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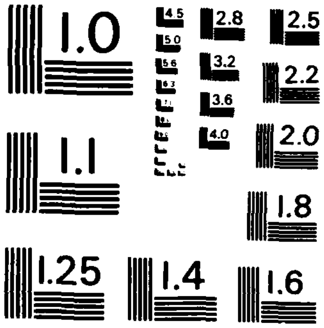

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An Optical Waveguide Humidity Detector

D. S. BALLANTINE* AND H. WOHLTJEN

Surface Chemistry Branch
Chemistry Division

**Geo-Centers, Inc.*
Suitland, MD 20746

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19 ABSTRACT (Continue on reverse if necessary and identify by block number)

An optical waveguide humidity detector is described that is reliable and inexpensive. It utilizes a cobalt chloride/poly(vinyl pyrrolidone) film on the surface of a thin walled glass capillary waveguide, and monitors the absorption change at 660 nm as the waveguide is exposed to $H_2O(g)$. The humidity response is an S-shaped curve with the inflection point between 65% and 80% RH; location of inflection point is correlated with $CoCl_2$ and PVP concentration in the film. The effects of reagent concentration and film thickness on detector response are described.

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D. S. Ballantine

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CONTENTS

AN OPTICAL WAVEGUIDE HUMIDITY DETECTOR

I. INTRODUCTION

The relative humidity of ambient air can have a significant impact on a number of physical processes of interest to many industries [1-9]. As a result, there has been great interest in recent years in the development of sensitive and reliable humidity sensors. Most current developments have centered around either electronic devices (e.g. moisture sensitive resistors, conductive cells), or colorimetric devices.

The electronic sensors tend to be sensitive to temperature as well as humidity, whereas the colorimetric reagent (e.g. metal salts; Co^{2+}, Cu^{2+}, V^{5+}) respond only to moisture. Most colorimetric reagents are suspended in gels or in adsorbent paper and subjected to simple visual inspection to determine the extent of reaction or hydration. Such inspections are highly subjective and quantitatively poor.

The use of colorimetric reagents coated on an optical waveguide to detect atmospheric vapors has been demonstrated [10]. An optical waveguide device has the advantage of higher sensitivity and quantitative precision. The development and testing of such a device for humidity measurements is described herein. Experimental results on response characteristics of films applied to the waveguide are included, and possible improvements of the device are discussed.

Manuscript approved July 23, 1985.

II. OPTICAL WAVEGUIDE DEVICE

A. Theory

The optical waveguide is theoretically related to internal reflection spectroscopy which has been described in detail by Harrick [11]. It takes advantage of the fact that light propagating by internal reflection through a medium (i.e. glass rod, optical fiber) can interact with a second, rarer material (i.e. thin film, solution, gas) that is in contact with the reflecting surface of this medium. This interaction is due to the creation of an evanescent wave that is perpendicular to the direction of propagation that penetrates into the rarer medium (see figure 1). The depth of penetration, d, is related to the angle and wavelength of the incident light and the refractive indices of the two media involved.

Also, the sensitivity of this technique is proportional to the number of internal reflections that occur. The more reflections that occur, the greater the number of interactions of the light wave with the rarer medium. The sensitivity is thus a function of the length and thickness of the waveguide - the thinner the material, the more reflections per unit length.

B. Device components

The waveguide humidity detector consists of an optical waveguide coated with a reagent/polymer film, a light source, a photodetector, and an associated electronics package.

Light sources were light emitting diodes (LEDs). They are relatively inexpensive, commercially available and emit light in 4 spectral ranges (red, orange, yellow, green).

Phototransistors were used as photodetectors. Like the LEDs, they are suitable for use in a small device, are relatively inexpensive and commercially available. The spectral response of the phototransistors used in this study drops off dramatically below 600 nm, so only the red (660 nm) and orange (635 nm) LEDs were used as light sources.

The waveguide consisted of a thin-walled glass capillary tube (~ 1.0 mm o.d. x 90 mm long; wall = 0.2 mm). One end of these capillary tubes was rounded off, which aided in focusing the transmitted light onto the phototransistor.

