of these firms.

The hair element with suitable accessories is widely used as a humidity controller in air-conditioning and other applications. The zero shift so evident in instruments measuring ambient humidity is less troublesome when the relative humidity about the element is maintained nearly constant (50, 62, 129). Controllers are available from a sizable number of industrial instrument firms.

A recent development in this country has been the use of goldbeater's skin in disk form by Serdex (139). It is claimed, but not yet generally accepted, that the performance is essential better than that of the human-hair type. See (134) for performance data at low temperatures; as for the hair hygrometer, the indication at temperatures below freezing of instruments reading correctly above freezing, is in terms of relative humidity of the vapor pressure of supercooled water.

Many organic materials are hygroscopic. Thus wood fibers have been used as a sensing element. Also plastics (152) in a form similar to bimetal have some application and perhaps are the most open to exploration. A cotton filament as a torsion element (53) has been tried. None of these seem to give essentially better, if as good performance as human hair and thus far have had only limited application.

4.3. Dewpoint Indicators and Recorders

When water vapor is cooled, a temperature is reached at which the phase changes to liquid or solid. At this temperature, condensation continues until an equilibrium between the vapor and liquid or solid phase is established. The temperature at which the vapor and liquid or vapor and solid phases are in equilibrium uniquely fixes the pressure of the vapor phase (saturation vapor pressure) and therefore determines the absolute humidity.

If the temperature at which water vapor must be cooled for it to be in equilibrium with its liquid or ice state is measured, then the humidity is obtained directly from it. The dewpoint method provides a convenient technique for ascertaining this temperature. Basically, the procedure is to reduce the temperature of a mirror until dew or frost just condenses from the surrounding air or gas sample. The temperature at the surface of the mirror at the instant dew or frost appears is defined as the dewpoint. If the temperature of the air or gas sample is measured and the initial humidity of the sample surrounding the mirror is kept unaltered, the initial relative humidity can be computed from a knowledge of the saturation vapor pressures at the two temperatures.

It should be noted that the formation of frost is not always positive because of the lack of a crystal nucleus, so that supersaturation may occur. Supersaturation is less likely to occur with respect to the liquid phase than with the ice phase. At a given saturation pressure, if ice does not form on the mirror, dew will form as the mirror temperature is lowered, hence there is always a little uncertainty whether the first clouding of the mirror represents the dewpoint (with condensed water) or the frost point.

Values of the saturation vapor pressure of water, at temperature above and below freezing, are readily available in various handbooks and compilations (1, 2, 4, 6, 15, 16, 17, 18, 128). There is some discordance in the values given in the listed references. However, for most applications in the field of humidity measurement or control, there is little to be gained in the use of any one table in preference to the others. The values given in table 2 are reproduced from the Smithsonian Meteorological Tables (16). At temperatures below 0° C, the saturation vapor pressures refer to water vapor in equilibrium over ice. Saturation vapor pressures of water vapor below 0° C in equilibrium over supercooled water are given in table 3 and are reproduced from the International Critical Tables (17).

The dewpoint instrument serves as a useful research tool for the determination of humidity in meteorology as well as for the determination of water vapor content in flue gases, gasoline vapors, furnace gases, compressed gages, and closed chambers. While the dewpoint instrument has been under considerable development in the past decade, principally along the line of improving the temperature control, means of indication, and automatic recording, it has been used in elemental form as far back as the early part of the last century. Dalton and Daniells used simple dewpoint hygrometers. Regnault (24) developed an instrument that has been used as a prototype and standard for many years in the measurement of atmospheric humidity. Essentially, it consisted of a thin polished silver thimble containing ether. Air was aspirated through the ether to cause evaporation and hence cooling of the thimble. The temperature of the ether at the appearance and disappearance of dew was observed and the mean taken as the dewpoint. A thermometer in a second thimble, near the first, gave the ambient temperature and, by comparison, the second thimble helped in the recognition of the appearance and disappearance of dew on the first thimble. Improvements and variations of the Regnault design were made by Alluard (25), and others (32, 41, 45, 55, 57).

The early models used ether for cooling and mercury-in-glass thermometers for temperature and measurement. Recent models have employed such cooling schemes as compressed carbon dioxide, dry ice, liquid air (for very low dewpoints) and mechanical refrigeration. In addition, metal mirrors are now commonly used, the

TABLE 2. *Saturation vapor pressure of water vapor in millimeters of mercury with respect to water above 0°C and with respect to ice below 0°C*

(Reproduced from the Smithsonian Meteorological Tables)

