

# Evaporated-Film Electric Hygrometer Elements<sup>1</sup>

Frank E. Jones

(February 14, 1962)

[This paper reviews the development at the National Bureau of Standards of an evaporated thin film electric hygrometer element and presents experimental data to illustrate characteristics of the element. These characteristics are explained, at least in part, in terms of physical principles, and especially with reference to the physical adsorption process.

The applicability of the evaporated thin film to upper air humidity sounding is discussed. The effects of such variables as film thickness, substrate temperature, and heat treatment in the film production processes on the characteristics of the hygrometer element are illustrated.] Of the fourteen compounds thus far investigated as the thin film material, results for barium fluoride, potassium metaphosphate, cerous fluoride, and lead iodide films are presented. Lead iodide films with electrodes deposited over the films are of particular interest due to the relative stability of the calibration with storage and the small temperature coefficient of electrical resistance. A plot of an upper air humidity sounding obtained with a barium fluoride element, indicating the rapid response and the high sensitivity of the element under flight conditions, is included.

## 1. Introduction

In upper air humidity sounding using the balloon-borne radiosonde there has been a need for an electric hygrometer element (a device which, through the variation of some electrical quantity such as resistance, is used to determine the moisture content in a gas sample) with a response sufficiently rapid to permit the accurate determination of atmospheric moisture distribution, especially where steep gradients or discontinuities exist. The approach at the National Bureau of Standards in developing such an element has been to experiment with materials which interact with water vapor mainly by physical adsorption, with its characteristic rapid rates and reversibility.

It is well known that the surface electrical conductivity of many materials varies with adsorption of water vapor. This property can be used to measure relative humidity. A plot of surface electrical conductivity against relative humidity at constant temperature is related to an adsorption isotherm since the conductivity has been found to depend upon the amount of water vapor adsorbed. A family of plots of electrical resistance against relative humidity at various temperatures for a solid adsorbent serves as a calibration for a device operating on the above principles. The thin film with its short diffusion paths is obviously an advantageous form in which to utilize a solid adsorbent for an application in which rapid response of some variable to the adsorption and desorption of a gas or vapor is desired.

To aid in the selection of humidity-sensitive film materials, consideration was given to such properties as the polarizabilities (the magnitudes of electric dipole moments induced by unit electric field) of

the constituents of the material; vapor pressure, decomposition temperature, ease of evaporation, and adhesion of the material to an insulating substrate; structure and stability of the deposited film, porosity of the film, and solubility of the film material in water; and the expected electrical resistance-relative humidity characteristics of the resulting device. On the basis of these properties, approximately 20 compounds were selected for experimentation. Potassium metaphosphate, strontium fluoride, strontium sulfate, cuprous chloride, barium fluoride [1],<sup>2</sup> cerous fluoride, didymium fluoride [2], lanthanum fluoride, neodymium fluoride, lead iodide, silver iodide, thallium iodide, cesium iodide, and cadmium iodide films have thus far been investigated.

## 2. Element Design

The film-type hygrometer element consists of the humidity-sensitive film, an insulating substrate on which it is deposited, and electrodes between which the resistance can be measured or otherwise utilized in an electrical circuit. The substrate material used in most of this work was microscope slide cover glass. The electrodes used in the potassium metaphosphate element [3] and the early work on some of the other materials were parallel strips of silver paint fired onto the glass. Due to the high electrical resistivities of elements of this type, especially at low relative humidities, closely spaced electrodes are needed to lower the resistance [4]. A sketch of an element and examples of various electrode configurations are shown in figure 1. The humidity-sensitive films are deposited over the electrodes in most cases, but evaporated film electrodes may be deposited over the films, and in later work this was done with significantly different results, to be discussed later.

<sup>1</sup> Sponsored by Bureau of Naval Weapons, Navy Department.

<sup>2</sup> Figures in brackets indicate the literature references at the end of this paper.

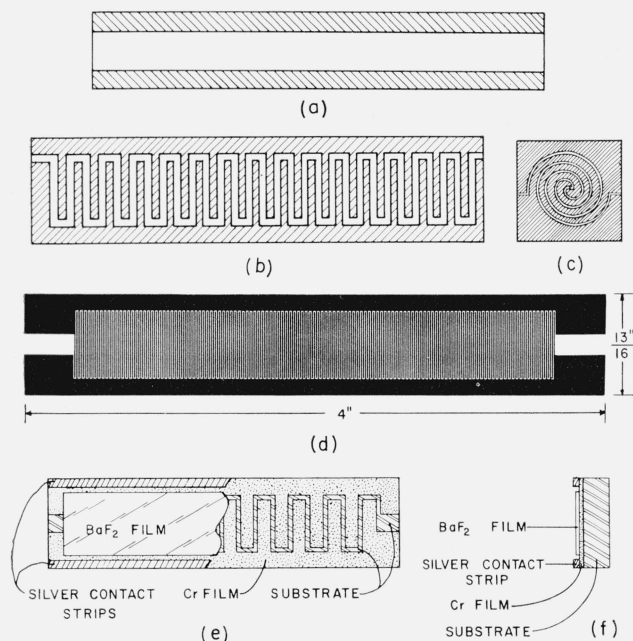


FIGURE 1. Examples of electrode configuration and element construction.

