NBS CIRCULAR 586

Electric Hygrometers

UNITED STATES DEPARTMENT OF COMMERCE

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Electric Hygrometers

Arnold Wexler

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This Circular is a review of the art of measuring the moisture content of air by the methods of electric hygrometry. The basis of these methods is the change in electrical resistance of a hygroscopic material with change in humidity.

1. General Introduction

Many, if not most, materials sorb and desorb water vapor as the ambient relative humidity increases or decreases. Associated with this sorption, there is usually a corresponding change in electrical resistance of the material. Materials which display a humidity-dependent change in resistance can be utilized as humidity sensors. However, for a sensor to be of practical use, it should have a reversible and reproducible humidity-resistance characteristic. Such sensors, or elements, when coupled with suitable measuring circuits constitute the electric hygrometer class of instruments. An electric hygrometer, therefore, may be defined as an instrument for determining the moisture content of air (or any gas) by the measurement of the electrical resistance of a hygroscopic material with change in humidity. In line with this definition, instruments that may use electrical meters or recorders or electronic devices in their circuitry, or that may require electric current for their operation, but that do not measure the resistivity or conductivity of a hygroscopic material are not discussed.

It is convenient to classify the sensors, in accordance with their basic principles of operation, into those that depend upon (a) the conductivity of aqueous electrolytic solutions, (b) the surface resistivity of impervious solids, (c) the volume resistivity of porous solids, (d) the resistivity of dimensionally-variable materials, and (e) the temperature of saturated salt solutions. These categories are not necessarily mutually exclusive nor do they include all possible ways in which resistance can be used for humidity sensing. They simply provide a basis for a description and discussion of many of the sensors that are in use or have been proposed.

2. Conductivity of Aqueous Electrolytic Solutions

2.1 General Theory

One type of electric hygrometer sensor is an aqueous solution of an ionizable substance. There are several variations of this type of sensor, but they all have the same theoretical basis of operation. Briefly, the electrical resistance of the sensor is a function of the concentration of the solution which, in turn, is a function of the ambient relative humidity and temperature. Some of the fundamental and theoretical considerations of sensor operation are discussed by Schaffer [1] [1] whereas Evans and Davenport [2] have studied, experimentally, the conduction mechanism.

If a nonvolatile solute is dissolved in water at a constant temperature, the equilibrium vapor pressure will be lowered below the saturation vapor pressure of pure water at that temperature. As the concentration of the solution is increased, the equilibrium vapor pressure is decreased. With many solutes, such as salts, a point is reached at which the further addition of solute to water will produce no further depression of the vapor pressure. The solution, at this point, will be saturated and the equilibrium vapor pressure will remain constant. Under certain conditions, a supersaturated solution can be produced, but, for the purposes of this discussion, it will be assumed the maximum solubility is reached at saturation.

For any given concentration and temperature of an aqueous solution, there is a corresponding equilibrium vapor pressure. If the solution is surrounded by an open space, there will be a continual flow of water vapor into and from the solution. If the vapor pressure of the space is greater than the equilibrium vapor pressure of the solution, there will be a net flow into the solution; conversely, if the vapor pressure of the space is less than the equilibrium vapor pressure of the solution, there will be a net flow of vapor from the solution into the space. This net vapor flow will continue until either the vapor pressure of the space and solution are equalized, or the water is evaporated completely from the solution. If a solution of finite volume is surrounded by an

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[1] Figures in brackets indicate the literature references at the end of this Circular.

infinite space of constant vapor pressure, only the concentration of the solution will change until the equilibrium vapor pressure of the solution equals that of the ambient space. The concentration of the solution, at equilibrium, is a measure, therefore, of the ambient vapor pressure or relative humidity. One method of determining the concentration of the solution is by measuring its electrical conductivity. Thus, an aqueous solution of an ionizable material can be utilized as an electric hygrometer sensor.

Some of the factors that influence or control the use, in this fashion, of an aqueous electrolytic solution are as follows:

(a) *Minimum relative humidity.* If the solute has a finite solubility in water, then at saturation, the solution will have attained its minimum relative humidity. If the ambient relative humidity is less than this minimum equilibrium relative humdity of the solution, the water will evaporate leaving only the solute. The equilibrium relative humidity for the saturated solution is the lower operational limit of the solution. Sulfuric acid is miscible with water in all proportions and has no minimum of this kind; this is the reason for its use in some sensing elements. With lithium chloride, a salt that is commonly used in sensors of the electrolytic class, the minimum theoretical relative humidity that may be measured is 14.7 percent at 0° C, 12.0 percent at 25° C, and 11.4 percent at 50° C [3]. With sodium chloride, the minimum theoretical relative humidity, over the range of 0° to 50° C, is 74.7 percent to 75.8 percent [3]. The proper choice of a salt depends, in part, on the minimum relative humidity that the sensor will be expected to measure.

(b) *High relative humidity.* There is a practical upper relative humidity operational limit for the solution. As the relative humidity increases, the dilution of the solution increases, until at a relative humidity of 100 percent, water vapor will be sorbed continually as the solution tends to approach infinite dilution. (In most practical sensors, the solution should not be exposed to a relative humidity of 100 percent.)

(c) *Hydrates.* Many solutes possess the property of forming chemical compounds with their solvents. If the solvent is water, then these compounds are known as hydrates. The formation of a hydrate will occur at a specified temperature and concentration. Solutes which form hydrates will exhibit discontinuities in their equilibrium vapor pressure data at the hydration temperatures. In addition, the solution conductivity at the hydration temperature will change markedly, and during the change, there will be an uncertainty regarding the ambient relative humidity.

(d) *Cryohydric point.* The addition of a nonvolatile solute to water lowers the freezing point of the water. As the concentration of the solution is increased, and the temperature lowered, a point is reached at which the solute is in equilibrium with both ice and liquid water. The maximum depression of freezing point is attained under this condition. The lowest temperature of freezing, for a given solute and water is known as the cryohydric point. If the temperature is decreased below this point, the solution will separate into pure solute and ice. The cryohydric point is the lowest theoretical temperature at which an aqueous solution of a finitely soluble solute can be used as an electric hygrometer.

(e) *Volume.* In theory, there is no limit to the volume of solution that may be employed. In practice, the volume should be kept as small as feasible. A small volume permits the solution to reach concentration equilibrium with the ambient relative humidity much more rapidly than a large volume. A small volume will respond to temperature changes more rapidly, and will affect the atmosphere of a confined space less, which is often an important consideration.

(f) *Polarization.* Either alternating or direct current can be used in the circuit for measuring the conductivity of the solution. If direct current is used, then the solution undergoes electrolysis, and there is a migration of ions to the electrodes. Associated with this migration of ions is the phenomenon of polarization. Polarization may be due to a chemical or physical change on the surface of the electrode, or to the deposition of a film of gas or oxide or other material, or it may be due to a change in concentration of the electrolyte in the neighborhood of the electrode. Polarization manifests itself by a change in the conductivity of the solution with time. If alternating current is used, then electrolysis is eliminated and polarization reduced or eliminated. However, the electrical capacitance of the solution, as well as that of the measuring circuit introduces a complicating factor. The physical dimensions of the solution may be varied to reduce the electrical capacitance and a measuring circuit may be used which balances out this capacitance. Unless this is done, the solution, for low ambient relative humidities, may approach a minimum conductance (maximum impedance).

(g) *Electrodes.* The electrodes employed should be materials that do not corrode or react with the electrolyte. Noble metals are usually the most satisfactory materials for use as electrodes.

(h) *Solution carrier or retainer.* Some convenient means must be provided for physically containing or supporting the solution and the electrodes. Of course an actual volumetric vessel or container may be used for this purpose. The surface of the solution in contiguity with the ambient atmosphere, should be as large as feasible for a given volume. If a vessel or container is used it will be limited usually to a fixed position to avoid spillage. Because of this and other limitations, volumetric containers are seldom, if ever, used. One approach is to apply a thin layer of solution, by brushing, dipping or spraying, to an impervious insulator on which electrodes have been affixed. Another approach is to disperse the solution in an inert binder of high viscosity or adhesiveness and then to apply a thin film of the resultant mixture to an impervious insulator. Natural or synthetic fibers or fabrics are more or less porous and will absorb and retain liquids. They can be impregnated therefore with a suitable electrolytic solution. In a similar fashion there are inorganic materials that are highly porous and these also can be impregnated with appropriate solutions.

2.2. Electrolytic Solution on Impervious Insulating Surfaces

a. Weaver Water Vapor Indicator

The use of an electrolytic solution on an impervious insulator as a moisture detector was studied as early as 1923 by Weaver and Ledig [4, 5]. They found that of the materials they investigated, sulfuric and phosphoric acids were the most useful, for with these acids, extremely low moisture contents could be detected. However, it was necessary to use alternating current in the measuring circuit to prevent polarization and to mix the electrolyte with gelatin or a similar binder to prevent "creeping" of the film of electrolyte after it has been coated on the surface of a detector. Even with these precautions, the calibration changed so rapidly that very frequent recalibrations were necessary. This method was little used until a need developed for measuring the moisture content of cylinders of compressed oxygen. Weaver and Riley [6] then devised a simple and rapid calibration technique whereby the resistance of the electrolytic film, soon after a measurement, could be translated into a measure of the moisture content.

The detector of the Weaver water vapor indicator comprises two closely spaced concentric platinum electrodes, separated by an insulating material, usually glass, and housed in a high pressure case such as an aviation engine spark plug. A small amount of electrolyte is applied to the detector and wiped across the surface, say, with a clean cloth, leaving a thin film. The detector is then exposed to an atmosphere of unknown humidity and the resistance of the film measured with an alternating current bridge or similar circuit. The detector is now exposed to a gas, such as air, oxygen, or nitrogen, the moisture content of which can be controlled in a known way. This is accomplished by saturating dry gas at a high pressure and expanding to a lower pressure. The pressures are adjusted so that the resistance of the detector in the atmosphere of known water vapor content is identical to that in the atmosphere of unknown humidity. In essence, this is a null method in which an electric hygrometer is used to balance an unknown humidity against a known humidity.

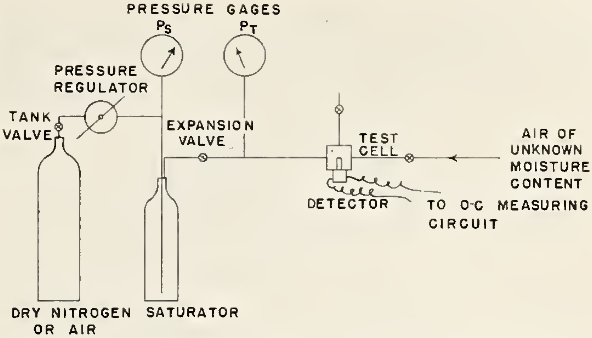

FIGURE 1. *Simplified flow diagram of Weaver water vapor indicator.*

Figure 1 is a simplified flow diagram of the apparatus. A pressure regulator is used to set the pressure in the saturator at any desired value, P_S, and an expansion valve reduces the pressure of the saturated gas to P_T. The saturator may be one or more high pressure metal cylinders filled with moistened pumice or gravel. The detector is inserted into a test cell which can be filled either with the test gas of known moisture content or with the atmosphere of unknown humidity. Alternatively, the detector may be inserted directly into the atmosphere of unknown humidity, and after a reading has been made, it then may be inserted in the test cell for calibration.