Temp, °C	0	1	2	3	4	5	6	7	8	9
−70	0.0019	----------	----------	----------	----------	----------	----------	----------	----------	----------
−60	.0080	0.0070	0.0061	0.0053	0.0046	0.0940	0.0035	0.0030	0.0026	0.0022
−50	.0294	.0260	.0229	.0202	.0178	.0156	.0137	.0120	.0105	.0092
−40	.0964	.0859	.0765	.0680	.0605	.0537	.0476	.0421	.0373	.0329
−30	.2878	.2591	.2331	.2094	.1880	.1686	.1511	.1352	.1209	.1080
−20	.7834	.7115	.6456	.5854	.5303	.4800	.4341	.3923	.3541	.3194
−10	1.9643	1.7979	1.6444	1.5029	1.3726	1.2525	1.1421	1.0406	.9474	.8618
−0	4.5802	4.2199	3.8868	3.5775	3.2907	3.0248	2.7785	2.5505	2.3395	2.1445
0	4.5802	4.924	5.291	5.682	6.098	6.541	7.012	7.513	8.045	8.610
10	9.210	9.846	10.521	11.235	11.992	12.794	13.642	14.539	15.487	16.489
20	17.548	18.665	19.844	21.087	22.398	23.780	25.235	26.767	28.380	30.076
30	31.860	33.735	35.705	37.775	39.947	42.227	44.619	47.127	49.756	52.510
40	55.396	58.417	61.580	64.889	68.350	71.968	75.751	79.703	83.820	88.140
50	92.639	97.33	102.23	107.33	112.66	118.20	123.98	130.00	136.26	142.78
60	149.57	156.62	163.96	171.59	179.52	187.75	196.31	205.19	214.41	223.98
70	233.91	244.21	254.88	265.96	277.43	289.32	301.63	314.38	327.59	341.25
80	355.40	370.03	385.16	400.81	416.99	433.71	540.99	468.84	487.28	506.32
90	525.97	546.26	567.20	588.80	611.08	634.06	657.75	682.18	707.35	733.28
100	760.00	----------	----------	----------	----------	----------	----------	----------	----------	----------

TABLE 3. *Saturation vapor pressure of water vapor in mm mercury with respcct to supercooled water*

(Reproduced from the International Critical Tables)

Temp, °C	0	1	2	3	4	5	6	7	8	9
−0	4.579	4.258	3.956	3.673	3.410	3.163	2.931	2.715	2.514	2.326
-10	2.149	1.987	1.834	1.691	1.560	1.436	---------	---------	---------	---------

warming of which by heat from the ambient atmosphere has been augmented by electric resistance or induction heating. The temperature of the mirror surface is frequently measured by thermocouples affixed several hundredths of an inch below the surface or actually on the surface of the mirror. While mercury-in-glass thermometers are still used, their high lag introduces an uncertainty in the temperature reading. In one instrument, the temperature is measured by a carbon dioxide vapor pressure thermometer in which the mirror is integral with the bulb (19). Visual observation of dew or frost has often been replaced by photoelectric detection of reflected or scattered light from the mirror and is indicated on an electrical meter, or automatically recorded. The output of the photoelectric circuit has been used also to control the heat input to the mirror and thereby to maintain the mirror temperature at the dewpoint. Photoelectric observation below the frost point has several advantages. Electronic circuits may be employed that automatically maintain a constant film thickness on the mirror. There can then be little question of whether the liquid or solid phase is involved, for supercooled liquid will not long exist under such conditions without changing to ice. There will be no supersaturation for lack of a crystal nucleus.

For information on these later forms of dewpoint indicators and recorders operating at atmospheric pressure, see (79, 95, 97, 102, 104, 110, 127, 135, 142, 144, 145, 146). Dewpoint indicators requiring visual observation and manual operating of the cooling system are available from dealers in scientific laboratory equipment. Dewpoint indicators and recorders employing photoelectric detection are made by a limited number of manufacturers.

Several dewpoint indicators have been developed that are of novel form or of specialized use. An instrument for use at high pressures is described in (133). In another instrument the sample of gas under test is pumped into a closed chamber and is then cooled by adiabatic expansion to a lower pressure. By repeated trials a pressure ratio can be secured so that a cloud or fog is just formed when the pressure is suddenly released. The dewpoint is computed from the ratio of the initial to final pressure and the measurement of the initial temperature. One version of this instrument (45) employs a vacuum pump for exhausting a reservoir into which the gas sample eventually is expanded. A commercial version (130) uses a small hand pump for compressing the gas sample and then expands the gas into the atmosphere. No adequate data on performance limits are available.

A polished rod or tube of high thermal conductivity, heated at one end and cooled at the other end so that dew forms on part of the rod (43) has been used to obtain the dewpoint. The temperature of the rod measured at the dew boundary is the dewpoint. There has been no commercial development of this device. Unpublished data indicate that it is unreliable at dewpoints below the ice point (0° C) because no satisfactory ice—no ice boundary is obtainable.

Use has been made of the change in conductivity between electrodes on a glass thimble for detecting the dewpoint (45, 59).