Clear plastic rods were used to manufacture optical couplers that were bored to accommodate the individual components (see fig. 2). These couplers held the optical components in a rigid, reproducible geometry which eliminated the need to strictly control the wavelength or angle of incident light. In addition, these couplers enhanced the transmission of light from the LED to the waveguide, and from the waveguide to the phototransistor.

Cells to hold the waveguide were fashioned out of plastic rods that were bored to hold the optical components. These cells have a very small dead volume, and were painted black to prevent the introduction of stray light.

The electronics package (figure 3) consists of a modulated LED power source and signal processor which amplifies, demodulates and filters the phototransistor voltage. A 3KHz RC timed, astable multivibrator circuit is used to pulse modulate the LED. Modulation of the light source is essential for reducing the effects of temperature drift in the phototransistor dark current. Without modulation, small variations in phototransistor temperature would produce unacceptable variations in the baseline signal. The phototransistor signal was amplified using an AC coupled op-amp and fed into an absolute value circuit and low pass filter which provided a DC voltage level proportional to the intensity of light striking the phototransistor. Small variations in light intensity produced by changes in the waveguide coating characteristics produced very easily measured changes in the output voltage of the electronics system. The system also was equipped with offset and gain controls to permit output signal adjustment to 0% and 100% transmittance conditions.

C. Reagent films

The colorimetric reagent selected for testing with this device was $CoCl_2 \cdot 6H_2O$. The anhydrous salt ($CoCl_2$) is blue, and exhibits a strong absorption peak at ~ 660 nm. When hydrated, the absorption peak shifts to 510 nm, characteristic of the $CoCl_2 \cdot 6H_2O$ complex. This behavior is completely reversible and is well suited for probing with LEDs that produce 635-660 nm wavelengths of light.

We were interested in determining the effect of various film parameters on the device response. For this reason, solutions were prepared in acetone/H_2O that contained varying concentrations of $CoCl_2 \cdot 6H_2O$ (from 30 mg/nl-230 mg/ml). Known weights of poly(vinyl pyrrolidone) (PVP) were then added to these solutions to produce solution containing 0.75 - 3.0% (w/w) of PVP. In addition, solutions of just $CoCl_2 \cdot 6H_2O$, and just PVP were prepared to examine the effect of each component on the overall response.

Prior to coating with reagent/polymer films, the waveguides were etched for 5 min. in a buffered, dilute HF solution. Reagent films were then applied using one of two different methods.

The first method involved dip-coating the waveguides by immersing them in a solution and slowly withdrawing them. As the solvent was evaporated using a heat gun, a light blue film of $CoCl_2$/PVP was deposited on the surface of the waveguides. The second method involved using an air brush to spray a light mist of reagent/solvent on the waveguide surface, which was then dried using a heat gun. The films produced by dip coating were thicker, and contained areas of high $CoCl_2$ concentrations, indicated by spots of darker blue color. Air brush films were generally thinner and more evenly distributed. Waveguides coated with these films were exposed to varying concentrations of water vapor at 22°C. The introduction of water vapor to the cell, and the acquisition of response data were controlled by the computer system described below.

D. Analytical system

A gas handling system was designed and constructed to control the introduction of vapor and/or diluting air to the sensor. Flow rates of water saturated air and dry air were controlled using variable rotameters. Introduction of clean, dry air or water-saturated air to the sensor was controlled by solenoid valves which had been interfaced to an Apple IIe microcomputer via the I/O game-controller. The % RH of water sautrated air was assumed to be ~ 98% when calculating the relative humidity of diluted vapor streams.

Voltage data from the phototransistor were collected by the Apple II via an A/D converter card. Voltage vs. time data were plotted using our own data acquisition program.

Before data were collected, a waveguide was inserted into the holder assembly, the LED was turned off, and the zero adjustments were made. The LED was then turned on, and the null adjustment was used to produce an output voltage just greater than 0 volts. The device was then ready for testing.

III. RESULTS AND DISCUSSION

Examples of typical humidity response curves are given in Figures 4a-c. Several features are of interest.

In general, the response follows an S-shaped curve, increasing rapidly in the range of 60-85% RH, and then gradually leveling off as 100% RH is approached. This behavior holds true for all $CoCl_2$/PVP films.