(a) Parallel strip electrodes. (b) Intermeshing-comb electrodes. (c) Spiral configuration [3]. (d) Fine-line intermeshing-comb electrode pattern (black area represents electrode area). (e) Sketch of top view of typical element. (f) Sketch of side view of typical element.

### 3. Evaporation Techniques and Procedures

Evaporated thin films are produced by thermal evaporation or sublimation in an evacuated chamber. The vapor deposits on substrates positioned in the chamber thereby forming the thin films. The conditions existing in the vacuum chamber before, during, and after the evaporation influence the initial structure and physical properties of the deposited films. Some of the influencing parameters and conditions which can be controlled or at least measured throughout the film production process and subsequent treatment are as follows: Residual pressure in the evaporator, composition of the residual gas in the evaporator, the nature and cleanliness of the substrate, the temperature of the substrate during the deposition, the heat treatment of the film and substrate after the deposition, the temperature of the evaporating source, the source-to-substrate distance, the angle between the evaporated "beam" and the substrate, the geometry of the source and of the support on which the substrates are mounted, the duration of the evaporation, the nature and number of nuclei or centers of nucleation on the substrate, and the thickness of the deposited film. Some of these conditions were controlled while others were measured during the deposition of the various substances.

The glass substrates are cleaned by conventional methods, such as a detergent-and-water wash followed by rinses in distilled water and in isopropyl alcohol and by vapor degreasing in an isopropyl alcohol degreaser. In the vacuum chamber, immediately before deposition of the film, a glow dis-

charge further cleans the substrates by removing adsorbed gases. Uniform film thickness for a batch of elements produced in the same evaporation is obtained by placing the substrates on a hemispherical rack with the source located on the same sphere, considering the evaporating source to approximate a "surface source" [5]. Effects of the variation of some of the other evaporation parameters will be illustrated later.

## 4. Characteristics of the Hygrometer Elements

### 4.1. Calibration

The resistance of the elements decreases with increasing relative humidity and, therefore, with the amount of water adsorbed on the humidity-sensitive film. Plots of logarithm of element resistance against known relative humidity at various temperatures are referred to as element "calibration curves." If mean calibration curves for groups of elements made under the same evaporation conditions are plotted, these curves may be used for these elements individually and for elements subsequently produced under the same conditions. Room temperature calibration curves for potassium metaphosphate, barium fluoride, cerous fluoride, and lead iodide elements are shown in figure 2.

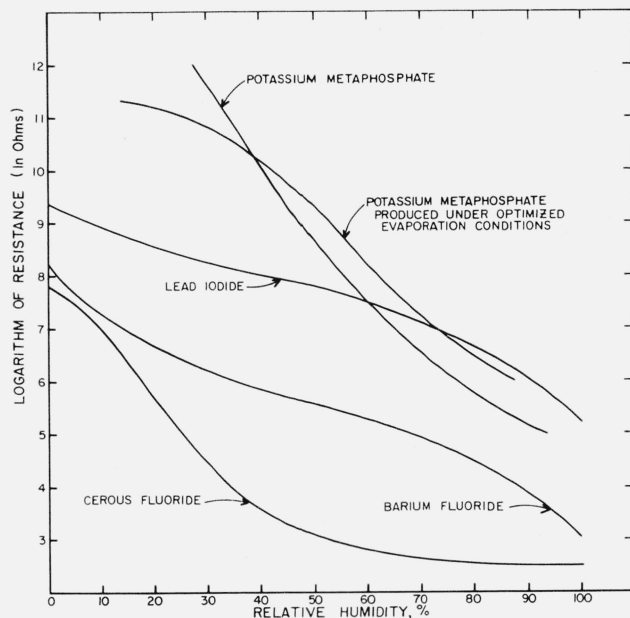


FIGURE 2. Room temperature calibration curves for various thin film elements.

The calibration curves are displaced vertically toward higher resistances at lower temperatures. The families of curves for potassium metaphosphate and barium fluoride elements over a temperature range of 40 to  $-40^{\circ}\text{C}$  are shown in figure 3. Each calibration is valid only for elements produced