The dewpoint method may be considered a fundamental technique for determining vapor pressure or humidity. However, the certainty of the dewpoint measurement is influenced by several factors, some of which are of such indeterminate nature as to make an estimate of the accuracy difficult. It is not always possible to measure the temperature of the mirror at the surface or to assure that no gradients exist across the surface. The visual detection of the inception of condensation cannot be made with complete assurance nor is it probable that two different observers would detect the dew or frost at the same instant. It is usual practice for the dewpoint to be taken as the average of the temperature at which dew or frost is first detected, on cooling of the mirror, and the temperature at which the dew or frost vanishes, on warming of the mirror. This procedure does not assure a correct answer since care must be taken to locate the thermometer, so that no temperature gradient exists from the cold source to the mirror face or to the gas as a whole. The photoelectric detection of the dewpoint usually depends upon achieving an equilibrium condition on the mirror surface during which the amount of dew or frost remains constant. It has been reported (146) that the dewpoint so measured, down to −35° C, agrees on the average to 0.1 deg C with the dewpoint measured visually with a Regnault instrument.

The uncertainty of measuring the dewpoint decreases with decrease in temperature. Below low 0° C uncertainty definitely exists if the eye is used for detecting the first sign of condensation, for it cannot distinguish or differentiate between the liquid and ice phase with the minute trace of water involved. With a photoelectric system in which the mirror alternately cools and then warms so that condensation forms and evaporates, the photocell is likewise incapable of determining whether the condensate is liquid or solid. With a photoelectric system in which a constant film thickness is automatically maintained on the mirror, ice will form on the mirror, for, as previously explained, supercooled water cannot long exist on a free and exposed surface.

Dewpoint instruments have been built with reported sensitivities of 0.1° C (27) and 0.01° C (97) and with reported accuracies of ±1 percent of the vapor pressure (27) at temperatures above freezing and ±1° C at −70° C (127).

4.4. Electrical Hygrometers

Dunmore. These hygrometers commonly depend upon the change in electric resistance of a hygroscopic material with change in humidity. In one design, largely developed by Dunmore (94, 99, 103), two parallel wires of a noble metal are wound upon a polystyerene cylinder or strip. A hygroscopic coating of polyvinyl acetate or polyvinyl alcohol and dilute lithium chloride solution is placed between the wires. At constant temperature the logarithm of the electrical resistance between the parallel wires varies approximately linearly with the logarithm of the relative humidity and is measured by a suitable Wheatstone bridge, preferably using alternating current, or other suitable electric circuits. The electric resistance at constant relative humidity is highly dependent upon temperature, especially at temperatures below 0° C.

The hygrometer was primarily developed for use in radiosondes in which the output is fed to a radio transmitter and controls an audio frequency. It is widely used for this purpose and is manufactured by a number of firms. An indicator and a controller for industrial use is now available commercially.

An elementary theory of the electric hygrometer has been proposed by Schaffer (132).

Similarly, as for the hair hygrometer, the chief defect has been in stability of calibration, which seems to have been overcome in the model for industrial use. The continuous application of direct current causes polarization with a resultant shift in calibration and ultimate deterioration. At temperatures above freezing, the response to humidity changes is rapid, but at lower temperatures, time lags are appreciable. Some data on the performance at low temperatures are given in (134 and 150). One of the advantages of this design is that it is remote indicating an adaptable for control. See also (113 and 114).

Dewcel. Another form of the electric hygrometer is the "dewcel", which is remote indicating and can be used for control (136, 154). Essentially it indicates the dewpoint temperature. The sensing element, similarly as the Dunmore element, has a parallel wire winding with the material between the wires kept wet with a wick impregnated with a saturated solution of lithium chloride. The element is heated by an electric current passed between the parallel wires until its temperature is such that the element neither loses nor gains moisture from the surrounding atmosphere. The electric resistance of the element increases if the temperature is above the equilibrium temperature, since the solution concentration increases by evaporation, and vice versa, and thus the vapor pressure of the solution on the element is automatically brought to and maintained in equilibrium with the surrounding vapor pressure. The temperature of the element, which is measured either by a resistance or liquid filled thermometer, determines the vapor pressure of the lithium chloride solution which in turn equals the pressure of the water vapor in the surrounding atmosphere. The scale can be graduated in terms of dewpoint insofar as the vapor pressures for saturated lithium chloride are accurately known. It is approximately 15 percent of that of water down to temperatures of about 0° C. With certain restrictions the dewpoint is measurable in the range −16 to +160° F. Stability of calibration under service conditions is claimed.

This instrument can be used for remote indicating, recording and control. It functions best in still air, and when the ventilation of the sensitive element becomes excessive (greater than 50 ft/min), suitable means must be used to reduce the ventilation, if accuracy is to be maintained.

Weaver. Weaver and Riley (147) have developed a type of electric hygrometer which has application in routine checking of water vapor content of gases, particularly those in high pressure cylinders.