With films composed of $CoCl_2$ only, the upper portion of the response curve (75-100%) also follows this pattern. Below 75% RH, however, there is a precipitous decrease in signal, until a large negative response (-300 mV to -600 mV) is reached between 60% and 70% RH. As 0% RH is approached, this negative signal gradually approaches zero volts.

To further determine the effect of the PVP binder on the response, the rate of signal increase was plotted as a function of % RH interval (5%), to obtain a simple derivative curve. These plots indicate the region of the curve with the greatest slope and were used to determine approximate inflection points in the S-curves. Examples of these plots are shown in figure 5.

The resulting inflection points ranged from 67-79% RH. To determine whether there was any significant trend in these data, the inflection points were correlated with different film variables.

Since the films varied in thickness and in concentration of components, the raw data was not suitable for meaningful comparisons. For example, a relatively thin film with a high concentration of cobalt chloride may have a high optical density and thus exhibit a large difference (Δ mV) between 0% and 100% T. A thicker film with a lower concentration of cobalt chloride may have a comparable optical density, but the relative response times, etc., may be quite different. To determine the effects of film thickness and component concentrations on the response behavior of the device, some type of correction must be applied to the raw data.

Since the amount of light transmitted through a given waveguide is dependent on the optical density of the film, waveguide responses were normalized to the film with the largest signal (mV) at 98% RH. Also, since more concentrated solutions of $CoCl_2$ would achieve a given optical density with a thinner film than less concentrated solutions, a correction factor was needed to account for film thickness. Since the thickness of the film was a function of the % PVP, this value was also used in determining the normalization factor for a given waveguide film. Also, since the $CoCl_2/H_2O$ equilibrium is related to the amount of water in the film at equilibrium, this correction factor would also correct for any variations in water concentration vs. film thickness.

The normalization factor (N.F.) applied to the inflection point data was then calculated using the equation

$$\text{N.F.} = \frac{(\Delta\ \text{mV})_{100\%\ \text{T},\ (x)} \cdot \text{PP}(\%)_x}{(\Delta\ \text{mV})_{100\%\ \text{T},\ (1)}\ \text{PP}(\%)_1} \qquad (1)$$

where $(\Delta\ \text{mV})_{100\%\ \text{T},\ (1)}$ = the signal at 100% T for film with largest response

$(\Delta\ \text{mV})_{100\%\ \text{T},\ (\chi)}$ = the signal at 100% T for film χ

$\text{PP}(\%)_\chi$ = the % PVP in solution used to prepare film χ.

$\text{PP}(\%)_1$ = the % PVP in solution used to prepare film 1.

The data used to calculate these N.F., as well as inflection points for these waveguides are given in Table I. Results are plotted in Figure 6.

The plot indicates some dependence of inflection point on optical density and % PVP. Although a straight line is drawn through the data, this relationship may not be linear. The data do indicate some degree of dependence of device response on film thickness. Further indications of the effect of film thickness are seen in figure 7. These plots are actual response vs. time graphs for the device using films of different thicknesses.

TABLE 1. Film Variables and Calculated Normalization Factors (N.F.)

Film Label	$[CoCl_2 \cdot 6H_2O]$ (mg/mL)	% PVP (w/w)	100% T (mV)	N.F.	Inflection Point (% RH)
AB#1	133	2.0	1900	0.83	75
AB#4	168	0.75	850	0.14	70
AB#5	67	1.0	825	0.18	69
AB#6	230	0.86	1210	0.23	67
AB#10	100	1.0	1300	0.28	70
AB#12	100	1.0	1820	0.40	75
AB#17*	200 (Thick)	1.5	3050	1.0	79
AB#18	200 (Thin)	1.5	2450	0.80	74
DIP#1	30	1.0	2480	0.54	71
DIP#10	100	1.0	1810	0.40	74
AB#15 (NH)	100	1.5	720	0.24	69
AB#16 (NH)	100	3.0	1050	0.69	77

* Highest transmittance (Δmv) at 298% RH. All other film responses are normalized against this value.