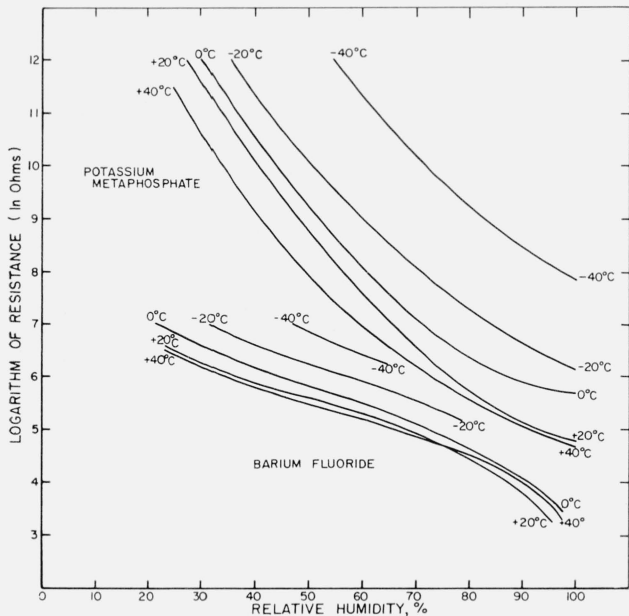


FIGURE 3. Calibration curves for potassium metaphosphate and barium fluoride thin film elements in the temperature range  $+40$  to  $-40$  °C.

with specified evaporation conditions and for a specified electrode configuration and film thickness. The range of resistance for the potassium metaphosphate element is from about  $4 \times 10^4$  to  $10^{13}$  ohms at room temperature and from about  $10^8$  to  $10^{15}$  ohms at  $-40$  °C. By optimizing the evaporation conditions, a potassium metaphosphate element can be produced with a range of from about  $10^6$  to  $10^{12}$  ohms at room temperature. These ranges pertain to elements with parallel strip electrodes, whereas the magnitude of the element resistance could be reduced by approximately  $10^3$  by the use of a closely spaced intermeshing-comb electrode configuration. The resistance range for barium fluoride elements with closely spaced electrodes is from about  $10^3$  to  $10^8$  ohms at room temperature. At  $-40$  °C, the range is from about  $10^4$  to  $10^{10}$  ohms. The effects of evaporation conditions on the room temperature calibration of potassium metaphosphate elements are illustrated in figure 4.

#### 4.2. Temperature Coefficient

It might be assumed that the negative temperature coefficient of resistance (that is, the increase in resistance with decreasing temperature) is in part due to two effects, namely, increased physical adsorption at lower temperatures, and the temperature dependence of the transport of current carriers through the film to the electrodes. In addition to the above effects, there are also other effects at the film-electrode, film-substrate, and electrode-substrate interfaces, and at the film surface. Calibrations for lead iodide and barium fluoride elements, with electrodes over or under the film at room temperature and at  $-30$  °C, are shown, respectively, in

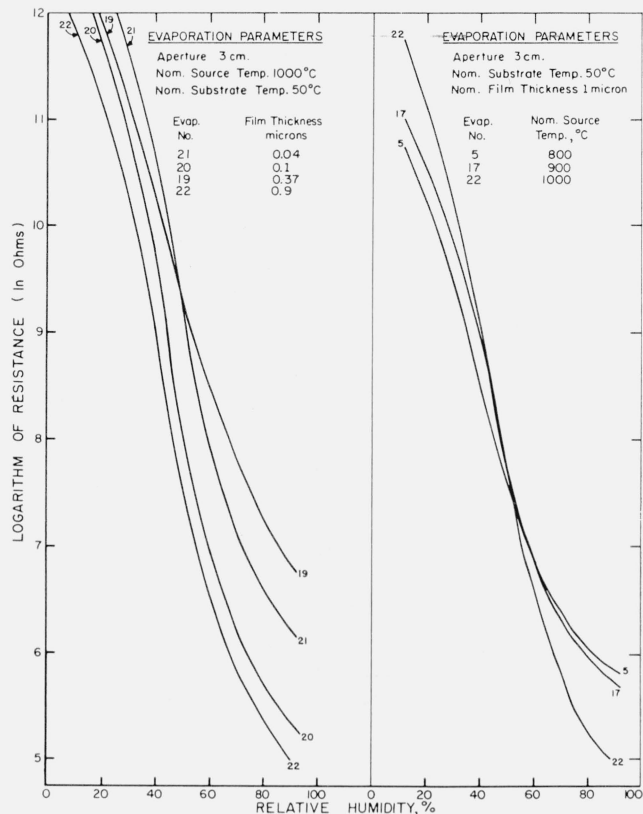


FIGURE 4. Examples of the effects of evaporation parameters on the room temperature calibration curves of potassium metaphosphate thin film elements.

"Aperture" refers to the diameter of a circular hole, in a baffle, delineating the evaporation source.

figures 5 and 6. The results indicate that in general the temperature coefficient of resistance is smaller for elements with electrodes over the film. This suggests the interesting possibility of producing an element with a greatly decreased temperature coefficient of resistance. Such an element would have the following advantages: A single calibration for the entire temperature range; lower resistance at lower temperatures, thus reducing the difficulty of resistance measurement; some latitude for electrode placement and dimensions; some latitude for decreased element size; and some latitude for element shape.

#### 4.3. Analogy With Physical Adsorption

Plots of logarithm of conductance against relative humidity for the potassium metaphosphate element and the barium fluoride element resemble typical adsorption isotherms [6], "Type V" for potassium metaphosphate and "Type II" for barium fluoride, as illustrated in figure 7. These two isotherms are believed to represent multimolecular adsorption (adsorption of more than one layer of water at the high relative pressures) and appear only in vapor (as differentiated from gas) adsorption [7]. It is interesting to note that these two isotherms are

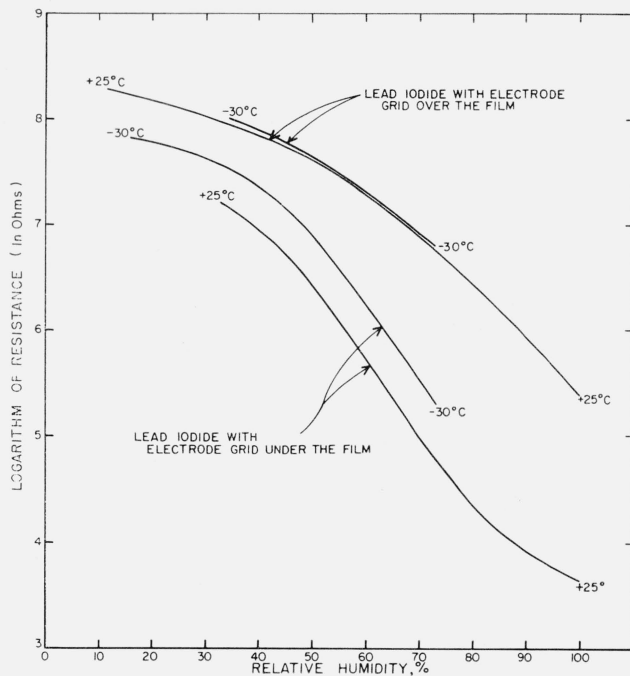


FIGURE 5. Example of the reduction of the temperature coefficient of resistance accomplished by placing the electrodes over the lead iodide film rather than under.

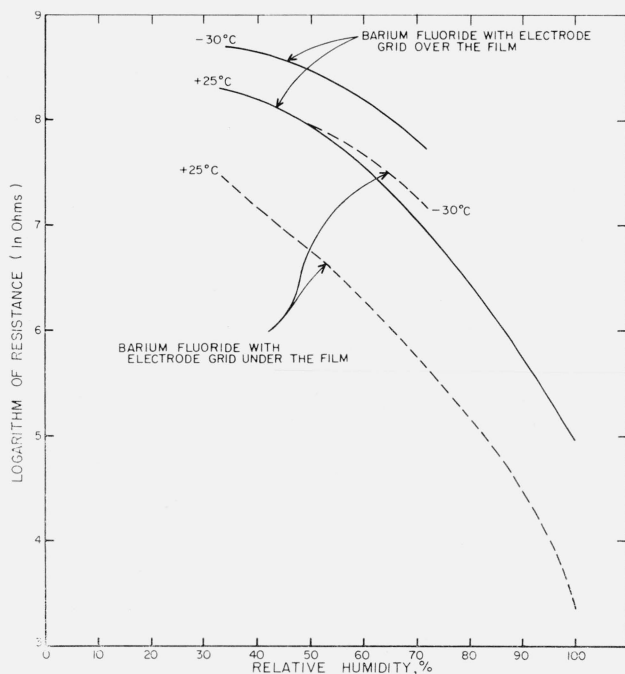


FIGURE 6. Example of the reduction of the temperature coefficient of resistance accomplished by placing the electrodes over the barium fluoride film rather than under.

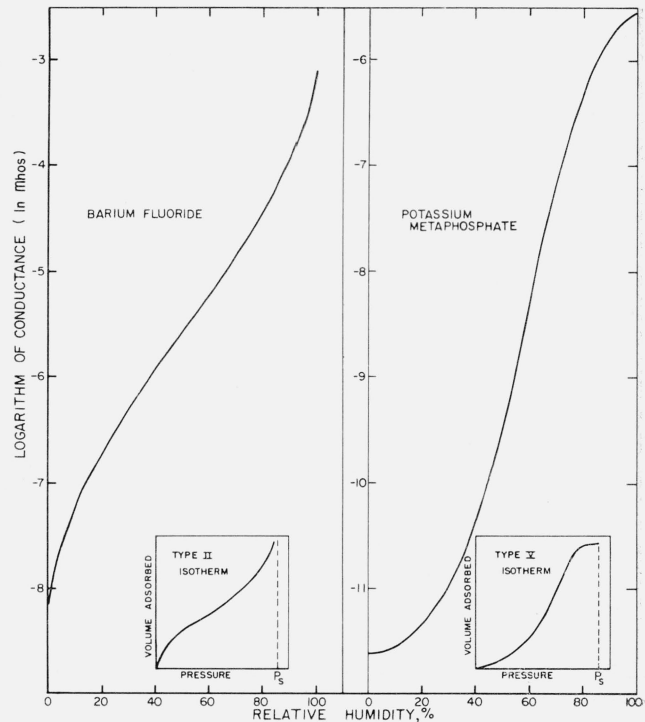


FIGURE 7. Illustration of the similarity between the shapes of plots of logarithm of thin film element conductance against relative humidity and the shapes of typical adsorption isotherm types.

typical of water vapor adsorption, Type II on hydrated portland cement and Type V on coconut charcoal [7]. This behavior is compatible with the physical adsorption process taking place on the film-type hygrometer element and suggests the desirability of performing physical adsorption measurements on the film materials to determine the adsorption isotherms and to correlate these isotherms with conductances (therefore, conductivities) determined under the same conditions.

#### 4.4 Hysteresis

Calibration curves are established by exposing the elements to a cycle of relative humidities. A plot of the logarithm of resistance for an individual element against relative humidity for the cycle is a hysteresis loop. On the branch of the loop representing increasing relative humidity, the resistance is higher than on the decreasing branch at the same relative humidity. The difference in indicated relative humidity between the two branches of the loop is taken as a measure of hysteresis. For the potassium metaphosphate element, the average hysteresis was approximately 3 percent relative humidity in the temperature range 0 to 40 °C; for the barium fluoride element, the median of the hysteresis values was approximately 1.5 percent relative humidity in the temperature range 40 °C to -40 °C. Humidity cycling tends to reduce hysteresis. With barium fluoride elements, expo-

sure to six cycles between the extremes of humidity at the calibration temperature, previous to the calibration cycle, reduces hysteresis significantly.

Hysteresis, both reversible and nonreproducible (nonreproducible if a different curve results from a repetition of the cycle) in the physical adsorption process has been studied by many investigators and several theories have been advanced [6]. Hysteresis in physical adsorption has been attributed to interference in multilayer formation due to porous structure of the adsorbent. Hysteresis of the hygrometer elements is nonreproducible. Humidity-cycling and evacuation in a vacuum chamber both result in reduction of hysteresis of the elements. The effect of humidity cycling on the hysteresis loop of potassium metaphosphate elements, and the room temperature hysteresis loop of barium fluoride elements are illustrated in figure 8. These results suggest instability of the film to sintering and to chemical change, and also suggest the possibility that adsorbed impurities on the film are at least partially removed by the cycling and evacuation.

#### 4.5. Response Time

The time required for the indication of the element to pass through a certain fraction of the total change in indication after the element has been subjected to an abrupt change in relative humidity is a measure of the speed with which the element responds to a change in ambient relative humidity. The times corresponding to 63 percent and 90 percent of a total change in indication are referred to as "response times" in this work. The response times depend upon temperature, the initial and final ambient relative humidities, the direction of change of relative humidity (increasing or decreasing), and other factors. The average 63 percent response times in the direction of increasing relative humidity for the potassium metaphosphate element are 0.1 sec at room temperature and 2 sec at  $-20^{\circ}\text{C}$ . Corresponding values for the barium fluoride element are approximately 0.1 sec at room temperature, 1 sec at  $-20^{\circ}\text{C}$ , and 3 sec at  $-40^{\circ}\text{C}$ . Corresponding values for the conventional lithium chloride electrolytic humidity element are 3 sec at room temperature, approximately 50 sec at  $-20^{\circ}\text{C}$ , and 480 sec at  $-40^{\circ}\text{C}$ . Typical  $-20^{\circ}\text{C}$  response curves for potassium metaphosphate elements, barium fluoride elements, and conventional lithium chloride electrolytic humidity elements are shown in figure 9. Comparison of the response times indicate that the thin film hygrometer elements represent a large improvement over the conventional element in this respect.

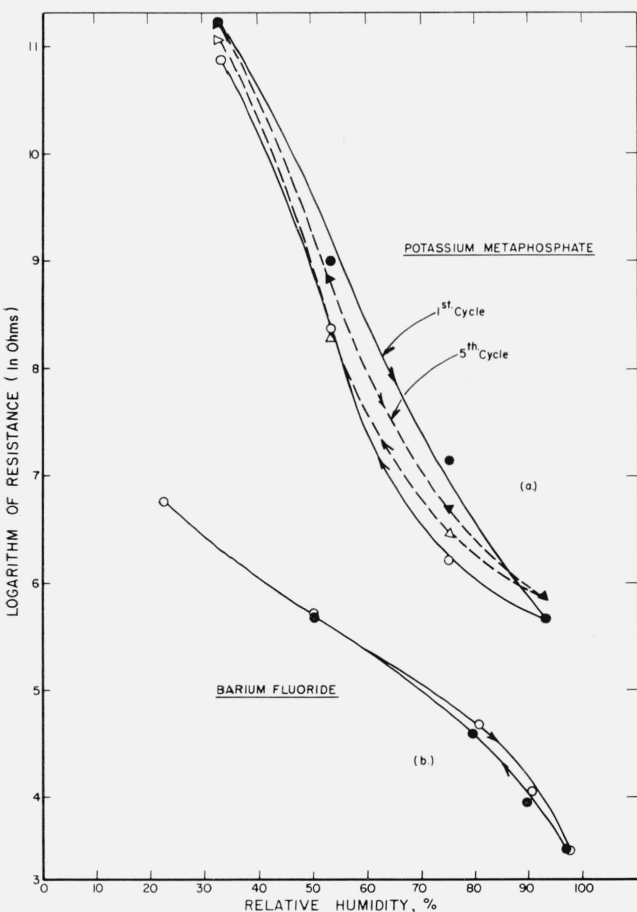


FIGURE 8. (a) Illustration of the effect of humidity cycling on the hysteresis loop of potassium metaphosphate thin film element. (b) Typical barium fluoride thin film element hysteresis loop after six humidity cycles.

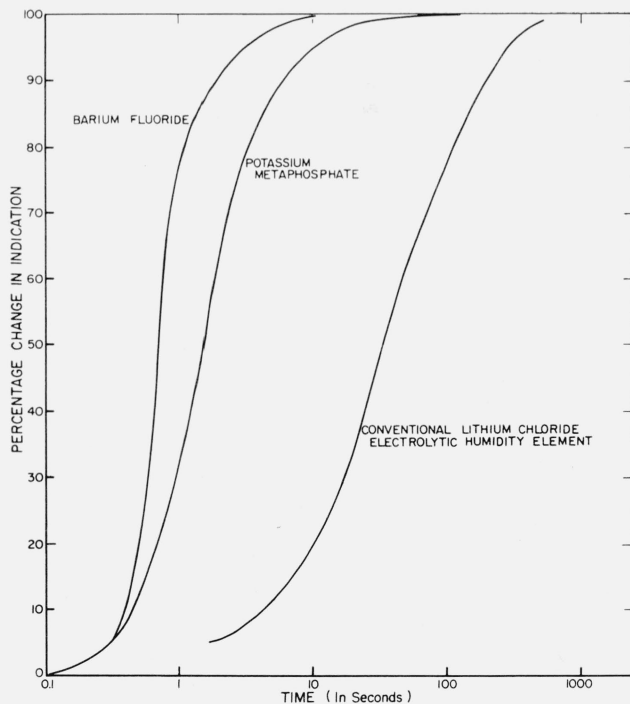


FIGURE 9. Typical response curves for barium fluoride and potassium metaphosphate thin film elements and the conventional lithium chloride electrolytic humidity element at  $-20^{\circ}\text{C}$ .

Plots of response time against potassium metaphosphate film thickness for various evaporation conditions are shown in figure 10. These plots indicate that the response was slower with increasing film thickness, presumably due, at least in part, to the mass transport of the water vapor into the micropore structure of the film. However, a minimum response time of the order of 0.1 sec at room temperature was approached as the film thickness was reduced. This result suggests the possibility that the response time is also influenced by other processes. Consideration of the response mechanism of the elements indicates that diffusion might be divided into at least three parts: Transport of water vapor through an aerodynamic boundary layer on the film resulting from the flow of air (250 m/min) across the surface; energy (heat of adsorption) transfer; and surface diffusion of water vapor into the micropore structure of the film. In each of these cases, the time required would contribute to the response time. If the thickness of the film became so small that diffusion into the film became negligible in its contribution to the response time, there would still remain the transport of the water vapor and the energy transfer through the aerodynamic boundary layer to contribute to response time.

It is possible that the observed minimum represents diffusion through the boundary layer and that the diffusion into the film is negligible. On this

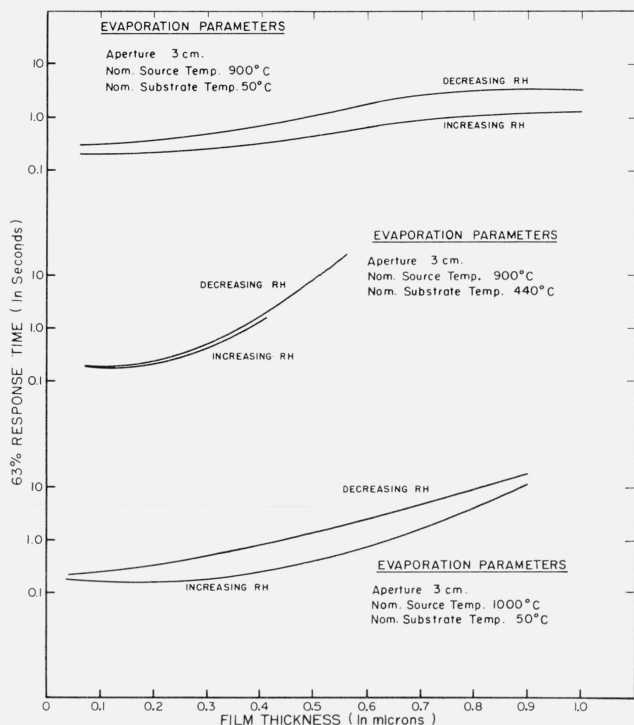


FIGURE 10. Examples of the variation of potassium metaphosphate response time with film thickness for several combinations of evaporation parameters.

"Source temperature" and "substrate temperature" refer to the temperature of the evaporating source and of the substrate, respectively, during the film deposition. "Aperture" refers to the diameter of a circular hole, in a baffle, delineating the evaporation source.

basis, then, it would be possible to greatly reduce the response time by introducing turbulence into the boundary layer since turbulent flow is much more efficient for transport of mass and heat than is laminar flow [8, 9, 10]. It would also be possible to reduce the boundary layer thickness by reducing the dimension of the element in the direction of the air stream. Morris and Sobel [11] have shown that the response time of the conventional lithium chloride element in an air stream depends on the orientation of the element relative to the direction of flow. A rough calculation based on a turbulent boundary layer and a smaller dimension in the direction of the air stream indicates that the response time of the potassium metaphosphate element might be reduced to the order of 1 msec at room temperature. This result would be expected to apply to other film-type elements also. The placement in the radiosonde and the nature of the flow across the element are, on the basis of this argument, areas in which the response time of the film-type element might be greatly improved.

#### 4.6. Film Thickness

The film thickness in the early potassium metaphosphate work at the National Bureau of Standards was  $0.075 \mu$  (approximately  $3 \mu$  in.), later work covered the thickness range from less than  $0.03 \mu$  ( $1 \mu$  in.) through  $2 \mu$  ( $80 \mu$  in.). The barium fluoride film thickness was  $0.30 \mu$  ( $12 \mu$  in.). The film thicknesses for the other materials thus far investigated generally lie within the range of the later potassium metaphosphate work. The response times for the potassium metaphosphate elements increased with increasing film thickness under similar evaporation conditions. However, altering the evaporation conditions resulted in generally different values of response time for the same thickness. The calibration curves for the potassium metaphosphate elements (fig. 4, for example) indicate that the logarithm of resistance-relative humidity characteristics of the elements are not simply determined by film thickness, but depend upon the combination of evaporation parameters. The barium fluoride film thickness of  $0.30 \mu$  was selected by experimentation as an optimum value which gave a favorable calibration curve without unduly sacrificing response time.

#### 4.7. Polarization

The film-type hygrometers tend to polarize when subjected to direct current, that is, the element resistance increases with time in a d-c circuit. Humidity cycling reduces this effect on the potassium metaphosphate element. It is possible that further investigation of electrode processes might result in further reduction in polarization. However, the more practical solution to the polarization problem is to use the element only in a-c circuits. For the barium fluoride element, it is desirable to use the element with symmetrical alternating current at low fre-

quencies, but not lower than 2 c/s, with voltage drops across the element preferably of the order of 1 v rms.

#### 4.8. Stability

One of the criteria for the selection of film materials is relative insolubility in water. The object of such a requirement is to minimize effects of exposure to high relative humidity and water immersion. Stability of the film material and its adhesion to the substrate and to the electrode are also of importance in this respect. Extended exposure of potassium metaphosphate elements for 1,470 hr over water in a sealed container resulted in increases in element resistance and a consequent error in the indication of approximately 15 percent relative humidity at saturation. Barium fluoride elements exposed to 97 percent relative humidity for 1,421 hr departed from the correct indication by a maximum of only 1.5 percent relative humidity. Subjection to a water spray in an air stream and 2-sec immersion in distilled water has no apparent harmful effect on the barium fluoride element. It is interesting to note that barium fluoride is more soluble in water than is potassium metaphosphate, although the high humidity exposure results would seem to indicate the contrary. However, there is electron diffraction evidence that an insoluble barium fluosilicate is formed on the barium fluoride film, which might in part account for these results. Cerous fluoride elements have been boiled in water with no apparent permanent damage. Other cerous fluoride elements have been frozen in ice to about  $-70^{\circ}\text{C}$  without apparent permanent damage.

The effects of long-term storage on the calibration of the elements are of importance in determining their "shelf life." Potassium metaphosphate elements stored in a dry atmosphere for approximately 1 year conformed satisfactorily to the original calibration. The barium fluoride elements, at least in part due to changes in structure and composition with time, increase in resistance with storage such that they should be put into use within 1 month after manufacture if the original calibrations are to be used. Lead iodide elements with electrodes over the films have been found to conform satisfactorily to the original calibration after at least 4 months storage in a dry atmosphere.

#### 4.9. Conduction and Capacitance

The mechanism of conduction on the film-type element is as yet not known. The results of some experiments and consideration of the adsorption process indicate that it is possible that the current carriers are transported in the adsorbed water film. The identification of the current carriers remains for future experimentation. However, the interesting possibility exists that at least part of the conduction is by proton transfer along the hydrogen bonds of the adsorbed water film, and that the humidity-sensitive film serves essentially only as an adsorbent. Ad-

sorption studies on the humidity-sensitive films with simultaneous determinations of conductivity could be expected to shed light on the conduction mechanism.

Although our emphasis thus far has been on the resistance of the element, the capacitance of the element also varies with relative humidity. The element can be considered to consist of a variable resistor in parallel with a variable capacitor. The capacitance of the element increases through two or more orders of magnitude from low to high humidities. Further study should determine the feasibility of using the capacitive component as a measure of humidity.

### 5. Flight Testing

In order to flight test the elements in radiosondes, a-c circuitry capable of handling the high resistances of the elements was developed and radiosondes were modified to accommodate the circuitry. A series of flights was planned to provide data on the response and sensitivity of the elements to changes in humidity in the atmosphere and to give an indication of the accuracy of the indication of the elements. On each flight, both a conventional radiosonde with a standard lithium chloride electrolytic element as the humidity sensor and a modified radiosonde with the thin-film element are carried aloft on the same balloon. A preliminary plot of one of these flights with the barium fluoride element is shown in figure 11. The apparent sensitivity and the rapid response of the

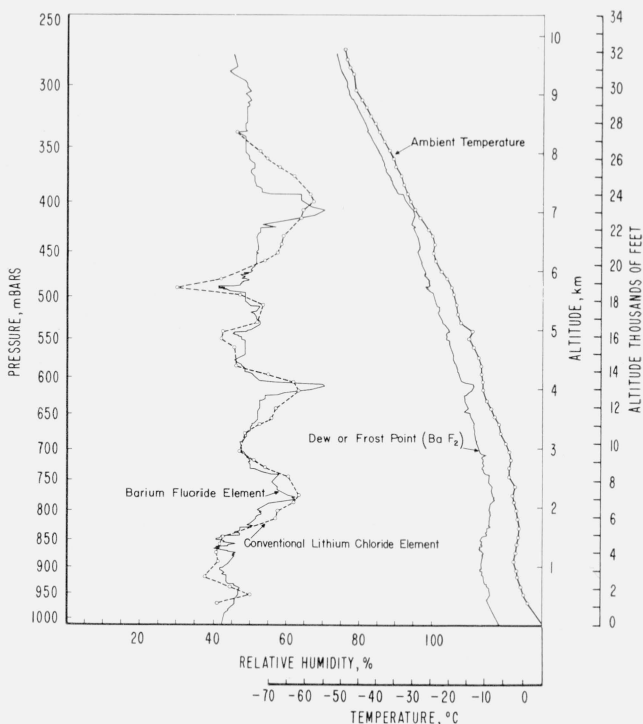


FIGURE 11. Plot of barium fluoride thin film element-conventional lithium chloride electrolytic element comparison flight.

barium fluoride element are indicated by the plot. In the future, detailed data will be obtained by analysis of magnetic tape records of the audiofrequencies transmitted by the radiosondes during the flights. Future flights can perform other functions such as: To compare different film-type elements under conditions of projected use; to provide response time data under both changing humidity and changing temperature conditions; to determine the effects of flow conditions, such as turbulence in the boundary layer, on response time; to determine the effects of dimensions and shape of the element on response time; and to provide information on the distribution of water vapor in the troposphere which could be correlated with the synoptic weather situation. The last of these functions includes the primary function of the element, and also includes research in the troposphere.

In summary, this paper has reviewed the development of a thin film humidity sensor at the National Bureau of Standards and has used the principles of physical adsorption to explain, at least in part, its characteristics. The development is not yet complete, and many areas of considerable interest and importance have been revealed in which further investigation is indicated.

## 6. References

- [1] F. E. Jones and A. Wexler, A barium fluoride film hygrometer element, *J. Geophys. Research* **65**, 2087-2095 (1960).
- [2] Lindsay Chemical Co., Code 482.
- [3] A. Wexler, S. B. Garfinkel, F. E. Jones, S. Hasegawa, and A. Krinsky, A fast responding electric hygrometer, *J. Research NBS* **55**, 71-78 (1955).
- [4] M. Auwarter, Electric hygrometer, U.S. Pat. 2,715,667 (1955).
- [5] L. Holland, Vacuum Deposition of Thin Films, pp. 146-148 (John Wiley & Sons, Inc., New York, N.Y., 1956).
- [6] S. Brunauer, The Adsorption of Gases and Vapors, p. 150 (Princeton Univ. Press, Princeton, N.J., 1945).
- [7] S. Brunauer and L. E. Copeland, Handbook of Physics, p. 5-103 (ch. 7, Surface tension, adsorption. Edited by E. U. Condon and H. Odishaw, McGraw-Hill Book Co., Inc., New York, N.Y., 1958).
- [8] R. C. L. Bosworth, Transport Processes in Applied Chemistry, p. 188 (John Wiley & Sons, Inc., New York, N.Y., 1956).
- [9] A. H. Shapiro, The Dynamics and Thermodynamics of Compressible Fluid Flow, vol. **II**, p. 1080 (Ronald Press Co., New York, N.Y., 1954).
- [10] T. K. Sherwood, Mass transfer and friction in turbulent flow, *Trans. Amer. Inst. Chem. Eng.* **36**, 818 (1940).
- [11] V. B. Morris and F. Sobel, Some experiments on the speed of response of the electrolytic hygrometer, *Bull. Amer. Meteor. Soc.* **35**, 226-229 (1954).

(Paper 66C-97)