Assume that the gas of unknown humidity, at an absolute pressure P_i, is expanded to an absolute pressure P_X at which pressure it produces a suitable reading on the detector. Assume also that the desired information is the moisture content of this gas at an absolute pressure P. If the pressure changes occur at constant temperature, and if the water vapor-gas mixture obeys the ideal gas laws, then the moisture content, W, at P is related to the moisture content W_X at P_X by

$$W = W_X \frac{P}{P_X}. \tag{1}$$

Let the gas, used in the calibration procedure, be saturated at an absolute pressure P_S and expanded to an absolute pressure P_C. If the saturation and expansion are isothermal, and if gas ideality is again assumed, then the moisture content W_C, at pressure P_C is related to the moisture content W_S, at P_S by

$$W_C = W_S \frac{P_C}{P_S}. \tag{2}$$

If the resistance of the electric hygrometer, that is, the water vapor detector, is the same at P_C with the gas of known moisture content as at P_X with the gas of unknown humidity, then the moisture contents of these two gases, at their respective pressures are equal, that is, $W_X = W_C$. Therefore, the moisture content of the gas of unknown humidity is obtained by substituting eq (2) into (1) to give

$$W = W_S \frac{P_C}{P_S} \frac{P}{P_X}. \tag{3}$$

The moisture content may be expressed in any of several ways: (a) water vapor density, in mass of water vapor per unit volume; (b) vapor pressure; or (c) relative humidity. The densities and vapor pressures of saturated water vapor are given in standard tables [7] so that for any given temperature, the appropriate value for W_S can be obtained. In terms of relative humidity W_S is always equal to 100 percent.

For many meteorological applications, where the moisture content of atmospheric air is to be measured, the detector will be exposed, usually, to the atmospheric air at atmospheric pressure and its moisture content will be desired at atmospheric pressure. Thus P is equal to P_X and eq (3) reduces to

$$W = W_S \frac{P_C}{P_S}. \qquad (4)$$

The quantity of vapor that exists in equilibrium with the liquid or solid phase of water, in the absence of any other vapor or gas, is a function solely of the temperature. In the presence of an inert gas, the nature of the gas and the pressure of the gas influences the equilibrium quantity of vapor. Weaver [6, 8] has shown that for such gases as air, oxygen, and nitrogen, for pressures up to 6,000 psi, and for temperatures of $-45°$ to $+38°$ C, an empirical relation may be used to account for the pressure effect. Thus, eq (3) becomes

$$W = W_S \frac{P_C P (1 - KP_C + K'P_C^2)(1 - KP + K'P^2)}{P_S P_X (1 - KP_S + K'P_S^2)(1 - KP_X + K'P_X^2)} \qquad (5)$$

and eq (4) becomes

$$W = W_S \frac{P_C (1 - KP_C + K'P_C^2)}{P_S (1 - KP_S + K'P_S^2)} \qquad (6)$$

where

$$K = 1.9 \times 10^{-4} \text{ and } K' = 1.4 \times 10^{-8}.$$

With phosphoric acid as the electrolyte on the detector, moisture concentrations as low as 8 μg of water vapor per liter are adequately measured and moisture concentrations as low as 3 μg/liter can be detected. With sulfuric acid as the electrolyte, concentrations as low as a fraction of a microgram per liter can be detected. In terms of dewpoint with respect to ice, these concentrations are approximately equivalent to dewpoints of $-62°$, $-69°$, and $-80°$ C. The thickness of the electrolytic film on the detector is not critical. However, a thick film is more sensitive, and slower in response, than a thin film.

The main use of the Weaver water vapor indicator is to measure low moisture contents, especially the moisture content of compressed gases. Because of the relative instability of calibration of the sensitive film on the detector, the preferred technique for procuring a reliable reading is to calibrate the film immediately after exposure to a gas of unknown humidity. A film may maintain its calibration without appreciable change for 15 min. The indicator can therefore be utilized to follow, for short intervals of time, changing humidity conditions. In general, it is not too well adapted for giving continuous readings of changing moisture concentrations for extended periods of time. The accuracy of this device depends, in large measure on (a) the accuracy of the water vapor content of the test gas at saturation, (b) the accuracy of the pressure measurements, (c) the accuracy of the pressure correction term, and (d) on the absence of moisture sources and sinks within the equipment. In the present state of development, the saturator, test cell, and detector are operated at room temperature. The temperature of these components varies, more or less, with ambient temperature. Errors in the temperature of these components, or differences in temperature, are reflected as errors in the indicated moisture content. For example, an error of 1° C in the temperature of the saturator, or a difference of 1° C between the saturator and test cell or detector that is not corrected for in the computation, will introduce an error of about 6 percent in the measured moisture content at an ambient temperature of about 25° C.

b. Dunmore Hygrometer

In exploring the possibilities of electric hygrometry for measuring the moisture content of the upper air during a radiosonde flight, Dunmore [9, 10] experimented with the use of various electrolytic solutions, such as calcium, zinc, and lithium chloride salts, sulfuric and phosphoric acid, and mixtures of these materials, coated on glass cylinders. As a result, he developed a hygrometer that consisted of a thin wall flint glass tube, 10 mm in diameter, 0.3 mm in thickness, and 12.7 cm long, roughened by sand blasting or etching, and having a bifilar coil of No. 38 AWG bare tinned copper wire, with a pitch of 20 turns per inch, wound on its outer surface. When coated with a dilute aqueous solution of lithium chloride, the resistance of the unit, between the two coil windings, was a function of the ambient relative humidity and temperature. Figure 2 is typical calibration. Although this hygrometer was subject to the same defects as that of Weaver and Ledig, Dunmore found that if he held it at a constant relative humidity prior to use, and calibrated it within a few days of use, it was capable of giving indications accurate to ±5 percent relative humidity. He also found that the long time aging or instability was due to either the oxidation or corrosion of the tinned copper electrodes and that the hysteresis was associated with the roughened surface of the glass. By using platinum or palladium electrodes and a smooth polystyrene base, he was able to improve the performance of the hygrometer so that it held its calibration to within ±3 percent for 6 months.

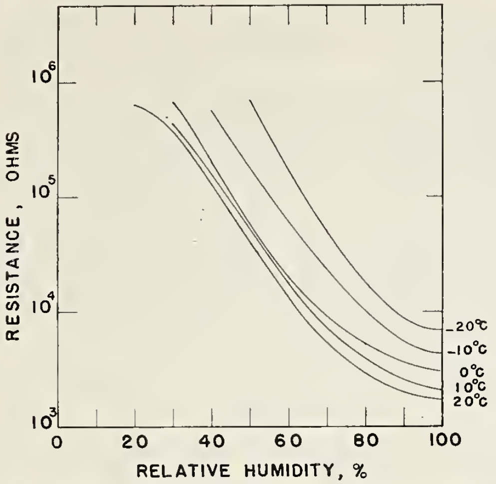

FIGURE 2. *Typical calibration of an electrolytic type of electric hygrometer.*

Roughened glass tube with bifilar coil electrodes coated with 5 percent (by volume of a saturated solution and water) lithium chloride solution. After Dunmore.

c. Larach Hygrometer

Although such electrolytes as lithium chloride, zinc chloride, phosphoric acid, and sulfuric acid have been favored for sensor use, there has been a continuing search for materials which have such improved characteristics as increased sensitivity, less temperature dependence, faster speed of response and less polarization. Solutions of the tetrachlorides of the metals tin, zirconium, hafnium, and lead, have been proposed by Larach [11] for use as sensors. A thin layer of such a solution is applied to an insulator, say a glass slide with fused silver electrodes, and heated at about 80° to 100° C until it partially dries and becomes tacky. A hygrometer element made in this way has a nonlinear relation between the logarithm of the resistance and the relative humidity, as shown in figure 3. The S-shape nature of this curve gives rise to the greatest sensitivity for the middle range of relative humidities and reduced sensitivities for both low and high humidities. The purported advantage of such a sensor is the reduction or elimination of polarization.

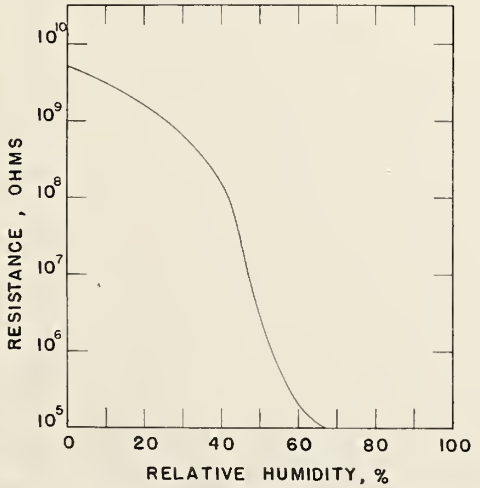

FIGURE 3. *Typical calibration curve of a Larach hygrometer.*

Insulator coated with a solution of the tetrachloride of either tin, zirconium, hafnium, or lead.

d. Gregory Hygrometer

An electric hygrometer has been developed by Gregory [12] in which glass wool yarn, impregnated with an electrolytic solution, is used as the sensitive element. One variant of this sensor is made by winding 9 feet of yarn around four platinum-clad nickel-iron core electrodes. The electrodes are connected in pairs. The yarn consists of 100 fibers, each about 25×10^{-5} cm in diameter; about 0.6 mg of calcium chloride in solution is spread over the yarn. Each fiber of the yarn acts as an impervious insulating surface, but the yarn, to some extent, is partially a porous medium so that solution is held and retained in the spaces between adjacent fibers. Such a sensor exhibits a near linear relationship between the logarithm of the resistance and the logarithm of the relative humidity, as shown in figure 4.

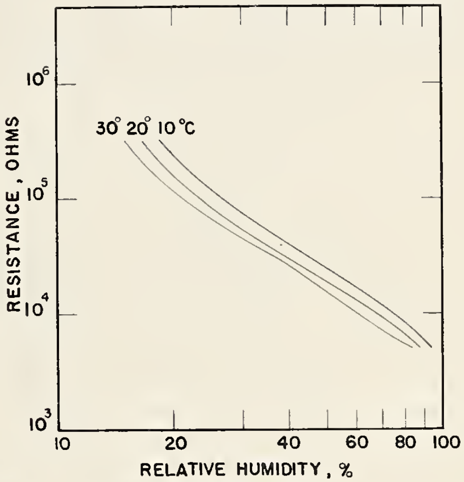

FIGURE 4. *Typical calibration curves of the Gregory hygrometer.*

Glass fibers coated with calcium chloride solution.

The range of this type of sensor has been extended to relative humidities of 1 percent or less by a modification in which the impregnated glass wool yarn is wound on a platinum electrode $\frac{1}{16}$ in. in diameter. A second electrode, comprising a platinum strip 0.001 in. in thickness and 0.01 in. in width is wound over the yarn. The conducting path is across the diameter of the yarn. Such an element can be made with a resistance that varies from 1.5 megohms at 1 percent relative humidity to 8,000 ohms at 10 percent relative humidity. Normal range elements, using the former construction, have been developed that have an over-all size of 10×6×6 mm [13]. These miniature elements are probably accurate to ±2 percent relative humidity. After a discrete change in relative humidity, at room temperature, the miniature element undergoes a 63 percent change in indication in 2 to 2½ min and a 90 percent change in indication in 3 to 5 min.