In the first plot, using an air brush film (AB#5), a relatively fast response time is exhibited at 70% RH. For a thicker, dipped film (DIP#1) the response time at 75% RH is considerably slower. It is evident that film thickness has a dramatic effect on the rate of response, with thinner films responding more rapidly.

Results obtained using the homogeneous $CoCl_2$/PVP films have been compared with results obtained using films of $CoCl_2$ only, a film of PVP only, and films obtained by coating first with $CoCl_2$ and then with PVP. The following qualitative observations were recorded.

1. An homogeneous film of $CoCl_2$/PVP exhibited much better response and a longer lifetime than a film obtained by coating first with $CoCl_2$ and then with PVP. Response curves also exhibited a smoother transition from high RH to lower % RH.

2. Films containing PVP were more stable; subsequent runs of individual tubes yielded similar responses after several weeks. Films of $CoCl_2$ alone showed decreased response after several hours of use. The cobalt chloride film powdered and showed poor adhesion to the waveguide surface.

3. Films of PVP alone exhibited no significant response to water vapor. It appears that the polymer film serves two purposes; first, it acts as a binder to ensure long life and good contact between the reagent film and the waveguide surfaces, and second, it acts as a protective, semipermeable membrane to regulate the introduction of water vapor to reagent.

IV. CONCLUSIONS

As a humidity sensor, the waveguide device shows relatively good precision within the range described (70-90%). It could be developed as is for use in specific cases where the desired humidity levels are within the range of good response.

Further development of the reagent/polymer film may extend the region of reliable response of the present device. Such film development could include the use of polymer/copolymer films of different hygroscopicity (e.g. poly(vinyl alcohol) (PVA), or poly(styrene sulfonic acid) (PSSA)), or different metal salts as reagents.

In addition, some form of temperature monitoring or control would be desirable to facilitate conversions from ppm (H_2O) to % RH and vice versa.

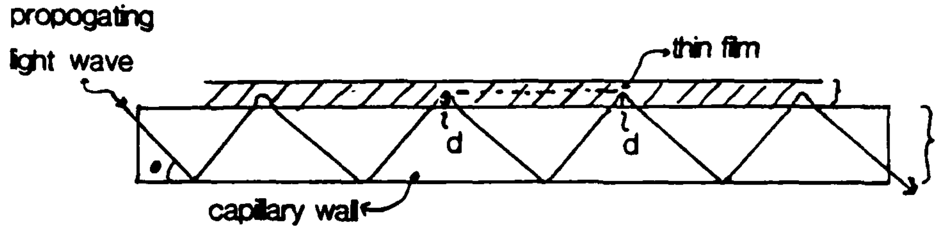


Fig. 1 — Diagram illustrating the interaction of an internally reflected light wave with a thin film coated on the surface of a glass capillary waveguide