The sensitive element is a film of electrolyte, usually phosphoric and sulfuric acid, with suitable electrodes for use in measuring the electric resistance of the film, all mounted in a small case, as an aviation engine spark plug, suitably modified. Since the electric resistance of the film is unstable, a comparison procedure is resorted to, in which the resistance of the film in equilibrium with the atmosphere to be measured is immediately matched by exposing to an atmosphere, the moisture content of which can be controlled in a known way.

In the primary use of the instrument, in measuring the dryness of aviator's oxygen, pressure control was found to be most convenient and is described here only in its most elemental form. Gas, usually nitrogen, is humidified 100 percent while at high pressure. A sample of this nitrogen, at atmospheric pressure, is passed through the cell and the resistance noted, usually as the reading of a galvanometer in an unbalanced alternating-current Wheatstone bridge. Then a sample from the compressed gas under test is passed through the cell, at a pressure which is reduced until the same reading is obtained. From the measured pressures and the known water content of the saturated sample, either the weight of water vapor per unit volume, vapor pressure, or relative humidity of the test sample can be computed.

The instrument is characterized by speed, the use of a small sample and greater sensitivity than is possessed by other instruments or methods comparable in these respects. It is available commercially.

Lichtgarn. The variation in electric resistance with relative humidity of selected underfired clays has been investigated by Lichtgarn. The performance data are incomplete as yet, and no elements appear to be commercially available (137).

Gregory humidiometer. Gregory (120) has utilized the electric resistance of cotton impregnated with LiCl or $CaCl_2$ solution to measure humidity. This method has been applied to the measurement of humidity on the skin and clothes of a human subject (131).

Burbidge and Alexander. The variation in electric resistance of cotton wool and human hair has been investigated by Burbidge and Alexander (51). The logarithm of the resistancy of these materials is proportional to relative humidity.

4.5. Gravimetric Hygrometry

a. Change in Weight of Drying Agent

The well-known gravimetric method is accepted as the most accurate for determining the amount of water vapor in a gas. The gas mixture of measured volume and known pressure and temperature is passed over a moisture absorbing chemical, usually phosphorous pentoxide for results of the highest accuracy, and its increase in weight determined. For the data, the weight of water vapor per unit volume and the relative humidity of the gas sample can be computed. Considerable care is required to obtain reliable data (3, 27, 66, 149). This method is employed only in fundamental calibration of instruments or exact determinations of water vapor content.

b. Change in Weight of Absorbing Material

In this type of hygrometer a moisture absorbing material such as human hair, or a chemical, or combinations of both to obtain a structure convenient to handle, is continuously weighed by a delicate balance with an indicator and calibrated humidity scale. The weight of the material must change only with change in the relative humidity of the ambient air (109, 118, 119). Instruments of this type are not known to be available commercially.

4.6. Thermal Conductivity

The difference in thermal conductivity between air (or other gases) and water vapor is utilized so that the temperature, and thus the electric resistance of a hot wire in a small cell varies with change in humidity of the air sample. Two hot wires, one in a reference cell exposed to dry air, are in a bridge circuit, the output of which is a function of the vapor pressure of water in the sample. The theory has been developed by Daynes (31) and Shakespear (34). A model was built by Leeds & Northrup (61, 76). This hygrometer is limited in sensitivity at low temperatures owing to the low vapor pressure of water vapor existing at these temperatures. It has considerable promise as a recorder of humidity in a closed space and in meteorology. It is limited by the fact that it is not specific for water vapor but indicates any change of composition of the gas entering the instrument.

Schwarz (138) has called attention to the possibility of subjecting the water-vapor sample to an inhomogeneous electric field in a thermal conductivity apparatus. Since the water molecule is a dipole, an additional circulation of the water vapor, in contrast to that obtained with air, is secured. This effect can be expected to add to the effect of differences in the heat conduction of air and water vapor. No development work appears to have been done on this possibility.

4.7. Spectroscopic Method

Instruments have been developed in which infrared bands which are absorbed by water vapor are compared in intensity with another band not so absorbed. The sample of air under analysis may be in a tube (116, 125) with the spectral bands obtained from a lamp or may be the entire atmosphere with the sun furnishing the spectral bands (124). The effect of water vapor upon the energy of the received radiation may be measured by phototubes or thermocouples. The instrument is not made commercially.

4.8. Index of Refraction

Some experimental work has been done on the variation of the index of refraction of a thin film of glycerine with water vapor content of the ambient air (29 and 48). The method, even if successfully developed, appears to have only limited application.

4.9. Measurement of Pressure or Volume

The volume of water vapor in a gas sample can be measured if its change in volume is measured at constant pressure before and after the water vapor is absorbed. Conversely, if the volume is held constant, the change in pressure gives the pressure of the water vapor. These methods are useful only in laboratory investigations. The difficulty of obtaining accurate determinations increases rapidly with decrease in temperature of the gas sample. See (1 and 8) for descriptions of a number of instruments of this type.

In one form of constant pressure apparatus a manometer and also a graduated tube containing an absorbing liquid, such as sulfuric acid, are connected to a gas container. In operation sulfuric acid is slowly admitted to the container to absorb the water vapor in the sample and at the same time in sufficient volume to maintain constant the absolute pressure of the gas, as indicated by the manometer and a barometer. The volume of acid admitted is the volume of water vapor in the sample, subject to corrections for lack of constancy of temperature or of the reference pressure.

If the apparatus just described is modified so that the sulfuric acid forms part of the original volume, a constant volume apparatus results. In this case the change in pressure as the water vapor is absorbed is the water-vapor pressure.

The tilting form of absorption hygrometer described by Mayo and Tyndall (33) is essentially a constant volume instrument. Here the absorbing material is installed in a piston which moves from one end of the cylinder containing the gas sample to the other as the cylinder is oscillated, thus forcing the gas through the absorbing chemical. This piston action reduces the time required for complete absorption of the water vapor. The fall in gas pressure which is measured is the water vapor pressure. The device is proposed as a working standard in calibration of hygrometers. It is not available commercially.

One version of constant-volume hygrometer (105) completely dispenses with an absorbing chemical and, instead, uses low temperatures to condense part of the water vapor content of a gas sample, and from a measurement of the temperature and reduction in pressure, permits the determination of the initial vapor pressure. In this instrument, two identical vessels, one containing dry gas and the other the gas sample of unknown water vapor content, are sealed and connected through a differential manometer. The vessels are then immersed in a liquid bath and gradually cooled until the differential manometer registers a pressure difference, indicating that condensation of water vapor has taken place in the gas sample. At this point the temperature and pressure difference are read. From the saturation pressure at the observed temperature and from the pressure difference, the initial water vapor content is then computed.

By employing a liquid-air trap, the moisture in a large volume of gas can be condensed and then suitably measured. The known volume of gas is passed through the trap and, while the low temperature is maintained, the trap is evacuated. The apparatus is then allowed to warm up, preferably in a thermostatted bath, and the vapor pressure measured. Experience with this method at this Bureau indicates that for frost points below −20° C, it is better than the direct determination of the frost point. When using this method with gases containing carbon dioxide, the temperature of the air trap is raised above −78° C before evacuation. This permits any condensed carbon dioxide to be vaporized and removed from the trap.

For additional information on absorption hygrometers, see (30, 85, 86, 101, 111).

4.10. Thermal Rise

The rise in temperature accompanying the exposure of dry cotton wool to moist air has been employed as a means of indicating humidity (see (36 and 45) for details).

4.11. Mobility of Ions

The change in the mobility of ions, produced by α-rays and γ-rays, due to the presence of water vapor has been investigated (45, 51). While a small effect has been observed, no practical hygrometer has been developed.

4.12. Dielectric Constant

Birnbaum has developed a recording microwave refractometer (153) of high sensitivity that can continuously sample and record the dielectric constant of a stream of air or gas. Since the dielectric constant of air varies with water-vapor content, this instrument may be employed as a recording hygrometer. The refractometer operates by comparing two identical cavity resonators. Into one of these cavities, the test sample is introduced. The resulting differences in resonance frequency between the two cavities is then a measure of the dielectric constant of the test sample. In addition to its high sensitivity, the refractometer has a time response, limited by the response of the recording milliammeter, of about one-half second to discrete changes in dielectric constant. A similar instrument has been reported by Crain (157).

4.13. Critical Flow

Wildhack (156) has proposed a means of measuring relative humidity which utilizes sonic, or critical, flow through small nozzles. Two sets of two nozzles in series are arranged in parallel, with critical flow maintained through all nozzles. At critical flow the mass flow through each nozzle is independent of the downstream pressure, and is directly proportional to the entrance pressure. An absorber of water vapor is placed between one series pair of nozzles, which reduces the mass flow and hence the gas pressure at the entrance to the downstream nozzle. Measurement of the difference in entrance pressures between the two downstream nozzles, of the absolute pressure of the gas at the entrance to the referenced downstream nozzle, and of the gas temperature, will serve to determine the relative humidity of the gas.

4.14. Diffusion Hygrometer

The difference in density of completely and partially saturated air, at the same temperature, has been employed to measure air humidity (49). Esentially, a column of atmospheric air is balanced against a column of saturated air. The difference in density of the two columns causes the lighter saturated air to diffuse upward into the atmosphere and the atmospheric air, because of its greater density to diffuse downward into a saturation chamber where it, in turn, becomes fully humidified. The rate of diffusion is then directly related to the vapor pressure of the atmospheric air and is detected and measured by means of the deflection produced in a suspended vane. It is claimed that this water vapor diffusion method can operate over a wide temperature range, is continuously indicating or recording, is easy to operate and is portable.

A different approach was used in the hygrometer described by Greinacher (122). His instrument is based on the difference in diffusion of water vapor and air through a semipermeable membrance. A porous clay plate cemented to an opening in the wall of an enclosed vessel containing a desiccant preferentially permits air diffusion and prevents water vapor diffusion. A differential manometer, communicating with the enclosed vessel and the ambient atmosphere (whose humidity is being measured), registers a pressure drop Δp_1 that is directly proportional to the partial pressure e of the water vapor in the ambient atmosphere. In order to avoid consideration of the constant of proportionality of the apparatus a similar vessel with an identical porours clay plate and manometer, but containing water instead of the dessicant, is employed. The pressure drop Δp_2 indicated by the latter arrangement is directly proportional to the difference between the saturation vapor pressure e_s and the ambient partial pressure e at the ambient temperature. The relative humidity is given by the relation.

$$RH = 100 \times \frac{e}{e_s} = 100 \times \frac{\Delta p_1}{\Delta p_1 + \Delta p_2}$$

Further theoretical consideration of this hygrometer are presented by Spencer-Gregory and Rourke (141). The instrument is reported to be extremely sensitive to rapid temperature changes which may give rise to erroneous readings.

4.15. Chemical Methods

Several methods are available for the determination of the moisture content in gases by chemical means. A very simple and qualitative indicator may be made based on the change in color, from blue to pink, of cloth or paper impregnated with cobaltous chloride, as the humidity increases. When a color comparison scale is employed with this indicator, a rough estimate of the relative humidity is obtained (75). Cobaltous bromide may similarly be used, with a threefold increase in sensitivity. The colors of these cobalt salts are affected by temperature as well as humidity. The quantitative measurement of water vapor has been successfully made by using cobaltous bromide as an indicator in a visual (112) and in a photoelectric (123) colorimetric method.

There is a series of compounds of ketones and Grignard reagents which can form internal ions accompanied by the development of intense color, induced by the presence of water. Some useful compounds are the complexes of Michler's ketone (tetramethyl-diaminobenzophenone) and Grignard reagent (ethyl magnesium bromide, methyl magnesium iodide, or phenyl magnesium iodide). An apparatus, employing the color change of these compounds, has been developed, primarily for detecting moisture in compressed oxygen (19). The apparatus and method involves sealing a measured amount of compound with dry sand in a glass ampule. Then, under a controlled and uniform rate of gas flow, the ampule is broken and the time for the movement of the resultant color front along a specified distance is measured. This time, for a given batch of ampules identically made, is a function of the moisture content, the temperature and rate of flow.

A method for the analytical determination of the water content in a wide range of materials was proposed by Karl Fischer in 1935 (84). His reagent, a solution of iodine, sulfur dioxide and pyridine in methanol, is the basis of titrimetric procedures that have been applied to moisture determinations in gases (20).

5. Test Methods

The testing and calibration of hygrometers involve the production and control of atmospheres of known relative humidity over a wide range of temperatures. While the methods of humidity production are varied, they may be classified, conveniently, into several categories. The equipment for producing the known relative humidity must be designed so that hygrometers to be tested can be conveniently exposed to the controlled atmosphere.

The sections below are restricted largely to the description of methods of producing a constant humidity of known amount useful for calibration of hygrometers.

5.1. Basic Methods

Relative humidity is related, through the fundamental gas laws, to such parameters as temperature, pressure, and water-vapor content. Several convenient and practical methods are available of directly establishing atmospheres of known relative humidity with sufficient precision and accuracy by the measurement and control of these parameters, without requiring auxiliary humidity measuring and sensing instruments.

The principle of divided flow may be employed, when flow is permissible, to produce any desired humidity. Apparatus, based on this principle, has been described in (76) for use at temperatures above freezing and in (134 and 149), for use at temperatures below 0° C (32° F). A stream of dry air is divided accurately, usually by means of a proportioning valve, into two parts. One part is saturated, with respect to water or ice; the other part is maintained dry. The two parts are then recombined in a test chamber and exhausted into the air. The relative humidity is given by the ratio of the division. A simplified schematic diagram of this method is shown in figure 1.

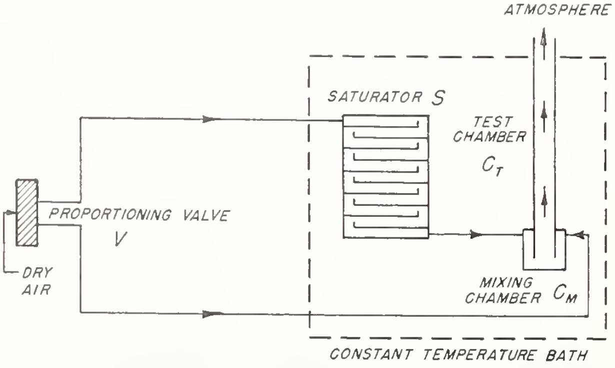

Figure 1. *Simplified schematic diagram of the principle of operation of the divided-flow humidity apparatus.*

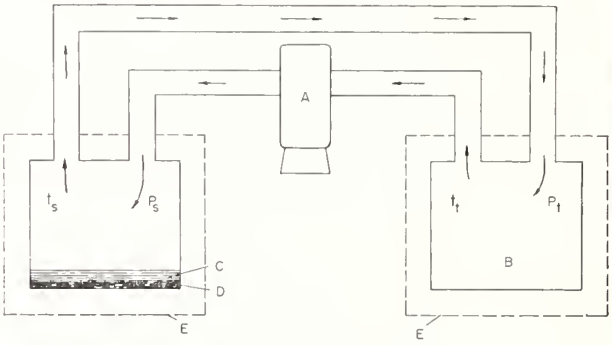

Figure 2. *Simplified schematic diagram of the two-temperature recirculating method of relative-humidity production.*

A, gas pump; B, test chamber; C, water; D, saturator; E, thermostatted bath.

In the recirculation or two-temperatures method, a stream of air is saturated at a controlled temperature and then the temperature of the mixture is elevated, without loss or gain in moisture. A measurement of the two temperatures serves to determine the relative humidity. To insure complete saturation at the lower temperature, the air stream is recirculated in a closed system from the saturator (at the lower temperature) to a test chamber (at the higher temperature) and back to the saturator. The temperatures must be accurately measured and controlled; for example, at 20° C (68° F) an error of 0.2° C (0.3° F) in either temperature measurement represents 1 percent error in relative humidity, which error increases at lower temperatures. Laboratory equipment of this type has been built (106, 155), but none is commercially available. The method is illustrated in figure 2.

In the two-pressure method (147) a stream of air (or some other gas) at an elevated pressure is saturated and the pressure of the saturated air is reduced as required to obtain any desired humidity. Since the desired relative humidity is required, usually, at atmospheric pressure, the elevated pressure is so adjusted that the air, upon expansion to atmospheric pressure, will be at the proper relative humidity. The pressure of the air and water vapor mixture is measured at both the elevated and reduced pressures, and so are the temperatures, if they differ. To insure that the saturator and test chamber temperatures remain the same, and also to provide a means of controlling and establishing any desired temperature, the saturator and test chamber are immersed in a thermostatted bath. To prevent condensation the saturated air temperature must not fall below the dewpoint, which may require heating the mixture at or before it flows through the pressure-reducing valve. Even at room temperature, control of the saturator temperature will be necessary if the air flow is appreciable. At constant temperature, the relative humidity is roughly the ratio of the two pressures, assuming ideal gas laws. More accurate computation of the relative humidity takes into account deviations from the ideal gas laws (147).

One type of saturator employed in this method consists of a cylinder filled with clean sand and water through which the air passes. Another type similarly consists of a cylinder into which water has been added, but the air in this type enters the cylinder tangentially to and above the water (or ice) surface and, after swirling around many times over the water, emerges through a central port at the top. A sketch of this method is shown in figure 3.

In the water or steam injection method for the precise control of relative humidity, moisture and dry air are mixed in desired proportions, using nozzles, orifices or other metering elements in conjunction with pressure reducers. See (67) for one application.

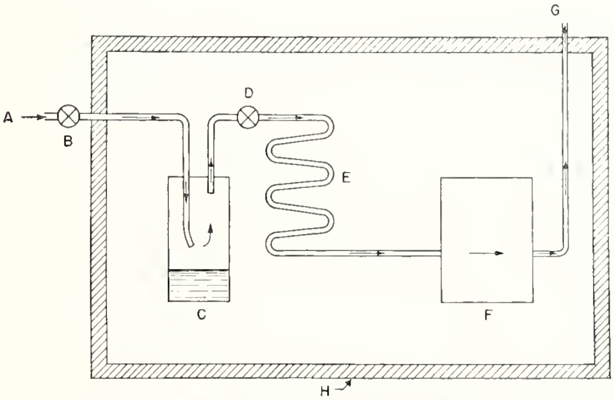

Figure 3. *Simplified schematic diagram of the two-pressure method of relative-humidity production.*

A, High-pressure source; B, pressure reducer; C, saturator (water or ice); D, valve; E, heat exchanger; F, test chamber; G, to atmosphere; H, thermostatted bath.

5.2. Secondary Methods

Very convenient methods exist for establishing atmospheres of known relative humidity which depend upon the equilibrium vapor pressure of water when a chemical is dissolved in it. These methods are ideally suited for controlling the relative humidity of a small closed space. Equilibrium conditions are more rapidly established when air circulation or stirring, as by means of a fan or blower, is employed. In all these methods, the test chamber should be kept free of hygroscopic materials, such as wood.

The saturated salt solution method is inexpensive and simple and produces constant relative humidities that are roughly independent of temperature. This method is used frequently for calibrating mechanical type hygrometers. A sealed chamber is required, for which a large glass jar or bell jar is often suitable. The salt solution is made up as a slushy mixture in a glass or enameled tray or in the glass jar, if used, with the solution spreading over as large an area as practicable. Distilled water and chemically pure salts must be used. The salts listed in table 4 have been found useful; for a list of others see (4). The data in table 4 are based partly on the vapor pressure data given in the International Critical Tables (17) and partly on dewpoint measurements made at this Bureau.

Table 4.—*Saturated salt solutions suitable for use in humidity control*

KNO_3=potassium nitrate
$NaCl$=sodium chloride
$Mg(NO_3)_2.6H_2O$=magnesium nitrate
$MgCl_2.6H_2O$=magnesium chloride
$LiCl$=lithium chloride

Temperature		Relative humidity of saturated salt solution				
		KNO_3	$NaCl$	$Mg(NO_3)_2.6H_2O$	$MgCl_2.6H_2O$	$LiCl$
°*C*	°*F*	%	%	%	%	%
0	32	97	76	54	34	19
5	41	96	76	54	33	16
10	50	95	75	53	33	14
15	59	95	75	53	33	13
20	68	94	75	53	33	12
25	77	93	75	52	33	11
30	86	92	75	52	32	11
35	95	90	75	51	32	11
40	104	89	75	51	31	11

Water-sulfuric-acid mixtures (39, 52, 63) produce atmospheres of relative humidity that depend on composition and temperature. Two techniques may be employed. The liquid may be exposed in a suitable tray in a sealed chamber to give the equilibrium vapor pressure of the mixture, or air may be bubbled or otherwise brought into intimate contact with the liquid. Wilson's data (39) are reproduced in table 5.

TABLE 5. *Relative humidity obtained from water-sulfuric acid solutions*

Relative humidity	Percentage of H_2SO_4 (by weight) at—			
	0° C	25° C	50° C	75° C
%				
10	63.1	64.8	66.6	68.3
25	54.3	55.9	57.5	59.0
35	49.4	50.9	52.5	54.0
50	42.1	43.4	44.8	46.2
65	34.8	36.0	37.1	38.3
75	29.4	30.4	31.4	32.4
90	17.8	18.5	19.2	20.0

Water-glycerine mixtures (63) will similarly produce atmospheres of known relative humidity. The techniques employed with water-sulfuric acid mixtures work equally well with water-glycerine mixtures. The relative humidity obtainable at 25° C from various water-glycerine solutions are given in table 6.

TABLE 6. *Relative humidity obtained from water-glycerine mixtures at 25° C*

Relative humidity	Glycerine (by weight)	Specific gravity
%	%	
10	95	1.245
20	92	1.237
30	89	1.229
40	84	1.216
50	79	1.203
60	72	1.184
70	64	1.162
80	51	1.127
90	33	1.079

5.3. Control Methods

In response to a sensing element, such as a mechanical hygrometer, electrical hygrometer, or psychrometer, the humidity of a closed space may be raised by water, spray or steam injection, by exposure to a water surface or wet wicks, or by the introduction of saturated or high humidity air (or gas), or the humidity may be lowered by chemical absorption, or the introduction of dry air (or gas). The controls that are used may be manual or automatic.

One type of controlled-humidity chamber design (32, 45) consists, essentially, of a sealed chamber, such as a bell jar, in which air circulation is obtained by means of a fan. Two trays, each with a tight cover that can be raised and lowered externally, are placed in the chamber. One tray contains a chemical absorbent, such as sulphuric acid, silica gel or Drierite, while the other contains distilled water, preferably with exposed cotton or linen wicks. The cover of the appropriate tray is raised until a hygrometer indicates that the desired relative humidity has been attained. The cover is then dropped and, since the chamber is sealed, the humidity remains constant. This chamber may be made automatic by using the output of a sensing element, through an appropriate circuit, to raise or lower the required cover.

See (8, 10, 12, 50, 54, 58, 62, 65, 92, 114, and 129), for additional suggestions and details.

5.4. Comparisons with Standards

While it is preferable to use atmospheres of known relative humidity for testing or calibration, it is often desirable to make spot checks of mechanical hygrometers and hygrographs under prevailing atmospheric conditions or even, in some cases, to test or calibrate hygrometers in chambers where the humidity is not known or only known approximately. Under these conditions, the readings of the instrument under test may be compared with those of a standard instrument.

It is generally considered that the primary standard in hygrometry is the gravimetric method of water vapor measurement. However, except for work of the highest order of accuracy, this method is seldom used as a working standard. On the other hand, proved designs of dewpoint indicators and recorders are frequently employed as working standards where accuracy is desired. Many models are in the nature of laboratory instruments, especially those depending on visual observation and manual temperature control, requiring skilled personnel for successful operation so that they are not usually used in routine calibrations. The dry- and wet-bulb psychrometer is particularly suited for rapid routine work. It should be used with caution in small enclosures, for evaporation from the wet-bulb may increase the relative humidity of the space being measured. If adequate ventilation is secured and proper precautions are observed, the psychrometer is calibrated merely by having its thermometers calibrated.

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