2.3. Electrolytic Solutions in Organic Binders

One difficulty with the direct application of aqueous electrolytic solutions to impervious insulating surfaces is the tendency for the solution to break up into globules of liquid, or to move or "creep", particularly when under the influence of such forces as gravity, and even to drip from the substrate surface. In order to keep the solution on the surface, the latter has sometimes been treated to make it rough, as, for example, the sandblasting or etching of glass when it is used as the insulator. If the surface treatment is too extensive, then the insulator may approach the category of a porous medium whereby the solution is retained in pores or capillaries of the insulator. An alternative method can be used to keep the solution on a smooth surface. The electrolytic solution is mixed with a binder, usually organic, that has excellent adhesive properties and the resultant mixture is applied to the insulating surface. What is particularly desired in such a binder is the ability to mix readily with the solution and to permit water vapor to diffuse rapidly through the mixture. A binder which forms a highly pervious structure on drying, and which has proved to be excellently suitable for electric hygrometer sensor use is partially hydrolyzed polyvinyl acetate [14,15]. Another good binder is polyvinyl alcohol [16]. Agar-agar, pectin, gelatin [17], alkyl aryl poly-ether alcohol [18], and methyl methacrylate [6] also have been used as binders. The addition of a binder increases the lag of the electric hygrometer because water vapor has to diffuse through the structure of the binder in order that equilibrium conditions may be attained. On the other hand, the binder may enhance the even distribution of solution on the substrate surface, leading to greater reproducibility between elements fabricated under uniform conditions. Then too, it has been established that a binder may act to reduce polarization, as in the case of partially hydrolyzed polyvinyl acetate and lithium chloride solution films [14]. Elements made with solutions in binders, when not exposed to severe temperature extremes, or to high relative humidities for extended intervals of time, will maintain their calibration and perform well for periods in excess of 1 year.

a. Dunmore Hygrometer

One of the most successful of the electric hygrometers of this type is that developed by Dunmore [14, 15]. In his early researches, Dunmore experimented with aqueous solutions on impervious insulators. It was not until he conceived the idea of combining a dilute aqueous solution of lithium chloride with an alcoholic solution of partially hydrolyzed polyvinyl acetate that he produced an excellent sensor that subsequently found wide application in meteorology and in industrial applications.

The early version of this sensor was made by coating a thin-walled aluminum tube with a polystyrene solution to form an insulating layer over the aluminum. In a later version, the aluminum tube was replaced with a polystyrene tube. A bifilar coil of No. 38 AWG bare palladium wire is wound on the tube; the two wires of the coil act as the electrodes. The unit is coated by dipping into a binder-electrolyte mixture of appropriate concentration and withdrawing at a constant rate. It is then aged under room conditions for 10 to 14 days, or inserted in an atmosphere of gently circulating air at 60 percent relative humidity at 26° C for 2 days. During the aging period, the resistance decreases and settles down to a final value.

By choosing the proper number of turns of wire, pitch, tube diameter, and concentration of lithium chloride, the resistance of the film can be made to vary over an appreciable range for a desired relative humidity range. Sensors have been designed that have the same resistance range, for increments of relative humidity of 16 percent; eight such sensors cover the range of relative humidities from 6 to 99 percent.

For radiosonde use, a single element has been developed that has a resistance range of 4,000 ohms to 6 megohms, as the relative humidity, at 20° C, goes from 100 to 15 percent. This element is a flat sheet of polystyrene, 3 x 11/16 x 1/32 in. with tin electrodes affixed to the long edges by sputtering. The element is coated, by dipping, in a binder and lithium chloride solution mixture. The calibration characteristics of such an element are shown in figure 5. At room temperature, with an air velocity of 768 ft/min parallel to the long edge of the element, the 63 percent speed of response is 3 to 6 sec and the 90 percent speed of

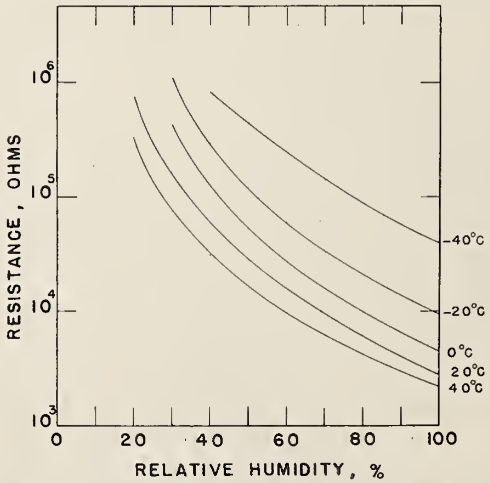

Figure 5. *Standard calibration curve of the narrow width, lithium chloride, electric hygrometer element used with the radiosonde.*

response is 25 to 35 sec. Temperature has a marked effect on the speed of response. At −20° C, the 63 percent speed of response, at air velocities of 525 ft/min is 50 to 150 sec [19]. Actually, the speed of response is an involved function of temperature, magnitude and direction of the relative humidity change, initial relative humidity, orientation of the element, and air velocity [19, 20].

The Dunmore hygrometer is manufactured commercially for industrial and scientific applications in both tubular and flat strip forms [21, 22, 23]. Units have been designed for special applications where small size is important [24, 25].

2.4. Electrolytic Solutions on Fibers and Fabrics

Most organic fibers are somewhat porous and have a capacity for absorbing liquids. When fibers are woven into fabrics, not only do the fibers absorb liquids, as they would singly, but the interstices between the fibers of the fabric can retain additional liquid. This ability of fibers and fabrics to absorb liquids lends itself readily to electric hygrometry, for an electrolytic solution can be used to impregnate these materials and so form humidity sensors. The fiber or fabric acts as a carrier for the solution. At the same time, it also inhibits the rapid equilibrium between ambient humidity and solution concentration, for as with the binder discussed above, water vapor has to diffuse through the capillaries within the fiber and the interstices between fibers.

It is possible to utilize such natural fibers as hair, cotton, silk, or such synthetic fibers as rayon, nylon, or saran [18]. Further, fabrics from these fibers or materials such as paper or asbestos cloth are suitable bases for treatment with electrolytic solutions [26, 27, 28, 30, 32, 33]. The electrolyte must be one that will not react with the base material. O'Sullivan [29] has been demonstrated that the conduction of cellulosic materials impregnated with salt is ionic.

a. Gregory Hygrometer

The Gregory hygrometer is an example of how an electric hygrometer of the salt-impregnated fabric type can be made and of how it may be expected to perform [30, 31, 32, 33]. In the version used by Ogden and Rees [33], a thin, grey, rectangular piece of cotton fabric, is boiled in a 1-percent solution of lithium chloride and allowed to air dry. This material is clamped, along each long edge by a thin piece of copper foil, leaving a narrow strip of exposed fabric ⅛×1 in. Contact and adhesion between the copper foil and the cloth is increased by using colloidal graphite as a bonding agent. The copper foil strips serve as electrodes. The weft threads are removed from the fabric to increase the porosity and improve the speed of response of the element. Copper wires are attached to the electrodes to function as leads, and both the wires and electrodes are insulated by coating with polystyrene cement. Figure 6 is a sketch of the unit.

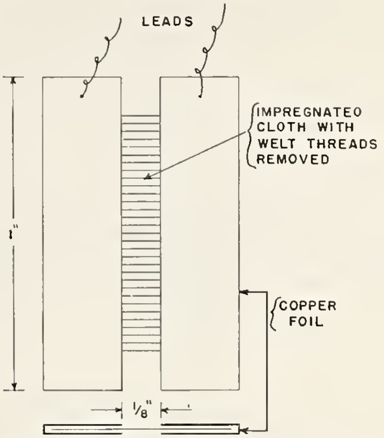

Figure 6. *Ogden and Rees version of the Gregory hygrometer.*
Cotton fabric impregnated with one percent lithium chloride solution. Copper foil electrodes.

A typical calibration curve for the hygrometer is shown in figure 7. There is a hysteresis effect and a temperature effect on the calibration. It is claimed that an accuracy of ±2 percent can be obtained from this hygrometer.

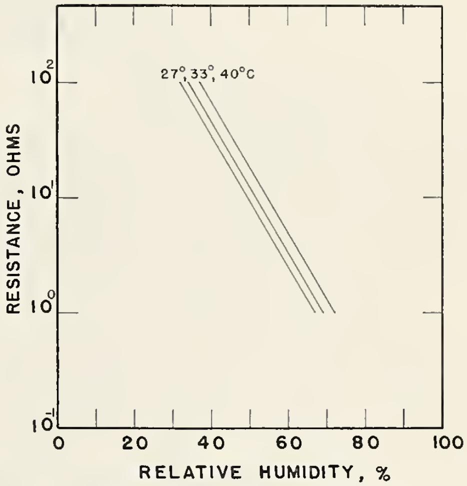

Figure 7. *Typical calibration of the Ogden and Rees version of the Gregory hygrometer.*

2.5. Electrolytic Solutions in Porous Ceramics

A porous ceramic can be impregnated with a salt solution to form a sensor in which the current flow is ionic. Such a sensor has been developed by White [34]. The core for this element is pure low-fired alumina. It is saturated with a solution of a salt such as lithium chloride or sodium dichromate. Two helical spiral coils of small diameter platinum wire are wound on the surface and so arranged that current can flow from coil to coil, in proportion to the resistivity of the impregnated core, and a heating current can be passed through one coil to raise the temperature of the core. The circuit is shown in figure 8. In this way, the temperature of the core can be adjusted to any desired value above ambient;

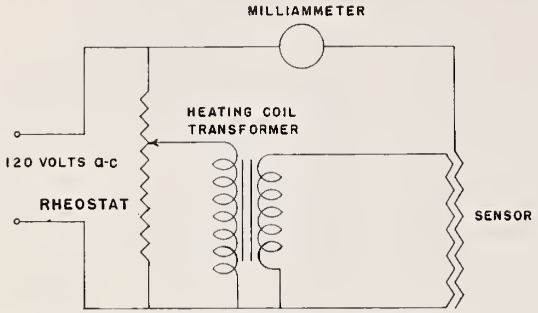

Figure 8. *Circuit diagram of the White hygrometer.*
Porous low-fired alumina core impregnated with salt solution.

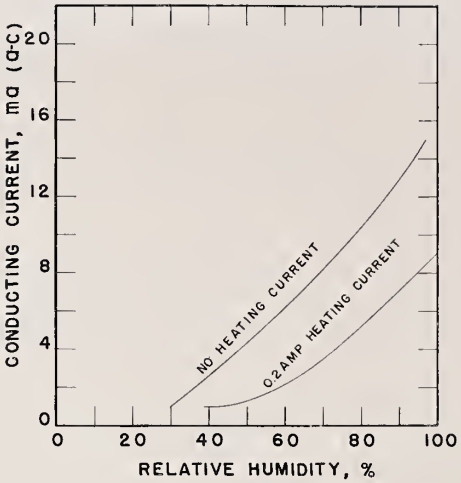

Figure 9. *Typical calibration curves for the White hygrometer.*

yet the sensor still functions in the usual fashion by a variation in resistance with relative humidity. Typical calibration curves, with and without heating current, are shown in figure 9. Within limits, variations in electrical characteristics from element to element, changes in ambient temperature, line voltage, and heater currents produce curves that are nearly parallel. This facilitates the use of slight changes in heater current to compensate for most of the variables encountered.