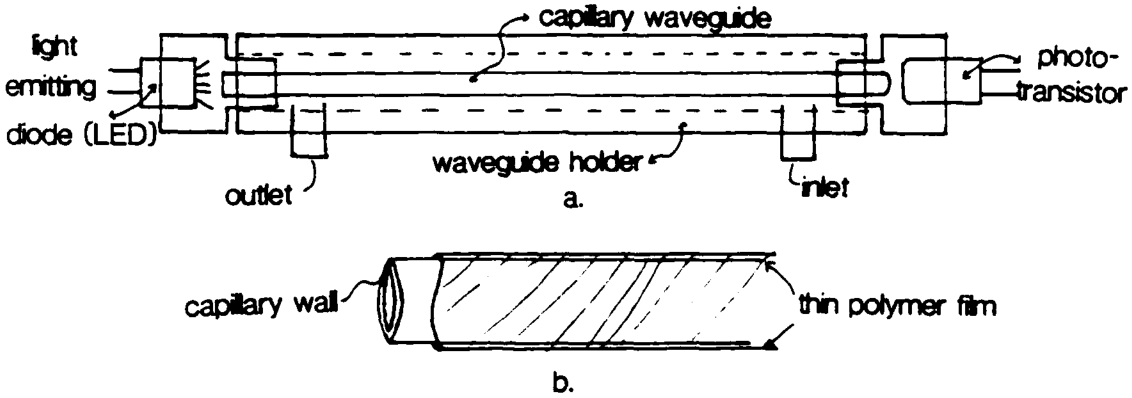


Fig. 2 — Diagram of the components comprising the optical waveguide detector

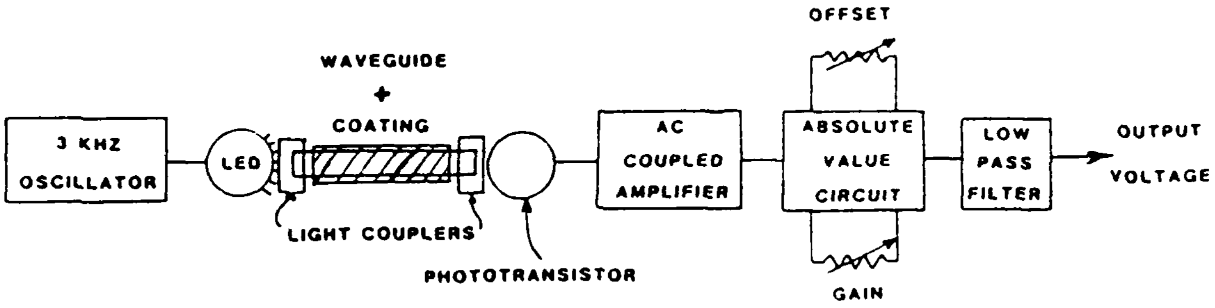
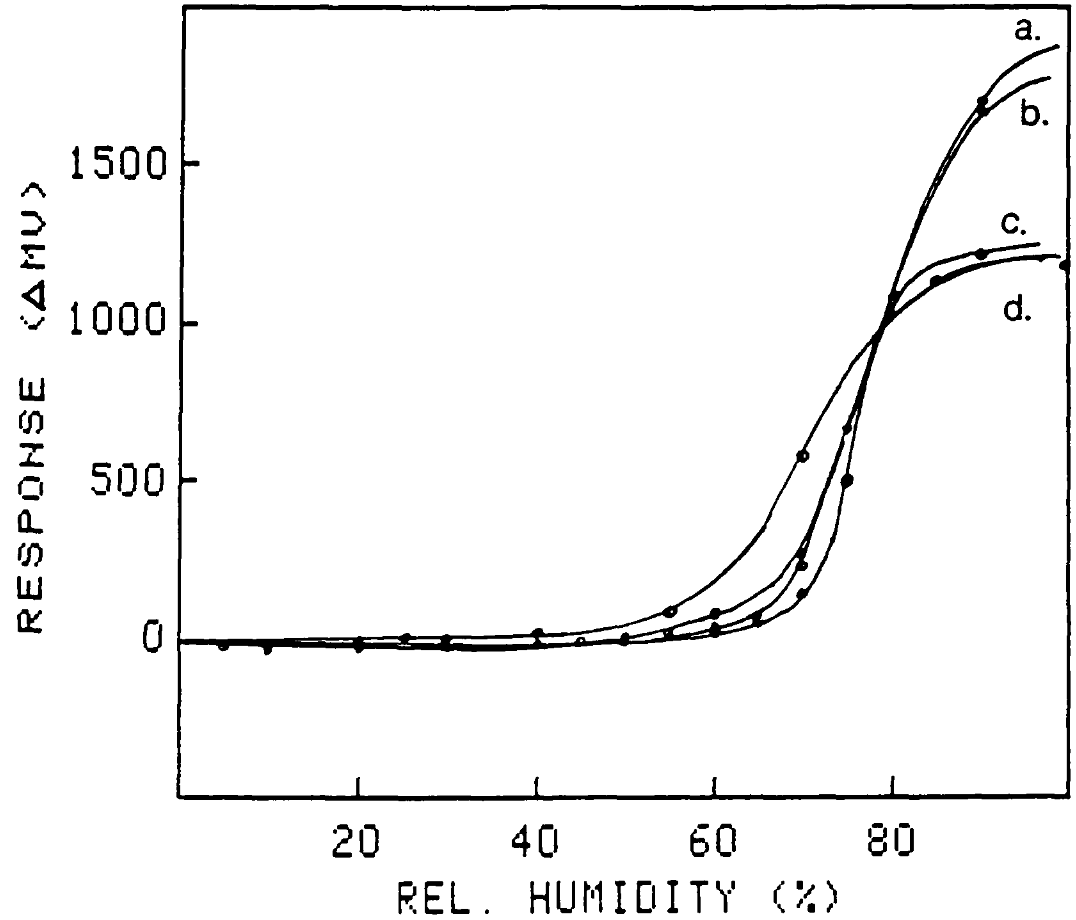
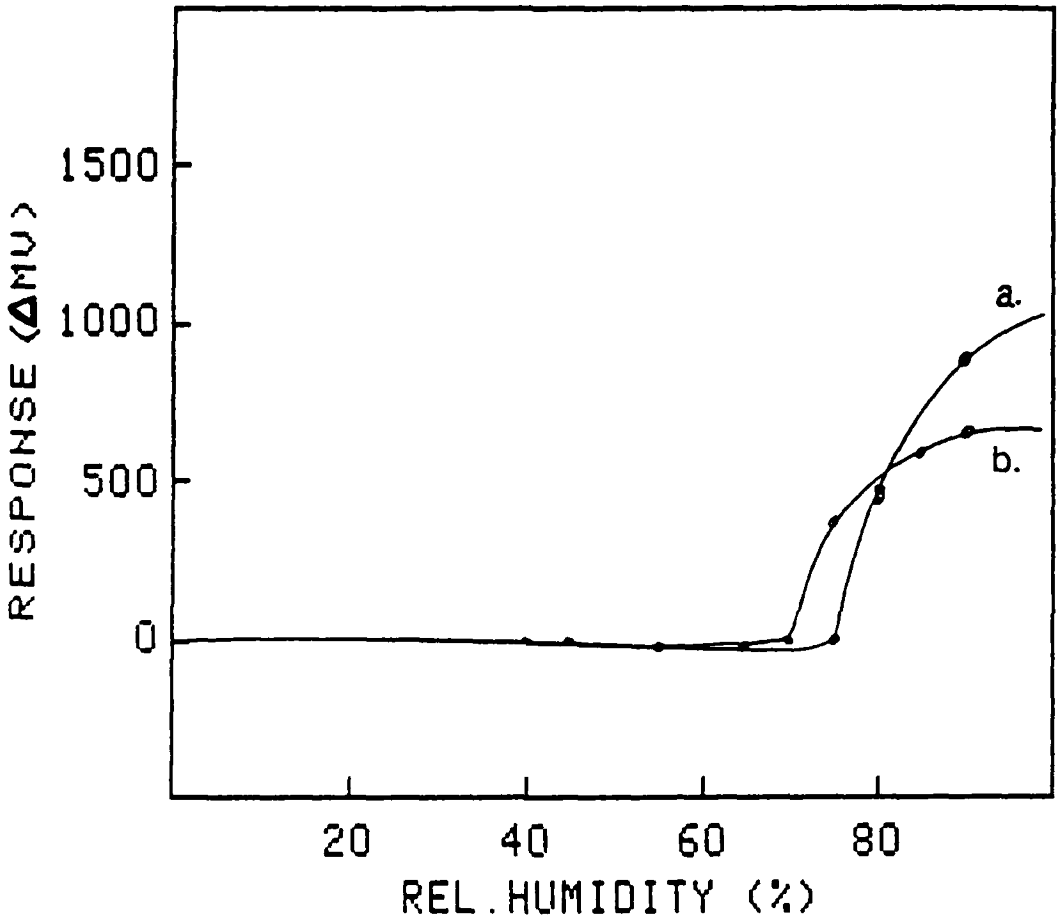


Fig. 3 — System diagram for the optical waveguide humidity detector



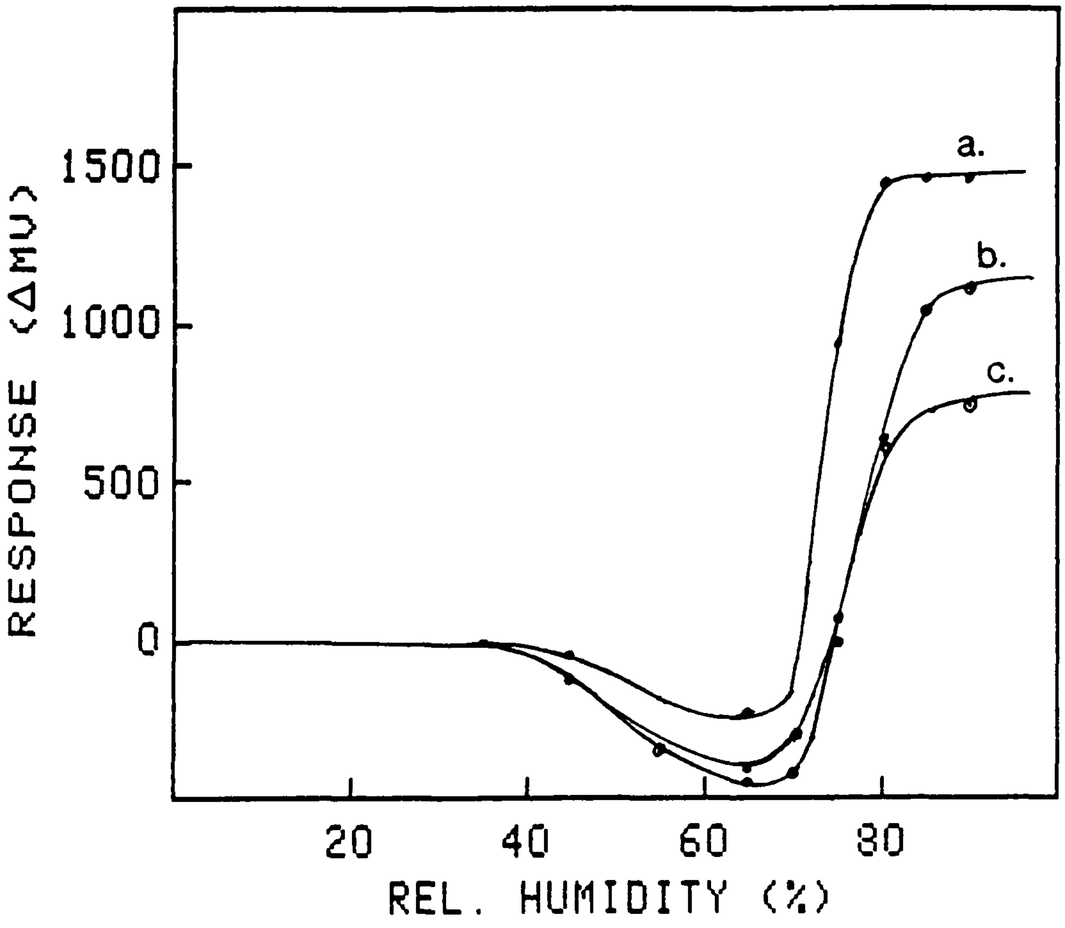
(a)

Fig. 4 — These S-shaped curves are typical of the waveguide device response (Δmv) vs relative humidity (% RH). The thin films coated onto the surface of the waveguide are of three types: (a) Films prepared from homogeneous $CoCl_2$/PVP solutions (H). The curves in 4a are for the following films: (1) AB#1; (2) AB#12; (3) AB#10; and (4)AB#6. (b) Films of $CoCl_2$ covered with a second film of PVP (non-homogeneous, NH). Curves in 4b are for the following films: (1) AB#16; (2) AB#15. (c) Films of $CoCl_2$ only, with no PVP binder (NP). Curves in 4c are for the following films: (1) AB#11; (2) AB#13; (3) AB#14.



(b)

Fig. 4 (Cont'd) — These S-shaped curves are typical of the waveguide device response (Δmv) vs relative humidity (% RH). The thin films coated onto the surface of the waveguide are of three types: (a) Films prepared from homogeneous $CoCl_2$/PVP solutions (H). The curves in 4a are for the following films: (1) AB#1; (2) AB#12; (3) AB#10; and (4) AB#6. (b) Films of $CoCl_2$ covered with a second film of PVP (non-homogeneous, NH). Curves in 4b are for the following films: (1) AB#16; (2) AB#15. (c) