promising avenues for further physiological experimentation. From this point of view, the present results indicate that neural as well as photochemical processes are involved in determining the time course of light adaptation, whether measured in conventional fashion or with the newer variable delay procedure. Furthermore, the long-term influence of the spatial parameters shown here suggests that such neural processes are complex and probably involve cerebral mechanisms (*7*). Further studies are necessary to clarify this point.

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6 January 1964

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## Liquid Film Hygrometer

Abstract. *An improved method of humidity measurement based on the dielectric constant of a liquid-solid mixture has shown agreement with a simple theory. The hygrometer has shown no measurable hysteresis and has identical time-response characteristics for increasing or decreasing humidity.*

Measurement of humidity continues to be a problem in chemistry, geophysics, and other sciences. Most hygrometers are slow to react and lack sensitivity for low humidities; some exhibit hysteresis. The responses of most humidity-measuring devices cannot be related to a suitable theory (*1*). We have succeeded in utilizing the equilibrium between water vapor and a hygroscopic liquid as the basis for a hygrometer which shows promise in alleviating some of these difficulties (*2*).

The equilibrium mole fraction of water in a nonionizing hygroscopic liquid can be related, in the ideal case, to the ambient relative humidity by Raoult's law:

$$\mathcal{R} = \frac{P_w}{P_T} = \frac{n_w}{n_w + n_s} \qquad (1)$$

where $\mathcal{R}$ is the relative humidity at instrument temperature $T$; $P_w$ is the partial pressure of water vapor, $P_T$ is the partial pressure over water at instrument temperature $T$; $n_w$ is the number of moles of water, and $n_s$ is the number of moles of solvent.

This liquid may be conveniently utilized as a coating on an inert granular solid, as in gas-liquid partition chromatography. Such heterogeneous mixtures can be formulated with up to 20 percent liquid phase by weight without having a tendency to separate or bleed. Both the bulk resistivity and dielectric constant of a solid-liquid mixture may be expected to vary with the number of moles of water, $n_w$, but the latter has proved to be more useful.

If the dielectric constant of the mixture is directly proportional to $n_w$, then for a capacitor containing this heterogeneous material as its dielectric,

$$P_w = \frac{B\Delta C\, P_T}{B\Delta C + n_s} = \frac{\alpha\Delta C P_T}{\alpha\Delta C + 1} \qquad (2)$$

where $B$ is the proportionality constant (moles per picofarad); $\alpha = B/n_s$ and represents the sensitivity constant (pf$^{-1}$); $\Delta C$ is the change in capacitance due to the addition of $n_w$ moles of $H_2O$ (pf).

Figure 1 shows the configuration of a hygrometer with a dielectric composed of a fluorocarbon (Fluoropak 80) coated with polyethylene glycol (Carbowax 400). The capacitor plates are a pair of parallel porous disks of stainless steel, which allow the sample gas to be passed through the capacitor. Because of the high ratio of surface area to mass, and because the liquid is dispersed in a thin layer (about 2500 Å) over the surface, equilibrium can be reached rapidly. The value of $\alpha$ for the hygrometer shown in Fig. 1 was 0.1 pf$^{-1}$, and the time for half response was 13 seconds at a flow rate of 15 lit./min and a temperature of 20°C. The results in Fig. 2 were obtained under the same experimental conditions; the right side of Eq. 2 is plotted against $P_w$, indicating the close agreement between equations and experiment. Capacitances were measured with a Tektronix type 130LC capacitance meter.

At low humidities ($\mathcal{R} < 0.1$), the response can be described by

$$\frac{P_w}{P_T} = \alpha\Delta C \qquad (3)$$

since $n_w << n_s$. For low humidity the time response can be described ideally by a simple exponential relationship:

$$\Delta C = \frac{P_w}{\alpha P_T}\left[1 - \exp\left(\frac{-KP_T}{n_s}\,t\right)\right] \qquad (4)$$

where $t$ is the time and $K$ is the diffusion coefficient for water vapor inside the packing.

Since time response and hysteresis are the main stumbling blocks of hygrometers in general, it is appropriate to examine the dynamic characteristics of this instrument. Figure 3 shows a tracing of the response of the liquid-film hygrometer to three step-changes of humidity (two increasing and one decreasing). The humidity changes were from $\mathcal{R} = 0$ to $\mathcal{R} = 0.09$ and back to $\mathcal{R} = 0$, so that the time response equation (Eq. 4) (requiring that $n_w << n_s$) should approximately apply.

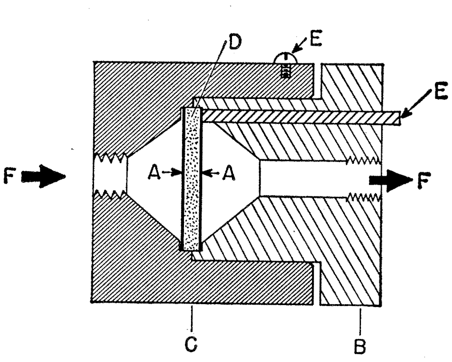

Fig. 1. Cross section of the hygrometer. *A*, Porous stainless steel capacitor plates; diameter, 1.5 cm; spacing, 2.0 mm. *B*, Teflon plug. *C*, Stainless steel body. *D*, Packing material. *E*, Electrical connections. *F*, Airflow.