The speed of response of the sensor is a function of ambient temperature and relative humidity. For high humidities and high temperatures, it is several minutes; at temperatures around 0° C and relative humidities under 30 percent, it is 1 hour or even longer.

3. Surface Resistivity of Impervious Solids

3.1. General Theory

The surface resistivity of some impervious materials, in particular, electrical insulators such as glass, porcelain, and plastics, varies in a marked way with ambient relative humidity. Water vapor is adsorbed on the surface of these materials, and retained by physical bonding forces, forming a thin film whose thickness, and possibly continuity, is a function of the relative humidity. This film of moisture provides a leakage path for current flow. There probably are minute quantities of soluble salts or gases present on the surface of the insulator which contribute to the conductivity of the film. The net effect is that the surface resistivity may decrease six or more decades as the relative humidity of the surrounding air increases from 0 to 100 percent. Because the material has an impervious surface, little or no water vapor will penetrate or diffuse into the body. The water vapor that is sorbed remains on the surface. It is to be expected, therefore, that the attainment of equilibrium between adsorbed water vapor and ambient relative humidity will be relatively fast. Materials normally classified as impervious are seldom completely so; there is usually some diffusion of water vapor into or out of the interior. Diffusion is a relatively slow process. Thus, a material may exhibit an initial fast response to a change in relative humidity, but also the time for reaching final equilibrium may be prolonged by the slow diffusion of a small amount of vapor.

The magnitude of the surface resistivity of an insulator is very high. This requires the use of special measuring circuits and techniques. Provided one can measure the high resistances involved, impervious insulators form a class of electric hygrometer sensors that are especially useful where fast response is needed.

3.2. Nonporous Insulators

One of the first to propose the use of an impervious insulator as a moisture detector was Pionchon [35]. His device was a glass tube, with silvered electrodes. With a voltage impressed across the electrodes, a galvanometer was able to detect the flow of current when the detector was moved from a dry to a moist atmosphere. Curtis [36] and Field [37] investigated the surface sensitivity properties of a large variety of insulating materials and showed that the resistivity decreased through several orders of magnitude as the relative humidity increased from 0 to 100 percent. These studies indicated that some materials take hours or days to reach equilibrium, due to their porous structure. The laws of film formation on glazed surfaces appear to be logarithmic [38].

Lubach [39] and Polin [40] proposed hygrometers that use glass, porcelain, glass wool, hard rubber, and ceramics as moisture sensors. Dunmore [10, 11] attempted to use glass tubing, roughened by sandblasting or etching, and wound with a bifilar bare copper wire coil for electrodes, as a sensor. Although he found that he obtained usable indications from such a sensor, he discarded it in favor of the electrolytic solution. Edlefsen [41] proposed the use of glass wool, in a cell with electrodes, for measuring relative humidity. A hygrometer employing a glass wool cell as a detector now appears to be commercially available [42]. This instrument has a relative humidity range of 42 to 100 percent, a temperature range of −40° to 80° C, and a corresponding resistance range of 100 megohms to 40,000 ohms.

3.3. Salt Film

Consider a thin film of salt deposited on an insulator and exposed to a constant relative humidity. If the ambient relative humidity does not exceed the equilibrium relative humidity of a saturated solution of the salt, then the film will sorb only enough water vapor that can be held by physical bonding forces. The quantity of adsorbed water vapor will be a function of the ambient relative humidity. The resistance of the film will be a measure of the ambient relative humidity.

A sensor of this type has an upper limit equal to the equilibrium relative humidity of the saturated solution of its salt. Thus, if the sensor is to be exposed to the full range of relative humidities, the salt should have an equilibrium relative humidity that is as close to 100 percent as possible. This implies that the salt should be practically insoluble in water. Even though the salt may be insoluble in water, or the sensor never exposed to relative humidities equal to or greater than that of the saturated solution of the salt, it is probable that some molecules of the salt ionize in the adsorbed water vapor and therefore contribute to the measured conductivity of the surface film.

Salt films, used in the manner described above, have been proposed or developed as electric hygrometer sensors by McCulloch [43], Auwarter [44], and Wexler et al. [45]. Anderson [46] had used a bead of calcium chloride, containing two copper wire leads separated by a 1 mm gap as a moisture detector. In a dry atmosphere, the resistance was 30,000 ohms; in the presence of water vapor the resistance dropped to 200 ohms. Fiene [47] designed detectors made with fused salt. He utilized the increased conductivity of the detector, when it formed a saturated solution, to designate the ambient relative humidity. Both Anderson and Fiene relied on the pronounced change in the resistance of a soluble salt, as it went into solution, and in this respect their sensors differ from those of McCulloch, Auwater, or Wexler et al.

a. McCulloch Hygrometer

The McCulloch sensor [43] consists of a coating of beryllium fluoride applied to a Pyrex tube on which there is a bifilar coil that functions as electrodes. The electrodes, 0.002-in. diameter nickel wire, are wound on a ¾-in. diameter Pyrex tube. Each electrode has 10 turns of wire and the two electrodes are spaced ¾-in. apart. The tube is dipped in a boiling 3 percent aqueous solution of beryllium fluoride, dried, and baked at about 300° C. The calibration of this sensor is shown in figure 10. The resistance at 97 percent relative humidity is about 3×10^5 ohms and at 30 percent is about 10^{12} ohms.

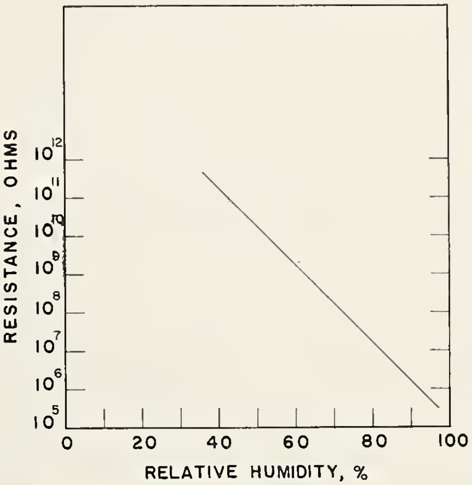

Figure 10. *Calibration curve of the McCulloch hygrometer.* Beryllium fluoride film on Pyrex.

b. Auwarter Hygrometer

In the Auwarter hygrometer [44], a thin film of a metallic fluoride, such as magnesium fluoride, aluminum fluoride or cryolite, is deposited, in vacuum, upon an impervious insulating material with spaced metallic electrodes. The film so formed has a thickness of the order of 4×10^{-4} to 10^{-5} in. The logarithm of the resistance, except at low relative humidities, is a linear function of the relative humidity. A speed of response, at room temperature, of less than 1 sec, is claimed.

c. Wexler et al. Hygrometer

In investigating the possibilities of improving the means for upper air humidity sensing with the radiosonde, Wexler and his associates [45] developed a fast responding hygrometer that uses, as the moisture sensitive material, a thin film of potassium metaphosphate deposited on an insulating base. In one form of the sensor, potassium metaphosphate is vacuum deposited on a glass slide, $3\times\frac{1}{2}\times\frac{1}{32}$ in., that contains parallel silver electrodes, $\frac{1}{8}$ in. wide, along the long edges. The thickness of the film is about 3 μin. Figure 11 shows the calibration curves of this sensor for the temperature range of −40° to +40° C. The logarithm of the resistance is approximately linear with relative humidity at constant temperature. The resistances vary from 4×10^4 to 10^{13} ohms. The manufacturing process is sufficiently well controlled so that elements, made in the same or in different batches, closely conform to a mean calibration curve. The standard deviation of an individual element from the mean calibration, over the −40° to 40° C range, is 2.9 percent relative humidity. The average hysteresis is 2.7 percent relative humidity. The polarization effect for reversed current loading (1-min cycles) is of the order of 0.3 percent relative humidity at the end of 2 hours; it is of the order of 2 percent for intermittent direct current loading (15 sec on, 45 sec off). The speed of response at room temperature, with an air velocity of 768 ft/min parallel to the long edge of the sensor, is about 0.1 to 0.4 sec for a 63 percent change in indication; at −20° C, with an air velocity of 800 ft/min, it is about 2 to 3½ sec.

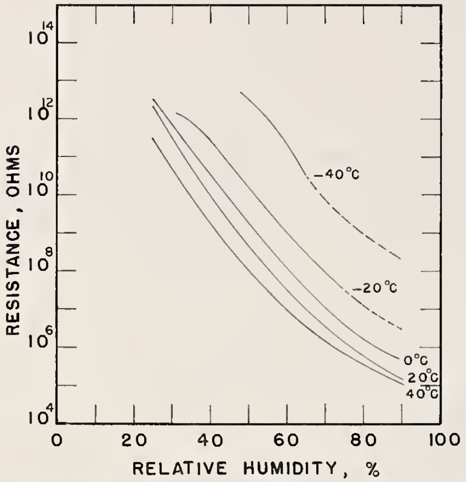

Figure 11. *Calibration of the fast responding potassium metaphosphate film hygrometer developed by Wexler et al.*

3.4. Oxide Film

a. Jason Hygrometer

Oxide layers can be formed on aluminum by anodization in acid electrolytes. These layers can be made porous in which state they offer a large surface area for the sorption of water vapor. As the water vapor is adsorbed or desorbed from the oxide film, there is a corresponding change both in its capacitance and resistance. This phenomenon has been utilized in the development of a capacitance-resistance hygrometer [48, 49, 50, 51, 52, 53].

Any method of anodizing which yields porous aluminum oxide films will produce sensitive elements; nonporous films show no great variation of capacitance or resistance with humidity change. After formation, aging occurs during which time the capacitance decreases and resistance increases until stabilization is attained. Elements formed in sulfuric acid still exhibit an appreciable sensitivity whereas those formed in other acids or by other processes appear to have lost their wide response to relative humidity.

Koller [53] was one of the first to propose the use of oxide films on metallic substances as humidity sensors. His element is made by electrolytically anodizing a plate of aluminum in sulfuric acid to form an oxide film 0.0004 in. thick. Gold leaf, 4 μin. thick, is placed over the oxide film and electrical leads are attached to both the leaf and the substrate.

A typical Jason sensor [49] is made by degreasing an aluminum rod, anodizing one end, and thoroughly washing off the electrolyte. The untreated surface is coated with an insulating layer which is made to overlay the oxide layer slightly. A thin porous conducting material is deposited over the oxide and extended over the insulation. This porous material may be a thin film of a colloidal suspension of carbon, or it may be a thin film of metal chemically or vacuum deposited. Wires are attached to the aluminum rod and porous conducting film, the rod and film being the electrodes of the element. The construction is shown in detail in figure 12.

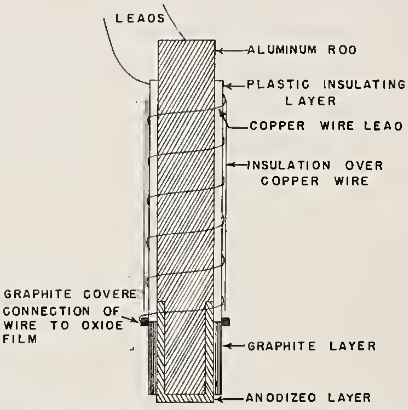

Figure 12. *Construction of the Jason hygrometer.*

The capacitance and resistance, as a function of relative humidity, are shown in the curves of figure 13. Cutting et al. [49] claim that the sensor is almost independent of temperature from 0° to 80° C. Underwood and Houslip [50] have found a pronounced temperature effect. With care in the construction, elements anodized simultaneously have the same calibration curve. At relative humidities of 90 percent or more, the response is slow and there is a small irreversible drift. This gives rise to positive hysteresis on returning to lower relative humidities. Prolonged exposure to saturation destroys the sensitivity of the element. Applied voltages greater than 80 percent of the formation voltage cause temporary breakdown of the oxide. Surface contamination by oil or grease interferes with proper performance.

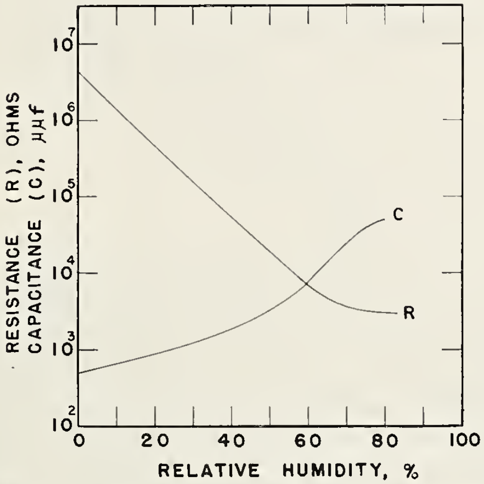

FIGURE 13. *Typical calibration of a Jason hygrometer.*
Aluminum oxide film on aluminum rod.

3.5. Ion Exchange Resins

A conventional ion exchange resin [54] consists of a high polymeric, cross-linked structure containing as an integral part of its structure polar groups of positive or negative charge (anion and cation exchangers, respectively). Associated with these polar groups are ions of opposite charge which are held by electrostatic forces to the fixed polar groups. One feature of such a resin is that it is hydrophilic. In the presence of water or water vapor, the electrostatically held ions become mobile, and, when a voltage is impressed across the resin, the ions are capable of electrolytic conduction. Materials such as cross-linked phenol formaldehyde, resorcinol formaldehyde, phenol furfural, cresol formaldehyde, xylenolformaldehyde, divinylbenzene-polystyrene copolymer, and similar high polymeric cross-linked plastics are capable of being made into ion exchange resins by suitable treatment with a variety of reagents including concentrated sulfuric acid, fuming sulfuric acid, sulfur trioxide and chlorosulfonic acid. As an example, polystyrene can be treated with sulfonic acid whereby the sulfonic radical is made an integral part of the structure whereas the hydrogen ion (anion) is bound to the radical by electrostatic forces. Any cation which will satisfy the condition that the resin be electrostatically neutral can take the place of, or exchange with, the hydrogen ion. Hence the name ion exchange resin.

a. Pope Hygrometer

An ion exchange resin can be adapted to humidity sensing, as demonstrated by Pope [55], for it sorbs water vapor from the ambient atmosphere and eventually reaches an equilibrium state with the surrounding relative humidity. Because such a resin is a highly porous material, water vapor will move through it by diffusion. Thus, if used in bulk form, an ion exchange resin would respond relatively slowly to changes in ambient humidity. However, rather than using it in bulk form, a thin layer is formed on the surface of, and integral with, the parent polymer. A base is chosen that is thermally stable and is a nonconductor. The surface is hygroscopic, insoluble in water, and electrically conductive. The principal difference between the base and the surface layer is that the latter contains polar constituents with electrostatically attached ions that have ion exchange properties. Electrodes can be attached to the surface of the resin to form the humidity sensor.

A typical hygrometer element is made from a rod of polystyrene which is submerged in concentrated sulfuric acid, at 100° C, using 0.5 percent, by weight, silver sulfate as a catalyst. The time of sulfonation may be varied from 1 to 60 min. depending on the conductivity desired at a given relative humidity. The greater the sulfonation time, the thicker the layer formed, and the slower the speed of response. After sulfonation, the rod is rinsed with water, boiled in sulfuric acid for 1 hour, rinsed again with distilled water, and air dried. Electrodes are added by painting with conductive metallic paint. Typical calibration curves, for elements made in this fashion, for different sulfonation times, are shown in figure 14. Figure 15 indicates the effect of temperature on the calibration.

Among the interesting characteristics of this type of hygrometer are the following: (a) the relative permanence of the sensitive surface layer when compared against films of electrolytic solution; (b) the ability of the element to operate at temperatures as high as 100° C; (c) the possibility of washing the surface with water or, perhaps, steam, if contamination interferes with the performance; and (d) the control of resistance range and speed of response by control of the sulfonation time, i. e., by control of the thickness of the porous layer of ion exchange resin.

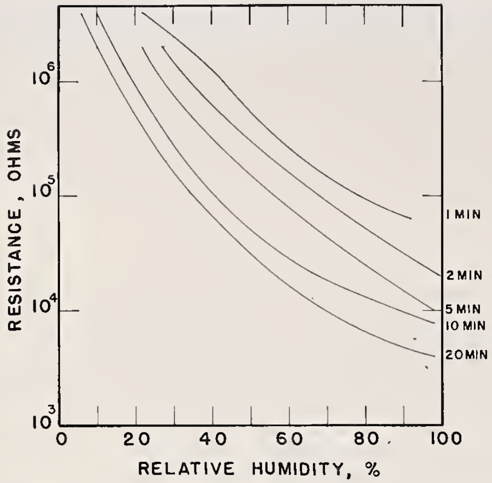

Figure 14. *Typical calibration, at 25° C, for the Pope hygrometer.*

Polystyrene base sulfonated for various times.

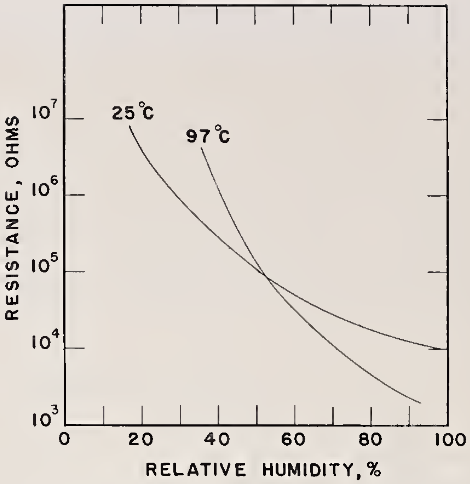

Figure 15. *Effect of temperature on the calibration of the Pope hygrometer.*

Polystyrene base sulfonated one hour.

4. Volume Resistivity of Porous Solids

4.1. General Theory

In a manner analogous to the use of the variation of the surface resistivity of impervious solid insulators with ambient relative humidity, the variations of the volume resistivity of some porous materials with ambient relative humidity can be utilized for humidity sensing. There are many substances that absorb water vapor, but relatively few that do so with sufficient reversibility and reproducibility [56, 57, 58]. Highly porous substances, as, for example, underfired clays, natural fibers, and textiles, have a high capacity for moisture absorption. Water vapor diffuses and permeates into the capillaries and pores of these substances, greatly affecting their volume resistivities. Unfortunately, the porous nature of these materials, which makes them so highly hygroscopic, often contributes undesirable characteristics that seriously detract from their usefulness as sensors. For one, the time involved for a porous material to reach equilibrium with any change in relative humidity is often excessively long. Then too, a porous material too often possesses hysteresis and drift. In spite of their shortcomings porous solids find some application as electric hygrometer elements.

4.2. Porous Insulating Materials

The variations in resistance of porous materials with relative humidity were first investigated because of their bearing on the insulating properties of dielectrics. Evershed [59], Curtis [36], and Kujirai [60] studied a large number of substances and determined that, in general, such materials decreased in resistivity by many orders of magnitude as the relative humidity increased from 0 to 100 percent. Further studies were made, not only on bulk insulating materials but also on textile materials and individual fibers [61, 62, 63, 64, 65, 66, 67]. The application of such materials to electric hygrometry was attempted in 1921 by Barr [68]. He made a sensor by gilding a glass tube, wrapping cotton around the tube, then winding gilt wire over the cotton. One model of this sensor has a resistance of 850 ohms at 90 percent relative humidity and 780,000 ohms at 33 percent relative humidity. The logarithm of the resistance is nearly linear with relative humidity. The lag is considerable. Parsons and Laws [69] used a piece of leatheroid wound around a metal cylinder; a bare metal wire is wound over the leatheroid and the resistance between it and the metal cylinder is used as an indication of ambient relative humidity. Burbridge and Alexander [70] devised hygrometers from both cotton and human hair. A layer of pure cotton wool, thin enough to be semitransparent, is placed between two electrodes in the form of a grid, as shown in figure 16. At constant temperature, the logarithm of the resistance is

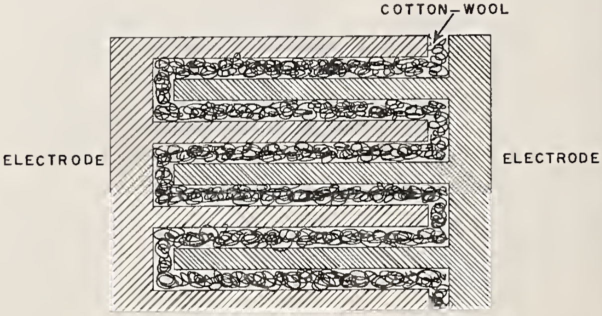

Figure 16. *Burbridge and Alexander cotton-wool hygrometer.*

linear with relative humidity. The resistance varies one decade for each 20 percent change in relative humidity. The lag is a function of the thickness of the layer; for one design of sensor, this is of the order of 5 to 6 min in air stirred by a fan. The hysteresis is about 2 percent. The hair hygrometer uses hair degreased by repeated extraction with alcohol. The logarithm of the resistance is nonlinear with relative humidity; the change in resistance is small in the 0 to 50 percent relative humidity range and greater at higher relative humidities. An alternate form of cotton sensor was proposed by Starkins [71]. Two separate lengths of cotton-covered copper bell wire are wound on a porcelain tube to form a bifilar coil. The copper wires act as electrodes and the cotton insulation changes its resistance with ambient relative humidity.

Both Cleveland [17] and Kersten [72] use hydrophilic gels as the humidity responsive material. Typical gels are gelatin, pectin and agar-agar. Films of gels are deposited on a rigid insulator or on clear photographic film containing electrodes.

Lichtgarn [73, 74] and others [75, 76, 77] have used underfired clays, sintered ceramics, and plaster of Paris. These are highly porous materials that are able to absorb relatively large amounts of water vapor. They can be fabricated in a diversity of shapes and forms. An attempt is usually made to devise an element that has as large a surface area, for a given volume, as practical. A sintered ceramic block 4×3×2 mm, is able to change in resistance from 1,000 megohms to 1 megohm for a relative humidity change of 10 to 95 percent [77].

5. Resistivity of Dimensionally-Variable Materials

5.1. General Theory

There is a class of electric hygrometer sensors that depends on dimensional changes to produce changes in resistance. Many materials change in length or volume or both as they absorb or desorb water vapor. The classic examples are hair, vegetable fibers, and wood. These materials are used in hygrometry to actuate mechanical systems that move pointers over dials for indicating relative humidity, or operate switches in humidity control systems. Materials, dimensionally-variable with relative humidity, may be coated or impregnated with conductive substances. The latter will expand or contract as the humidity sensitive materials expand or contract. By the proper choice of the conductive substance, a measurable change in resistance is achieved. Consider a film whose conductivity depends on the presence of discrete particles of carbon, metal dust, or other electronic (as opposed to ionic) conducting medium. As the film expands, the particles separate and the resistance increases; as the film contracts the reverse occurs. Dimensionally-variable humidity sensitive materials expand with increasing relative humidity and contract with decreasing relative humidity. A particle type of conducting film or conducting impregnation on such a material will therefore increase in resistance with increasing relative humidity and decrease in resistance with decreasing relative humidity. This behavior is the inverse of that observed with electrolytic-film sensors, surface-resistivity sensors, or volume-resistivity sensors. Now, in addition to the change in resistance due to the dimensional changes in the conducting film or impregnation, there is the resistance change in the humidity sensitive base material. Thus the resistance of this humidity sensor is made up of two parallel resistances. As one increases, the other decreases. Depending on the relative magnitudes of these two resistances, the measured resistance may be monotonic with relative humidity, or it may go through a maximum so that a single value of resistance may correspond to either of two relative humidities.

5.2. Carbon Element

Dimensionally-dependent resistance sensors were made by Welco [78] using, for hygroscopic materials, hair, cellophane, and paper and coating them with India ink. The cellophane and paper elements were 20 cm×1.25 cm whereas the hair element consisted of 27 segments in parallel, each 2.5 cm in length, degreased by boiling in ethyl ether. These sensors had limited humidity and resistance ranges.

Smith and Hoeflich [79] have described the development of a carbon film hygrometer element that uses a plastic binder as the material that is dimensionally variable with relative humidity. A polystyrene strip, 100 mm long, 18 mm wide, and 1.2 mm thick, serves as the blank on which the sensitive film is deposited. There are two metal (tin) electrodes along the long edges. The clear space between the electrodes is 11 mm. A mixture composed of 45 percent carbon, 32 percent hydroxyethyl cellulose, 16 percent polyoxy ethylene sorbitol, and 7 percent alkyl aryl polyether alcohol is sprayed on both sides of the blank. The hydroxyethyl cellulose functions as a binder. It changes its volume with relative humidity and in doing so, alters the relative positions of the conducting carbon particles. The polyoxy ethylene sorbitol is a humectant type plasticizer that modifies and controls the sensitivity of the element. The alkyl aryl polyether alcohol is a non-ionic dispersing agent which is needed to insure a uniform distribution of carbon in the film.

The calibration for a typical carbon film hygrometer element is shown in figure 17. The element has low sensitivity at low relative humidities. As the relative humidity increases the sensitivity increases. At relative humidities of 80 percent or

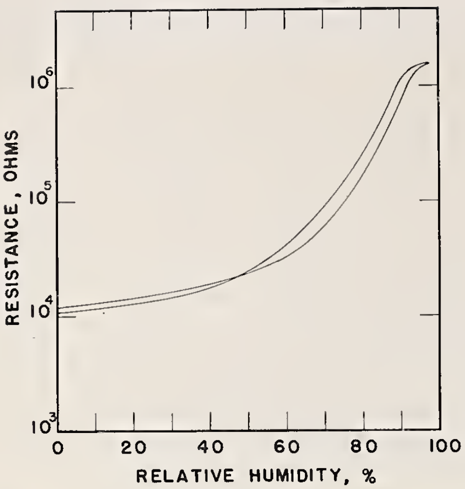

Figure 17. *Calibration curve for a typical carbon film sensor at temperatures between 0° and 40° C.*

above, there is a decided tendency for the calibration curve to have a "hump," that is, to undergo a reversal so that for a range of resistances, there are two values of relative humidity for each value of resistance. To avoid this "hump" requires the careful elimination of even small traces of ionic substances. Thus, in making elements of this type, deionized or freshly distilled water is used, the dispersing agent is cleaned by dialysis, and the binder is specifically prepared to be free of ionic content.

With this element, there is an average hysteresis of about 5 percent relative humidity, the hysteresis being more pronounced at lower relative humidities. There is relatively little polarization. This is due, possibly, to the fact that the mechanism of conduction is primarily electronic rather than electrolytic. The speed of response, at −20° to −30° C, for a 90 percent change in indication, is about 30 to 60 sec.

When the element is exposed to atmospheric air over a period of time, it tends to acquire impurities and to shift in calibration. For such long time exposures, a protective moisture-permeable envelope should be used. There is, of course, an accompanying large increase in lag, for now the moisture has to diffuse through the envelope.

6. Temperature-Controlled Saturated Salt Solutions

6.1. General Theory

Consider a saturated salt solution in a closed space. If equilibrium conditions prevail, the partial pressure of the water vapor in the space will be uniquely determined by the temperature, as the temperature of the solution is increased from its freezing point to its boiling point. At any given temperature, this partial pressure will be less than the saturation vapor pressure of pure water. Now let the saturated salt solution, at some given temperature, be exposed to an ambient atmosphere having a higher vapor pressure than the equilibrium vapor pressure of the saturated salt solution. Normally, there will be a net flow of vapor from the ambient atmosphere to the saturated salt solution, with a dilution of the latter until the vapor pressures are equal. On the other hand, if the temperature of the saturated salt solution be increased, a point will be reached where two vapor pressures will be equal whereas the solution will remain at the same concentration. A measurement of this temperature determines the ambient vapor pressure. Similarly, if the saturated solution, at some given temperature, is exposed to an ambient atmosphere with lower vapor pressure than the equilibrium value of the saturated salt solution, the temperature of the latter can be reduced until the two vapor pressures are equal, and a measurement of the solution temperature determines the vapor pressure. If there were some means for determining when the vapor pressures equalize it would be possible to use the temperature of the saturated salt solution as a hygrometric indicator.

The conductivity or resistance of a salt solution is a good indicator of its concentration. As the concentration increases or decreases, the resistance increases or decreases. Now, consider a saturated solution in which suitable electrodes are arranged so that its resistance may be measured. If the vapor pressure of this solution is in equilibrium with the ambient atmosphere, then the resistance remains constant; if the vapor pressure of the solution is greater than that of the ambient atmosphere, water vapor will evaporate and the resistance will increase; and conversely, if the vapor pressure of the solution is less than that of the ambient atmosphere, water vapor will be sorbed by the solution with a corresponding decrease in resistance. By adjusting the temperature of the saturated solution, a point will be reached at which the resistance remains constant. The temperature of the solution is now a measure of the ambient vapor pressure.

6.2. Dewcel

The temperature-controlled saturated solution principle has been successfully utilized in a form of hygrometer known as the "dewcel" [80]. A thermometer bulb (usually of the resistance or vapor pressure type) is surrounded by a glass wool wick impregnated with a saturated solution of lithium chloride. Two silver wire electrodes are wound on the outside of the wick to form a bifilar coil. Alternating current is impressed across the electrodes, through a ballast tube, as shown in the circuit diagram of figure 18. The flow of current through the solution generates enough heat to raise the temperature of the device. As the temperature increases, water evaporates

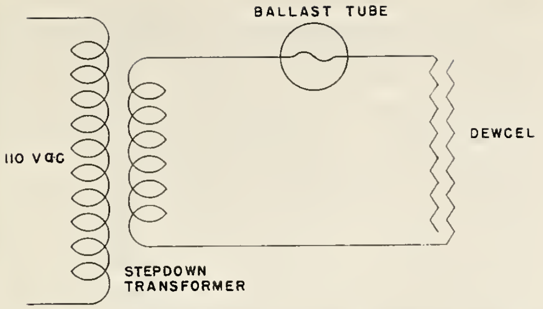

FIGURE 18. *Circuit diagram of the "dewcel" hygrometer.*

from the solution, the resistance increases, the current decreases, and the heat generated by the current flow decreases. The device then tends to cool because of the decrease in heat input. Thus, the application of current to the saturated solution provides automatic temperature control. The solution attains a temperature that corresponds to a constant resistance, which, of course, means that the solution and ambient vapor pressures are equal. The temperature, as measured by the thermometer, can be indicated or recorded.

Figure 19 is a plot of the vapor pressure, as a function of temperature, of pure water and of a saturated solution of lithium chloride. These curves show the relation between the measured dewcel temperature, the ambient vapor pressure and the ambient dewpoint. For example, if the equilibrium temperature of the dewcel is 51° C, then the ambient vapor pressure is 10 mm of Hg, as obtained from the lithium chloride curve. The dewpoint is read from the ordinate, by intersecting the water curve at the same vapor pressure. For the above case, the dewpoint is 11° C.

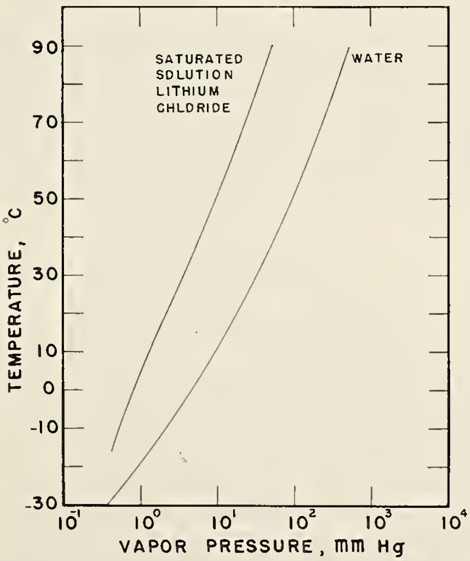

FIGURE 19. *Vapor pressure as a function of temperature, for water and a saturated solution of lithium chloride.*

There are several important considerations regarding the design and use of the dewcel. The speed of response of the unit depends primarily on the rate at which it can be heated or cooled. Hence, the thermal mass must be small if high lags are to be avoided. When the dewcel is exposed to high ambient vapor pressures, with no power across the electrodes or after a power failure, all the salt may dissolve to form a dilute solution. The wick must be of sufficient absorbency to retain the salt and to prevent any loss from dripping. However, if there is a loss of salt, it can be easily replenished without disturbing the fundamental calibration. After a period of inoperation, and particularly after applying fresh solution or exposure to high humidity, the resistance of the solution may be relatively low. On applying current to the electrodes, there may be a high enough flow of current to damage the structure. To avoid this, a ballast resistor is used in the input circuit as a current limiting device. The dewcel functions best in still, or near still air. High air speeds, say above 50 ft/min conducts too much heat away from the device, lowering the equilibrium temperature and shifting the calibration.

There is a limited range of humidities that the dewcel can measure at any ambient temperature. This range in terms of relative humidity, extends from 100 percent to the equilibrium value of the saturated salt. At room temperature, the range is 100 to 11 percent; at lower temperatures, the range narrows as indicated in the curve of figure 20. The lowest ambient temperature, at which the dewcel will operate is, theoretically the freezing point of a saturated solution of the salt, that is −80° C. Actually, the practical minimum temperature is about −29° C (−20° F).

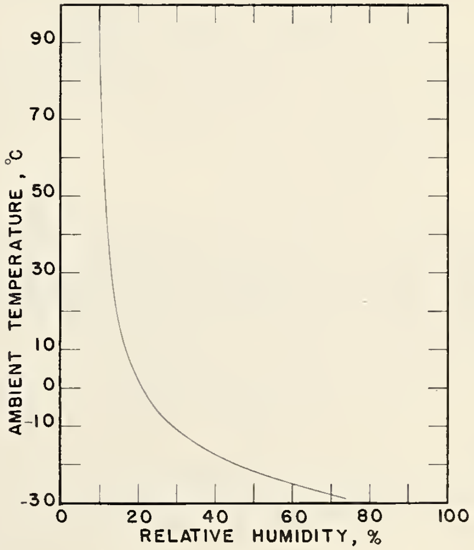

FIGURE 20. *Minimum relative humidity that can be measured with the "dewcel" at various ambient temperatures.*

The dewcel has been investigated for its applicability to meteorology [81]. The accuracy of the instrument is about ±3° F in dewpoint. The speed of response is 0.8 to 3.5 min for a 98 percent change in indication.

6.3. Wylie Hygrometer

A form of hygrometer has been proposed by Wylie [82] which differs from the dewcel in that a single crystal or a transparent group of crystals is used on which a thin film of saturated solution forms rather than a wick impregnated with a saturated salt solution. Further, whereas in the dewcel the solution can be temperature controlled only above ambient, in the Wylie hygrometer there is provision for both heating above and cooling below ambient.

One construction of the hygrometer consists of a small isothermal metal enclosure, about 1 in. long and 1 in. in diameter, in which a suitable ionic crystal is mounted between two chemically inert electrodes. The gas under test is forced through the enclosure after it has been brought to the enclosure temperature by passing through channels cut in the enclosure or by passing through an attached coil of metal tubing. The enclosure is cooled by passing a refrigerant through appropriate channels. Compressed carbon dioxide gas, expanding through a small needle valve, serves as a satisfactory refrigerant. An insulated coil of resistance wire, wound directly on the metal enclosure, is used to provide heat electrically. The temperature of the enclosure is measured with a resistance thermometer wound directly on it or with a directly attached thermocouple.

The conductivity of the crystal is measured on a deflecting type of instrument, or, by electronic means, is made to control the heating and cooling of the enclosure. Crystals of such salts as potassium sulfate or lithium chloride can be used. With potassium sulfate, the equilibrium relative humidity at room temperature is 97 percent; with lithium chloride it is 12 percent. With the former salt, cooling is generally necessary whereas with the latter, heating is usually required.

7. Electrolysis of Water

7.1. General Theory

Water is electrolyzed into gaseous oxygen and hydrogen by the application of a voltage in excess of the thermodynamic decomposition voltage (2 v). The mass of water electrolyzed is directly related to the electrolysis current by Faraday's law.

$$M_{\mathrm{H_2O}}=\frac{It}{96500}\times\frac{W_{\mathrm{H_2O}}}{Z} \tag{7}$$

where

$M_{\mathrm{H_2O}}$=mass of water, grams

I=electrolysis current, amperes

$W_{\mathrm{H_2O}}$=gram—molecular weight of water

Z=valance

t=time, seconds.

Consider, now, a mixture of air and water vapor and let the water vapor be electrolyzed completely. From the perfect gas laws and Amagat's law of partial volumes, it follows that

$$\frac{V_{\mathrm{H_2O}}}{V_{\mathrm{air}}}=\frac{M_{\mathrm{H_2O}}}{M_{\mathrm{air}}}\times\frac{W_{\mathrm{air}}}{W_{\mathrm{H_2O}}} \tag{8}$$

or

$$M_{\mathrm{H_2O}}=\frac{V_{\mathrm{H_2O}}}{V_{\mathrm{air}}}\times\frac{W_{\mathrm{H_2O}}}{W_{\mathrm{air}}}\times M_{\mathrm{air}} \tag{9}$$

where

M_{air}=mass of air, grams

$V_{\mathrm{H_2O}}$=partial volume of water vapor, cm^3

V_{air}=partial volume of air, cm^3

W_{air}=gram—molecular weight of air.

The current flow, during electrolysis is

$$I=\frac{96500}{18.016}\times 2\times\frac{V_{\mathrm{H_2O}}}{V_{\mathrm{air}}}\times\frac{W_{\mathrm{H_2O}}}{W_{\mathrm{air}}}\times\frac{M_{\mathrm{air}}}{t} \tag{10}$$

or

$$I=6660\,\frac{V_{\mathrm{H_2O}}}{V_{\mathrm{air}}}\times\frac{M_{\mathrm{air}}}{t}. \tag{11}$$

Thus, the current flow is directly proportional to the volume ratio of water vapor to air and to the mass flow of air. If the mass flow of air is kept constant, then the current flow is directly proportional to the volume ratio. If the volume ratio is expressed in parts of water vapor per million parts of air, equation (11) becomes

$$I=0.00666\ \mathrm{ppm}\times\frac{M_{\mathrm{air}}}{t}. \tag{12}$$

7.2. Keidel Hygrometer

Keidel [86] has described a hygrometer that operates by electrolyzing, continuously and quantitatively, the water vapor content of a water vapor-gas mixture. Figure 21 is a flow diagram of the instrument. A sample of water vapor and air enters the instrument, under pressure, and is divided into two parts. A constant mass flow of dry air is maintained in the electrolytic cell while the remainder of the sample is by-passed,

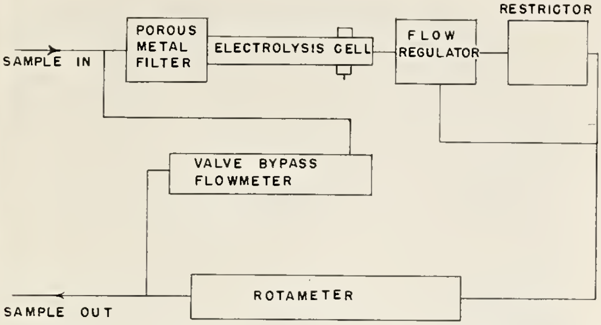

Figure 21. *Flow diagram of the electrolysis hygrometer.*

through a flowmeter, and exhausted at the outlet. The part of the sample that passes through the cell, then flows, in turn, through a pressure regulator, an adjustable restrictor, a flowmeter and finally exhausts at the outlet. The flow through the sample flowmeter is adjusted to 100 cm^3/min at a pressure of 760 mm of Hg and a temperature of 25° C. Under these conditions, the electrolysis current is 13.2 μa/ppm.

The electrolysis cell is a Teflon tube, the inside of which is coated with a thin, viscous film of partially hydrated phosphorous pentoxide. Two platinum wire electrodes are spirally wound on the inside of the Teflon tube in contact with the film. The film absorbs the water vapor from the sample gas. The application of a d-c potential across the electrodes electrolyzes the water and the resultant current is measured on a microammeter, or, if desired, recorded.

This instrument has full scale ranges of 10 to 1,000 ppm. It is claimed that the accuracy is 5 percent of the indication from 1 to 1,000 ppm. If the efficiency of electrolysis is 100 percent, then the accuracy is limited by the constancy of the mass flow of the air and performance of the electrical components. The speed of response, for a 63 percent change in indication, is about 1 min. in the increasing humidity direction and about 2 min in the decreasing direction. The response time varies with water vapor concentration, applied cell voltage, and film thickness.

Because the sample flow through the cell is controlled on a volumetric rather than a mass basis, and measured on a rotameter, there is a temperature effect. If the instrument is used at other than its design temperature, the correction is 0.3 percent per ° C.

8. Measuring Circuits

There are several simple circuits that are commonly used to measure the resistance of the sensor, or, a related parameter, such as current. The output of the circuit is displayed on a meter or a recorder, sometimes in the measured variable, but more often in units of relative humidity.

The d-c ohmmeter and the d-c Wheatstone bridge are two standard circuits for measuring resistance. They are not, however, well suited to electric hygrometry, for a preponderance of the better sensors are wholly or partly ionic conductors and so are subject to polarization. With d-c circuitry, even with small impressed voltages on the sensor, there is a significant error due to polarization. Except in specialized applications, d-c circuitry is to be avoided. The outstanding exception is the radiosonde where pulsating d-c is applied to the sensor. Because a radiosonde flight normally is of no more than 2 hours duration, the amount of polarization that occurs in this time can be tolerated.

Figure 22 is a diagram of a typical a-c circuit [14]. The transformer reduces the 110 input voltage to a desired lower value, sometimes to 100 v although it may be much lower. The limiting resistor prevents the current through the sensor from exceeding a maximum value. With Dunmore sensors, the current is limited, preferably, to 100 μa. The lower the maximum current, the greater the life of the sensor. A rectifier converts the alternating current to direct current so that it can be measured on a d-c microammeter. Alternatively, or in addition, a dropping resistor can be used in the d-c part of the circuit and the voltage drop across it recorded on a strip chart potentiometer. With this circuit, there is a loss in sensitivity at both low and high resistances. A typical sensor calibration curve, in terms of indicated current, is shown in figure 23. Dunmore elements are often used in sets of eight, each covering a relative humidity span of about 16 percent, the set covering about 7 to 98 percent. The salt solution concentration of each element is so chosen that the same resistance range is encompassed by each element for its limited relative humidity span. Thus, the calibrations, with the same circuit, will appear as parallel displaced curves of the same shape as in figure 23.

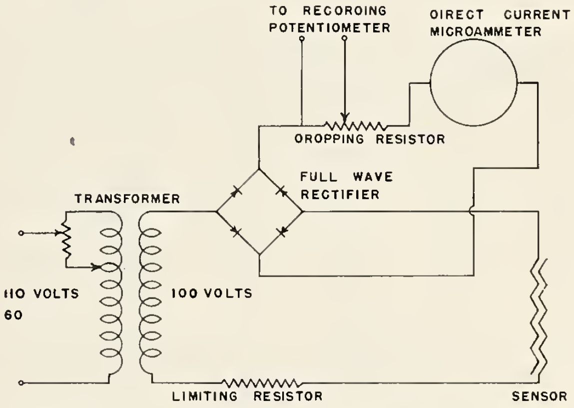

Figure 22. *Alternating current measuring circuit.*

It is occasionally advantageous to make the entire relative humidity range correspond to the

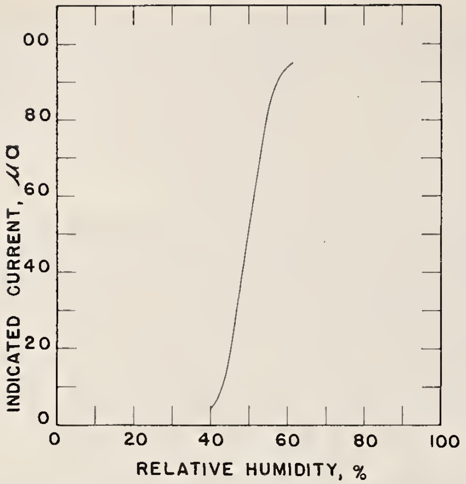

Figure 23. *Typical calibration of a limited range Dunmore sensor when used with the a-c measuring circuit of figure 22.*

range of the indicating and recording instrument. Dunmore [14] has described an arrangement of sensors and resistors, as shown in figure 24, which accomplishes this. A set of five sensors, with appropriate resistors, will produce a calibration curve, in terms of resistance versus relative humidity, of the type shown in figure 25. At high relative humidities the resistance of sensors B, C, D, and E are very low, but resistors R_2, R_3, R_4, and R_5 prevent any significant current flow; sensor A and resistor R_1 control. At low relative humidities the resistances of sensors A, B, C, and D are sufficiently high so that sensor E, in combination with resistors R_1, R_2, R_3, R_4, and R_5 control. At intermediate relative humidities, sensors B, C, and D control in a like manner.

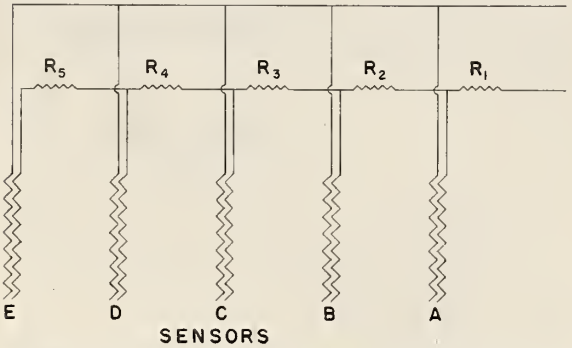

Figure 24. *Arrangement of limited range sensors and resistors to cover full relative humidity range.*

A standard a-c Wheatstone bridge circuit can be employed for the measurement of sensor resistance. Weaver [6] has used several different variants of the a-c bridge with his sensor. For extremely high resistances, say 10^6 ohms and greater, simple a-c circuits, such as that of figure 22, are unsuitable because the sensor capacitance becomes the controlling factor, limiting the upper value of the resistance that can be measured. The standard d-c circuits are often unsuitable too because the high voltage required to give a measurable current flow results in polarization. In addition, to cover the many decades of resistance of some sensors a range switch is necessary. Garfinkel [83] has devised an interesting electrometer circuit, figure 26, which impresses about 1.25 v on the sensor, limits the current flow to about 100 μa, and yields an output that is proportional to the logarithm of the sensor resistance. Thus, eight decades of resistance can be indicated on the scale of an output meter or recorder without range switching. There is also a provision for adjusting the zero and range.

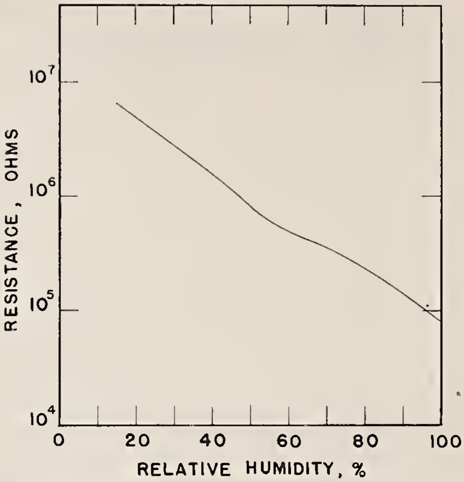

Figure 25. *Typical calibration curve at 24° C of five limited range Dunmore elements arranged as shown in figure 24.*

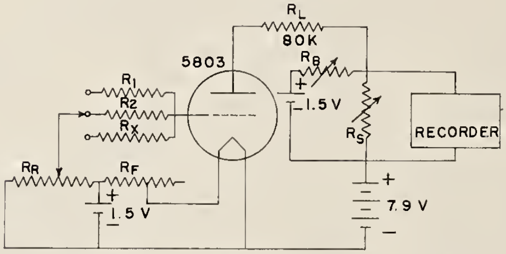

Figure 26. *Garfinkel electrometer circuit.*

R_1 and R_2 are precision resistors used for calibration. R_F and/or R_R are used to adjust or compensate for changes or drifts in calibration. R_X is the unknown (electric hygrometer sensor). R_S and R_R are adjusted so that the full range of the recorder corresponds to the full range of R_X.

There are other circuits and schemes that may be used with electric hygrometer sensors, but the above ones indicate some of the main types. Because sensors usually have a temperature coefficient, circuits have been designed to automatically correct or compensate for this [84, 85].

9. Discussion

There are certain advantageous features in the use of electric hygrometry in meteorology. The sensor is small and relatively inexpensive, although the cost of the measuring circuit may not necessarily be low. The indications are in terms of electrical quantities so that remote indicating or recording is feasible. On the other hand, except for the temperature-controlled saturated solution and water electrolysis types, the electric hygrometer is an empirical device that requires a calibration. Furthermore, it usually has an appreciable temperature coefficient so that the calibration must cover a range of temperatures and, with each measurement with the hygrometer, there must be a temperature measurement. To a limited extent, the hygrometer circuit can be designed to compensate for temperature, obviating the necessity of a direct temperature measurement.

Several other factors influence the performance of the electric hygrometer. Polarization introduces an error, but this can be avoided by the use of a-c circuitry. Exposure to saturated air, fog or clouds, or wetting as by rain, is usually deleterious to a sensor. Contamination of the sensitive surface, especially by ionizable materials, will shift the calibration if not ruin the sensor.

These are some of the gross characteristics of the electric hygrometer that must be assessed for a given application. Within its limitations, the electric hygrometer is an extremely useful instrument.

Among the various sensors, there are relative advantages and disadvantages. The Weaver water vapor indicator, for example, is an excellent instrument for measuring very low humidities, but is not too well suited to continuous recording. It is best used in situations where discrete measurements are to be made. It requires an operator. Those sensors that use an aqueous solution, without binder, on an impervious surface are inherently faster in response than the binder type or the impregnated fiber, fabric, or ceramic. When high speed of response is required, the former sensors are the logical choice of the electrolytic solution class. However, the stability and life of the former may be expected to be less than the latter.

Of all the sensors, those that depend on surface adsorption will probably have the fastest response. The dry salt films appear to be best in this regard. They have one major limitation. It is their high resistance. To measure the high resistances requires special circuitry and handling. The oxide film sensor, as in the Jason hygrometer, has a more reasonable resistance range, but it has such drawbacks as an upper relative humidity limit, hysteresis, and loss of sensitivity after extended exposure to high humidity.

Sensors whose function is based on volume resistivity tend to be very sluggish in response, to exhibit hysteresis and drift. They can usually be made to have any desired resistance range.

The carbon element is difficult to make without a high relative humidity "hump". Because it conducts electronically, rather than ionically, it is free of polarization. It appears to be faster in response than the lithium chloride hygrometer and to have less of a temperature coefficient.

With all these sensors, the performance at low temperatures is related to the lag. With decreasing temperature, the lag increases exponentially. Sensors which will adequately respond at normal temperatures may become so sluggish at low temperatures that their indications have little value. Elements through which water vapor diffuses, must be made very thin in cross section to reduce their inherently high lag; even then, the speed of response may be too slow for these elements to be of practical value in meteorology. Surface resistivity sensors have an obvious advantage here, for they depend on surface adsorption rather than volume adsorption and diffusion. They, too, slow down at low temperatures, probably because there is some volume adsorption accompanying the surface adsorption.

The hygrometers using a temperature controlled saturated salt solution or a water electrolysis cell are based on quantitative laws. The latter is capable of measuring very low moisture contents and so may be adaptable to upper air or arctic meteorology.

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THE NATIONAL BUREAU OF STANDARDS

The scope of activities of the National Bureau of Standards at its headquarters in Washington, D. C., and its major field laboratories in Boulder, Colorado, is suggested in the following listing of the divisions and sections engaged in technical work. In general, each section carries out specialized research, development, and engineering in the field indicated by its title. A brief description of the activities, and of the resultant publications, appears on the inside front cover.

WASHINGTON, D. C.

Electricity and Electronics. Resistance and Reactance. Electron Devices. Electrical Instruments. Magnetic Measurements. Dielectrics. Engineering Electronics. Electronic Instrumentation. Electrochemistry.

Optics and Metrology. Photometry and Colorimetry. Optical Instruments. Photographic Technology. Length. Engineering Metrology.

Heat and Power. Temperature Physics. Thermodynamics. Cryogenic Physics. Rheology. Engine Fuels. Free Radicals Research.

Atomic and Radiation Physics. Spectroscopy. Radiometry. Mass Spectrometry. Solid State Physics. Electron Physics. Atomic Physics. Neutron Physics. Nuclear Physics. Radioactivity. X-rays. Betatron. Nucleonic Instrumentation. Radiological Equipment. AEC Radiation Instruments.

Chemistry. Organic Coatings. Surface Chemistry. Organic Chemistry. Analytical Chemistry. Inorganic Chemistry. Electrodeposition. Gas Chemistry. Physical Chemistry. Thermochemistry. Spectrochemistry. Pure Substances.

Mechanics. Sound. Mechanical Instruments. Fluid Mechanics. Engineering Mechanics. Mass and Scale. Capacity, Density, and Fluid Meters. Combustion Controls.

Organic and Fibrous Materials. Rubber. Textiles. Paper. Leather. Testing and Specifications. Polymer Structure. Plastic. Dental Research.

Metallurgy. Thermal Metallurgy. Chemical Metallurgy. Mechanical Metallurgy. Corrosion. Metal Physics.

Mineral Products. Engineering Ceramics. Glass. Refractories. Enameled Metals. Concreting Materials. Constitution and Microstructure.

Building Technology. Structural Engineering. Fire Protection. Air Conditioning, Heating, and Refrigeration. Floor, Roof, and Wall Coverings. Codes and Specifications. Heat Transfer.

Applied Mathematics. Numerical Analysis. Computation. Statistical Engineering. Mathematical Physics.

Data Processing Systems. SEAC Engineering Group. Components and Techniques. Digital Circuitry. Digital Systems. Analog Systems. Application Engineering.

● Office of Basic Instrumentation ● Office of Weights and Measures

BOULDER, COLORADO

Cryogenic Engineering. Cryogenic Equipment. Cryogenic Processes. Properties of Materials. Gas Liquefaction.

Radio Propagation Physics. Upper Atmosphere Research. Ionospheric Research. Regular Propagation Services. Sun-Earth Relationships.

Radio Propagation Engineering. Data Reduction Instrumentation. Modulation Systems. Navigation Systems. Radio Noise. Tropospheric Measurements. Tropospheric Analysis. Radio Systems Application Engineering.

Radio Standards. High Frequency Electrical Standards. Radio Broadcast Service. High Frequency Impedance Standards. Calibration Center. Microwave Physics. Microwave Circuit Standards.


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