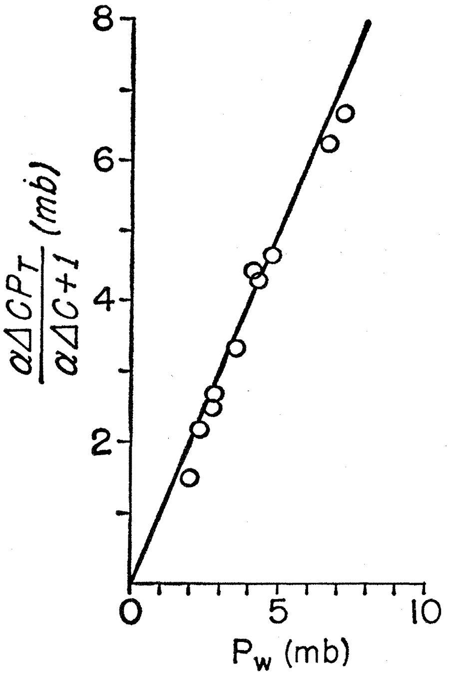

Fig. 2. Data from the hygrometer shown in Fig. 1.

The instrument conditions were the same as described earlier: 15 lit./min at 20°C. From these data, the following can be ascertained. (i) The output returns to zero when the humidity returns to zero. (ii) The time response is exponential. (The reader may verify this for himself by making a graph of log $[1 - (\alpha\Delta C/\mathcal{R})]$ versus time. The resultant plot is nearly linear in agreement with Eq. 4.) (iii) The response time is the same for both increasing and decreasing humidity. (iv) By virtue of (i) and (iii), hysteresis is very small.

At relative humidities above 0.1, the response can be described by an expression where the assumption that $n_w << n_s$ is not made. Experimentally, the response is not exponential; however, the times for half response for increasing and decreasing humidity are still identical. Further, the output reliably returns to zero at $\mathcal{R} = 0$, indicating a lack of hysteresis at these higher humidities. If the relative humidity at the temperature of the instrument exceeds about 0.7, the liquid phase begins to flow and irreversible changes occur in the sensor. In order to measure these higher humidities, the sensor and ancillary plumbing must be operated at an elevated temperature.

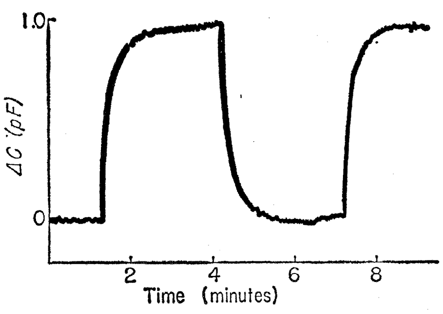

Fig. 3. Dynamic response to step-changes of humidity, $\Delta C$(pf) versus time (minutes) for changes in relative humidity of 0 to 0.09 and back to 0, at 20°C.

Data have been obtained which show that the response time is independent of humidity but strongly dependent on both flow rate and temperature. The dependence on flow rate is probably due to the variation of the diffusion coefficient, $K$, with gas velocity. The effect of temperature arises in the dependence of $P_T$ on temperature. By operating the instrument at 50°C and 15 lit./min, the time for half response is reduced to less than 1 second. Since $P_T$ has been increased by almost an order of magnitude, some loss of sensitivity is encountered. However, sensitivity is still sufficient for measuring 0.1 mb of water with a signal noise ratio of 10. Experiments are now being conducted to determine the form of these temperature and flow rate dependences.

The accuracy of the liquid-film hygrometer is essentially dependent on three factors: noise, drift, and calibration. The noise is independent of humidity and represents about 0.01 mb of water vapor. The drift (indicating decreasing capacitance) corresponds to about $-0.1$ mb/hr. Most of this is due to the evaporation of the liquid phase. This evaporation drift, however, amounts to a change of only about 1 percent in the sensitivity coefficient ($\alpha$) per 100 hours because of the large mass of liquid in the sensor (about 0.1 g) and the high dielectric constant of polyethylene glycols.

Calibration remains as the real problem in the accuracy of any hygrometer. Typical calibration devices are subject to inaccuracies of a few to several percent of $P_w$. For instance, other data show that the errors in Fig. 2 are the result of inaccuracies in the flowmeters used in combining a dry and saturated stream of air to produce the desired humidities. However, since the indicated humidity for a fixed reference point is repeated within 3 percent, relative errors are smaller than absolute errors. A field model of this hygrometer has been built and it includes a temperature-controlled sensor and sample flow. This instrument has proved useful in the measurement of (i) fluctuating humidities; (ii) humidities near and above saturation; and (iii) partial pressures of water vapor in the realm of 0 to 1 mb at room temperature.

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## Analysis of Variance of Migmatite Composition II: Comparison of Two Areas

Abstract. *To obtain comparison with previous results an analysis of variance was made on measurements of proportion of granite and country rock in a second Colorado migmatite. The distributional parameters (mean and variance) of both regions are similar, but the distributions of variance among the three levels of the nested design differ radically.*

In a recent report (*1*) we presented an analysis of variance of the composition of a migmatite in northern Colorado with respect to the ratio of country rock to discrete small bodies of granite. The variance was partitioned into three components: regional (between groups of outcrops), areal (between outcrops), and local (between sample points within outcrops). Since there were no similar data for any other migmatite, we were without a basis for deciding whether or not the basic distributional characters ($\overline{X}$, $S^2$, and so forth) were typical for such rocks. We were also unable even to speculate whether the unexpected results from Poudre Canyon, such as the absence of any significant regional variation in composition, were strictly local.

During the summer of 1963, while examining migmatite areas in the western United States as possible sites for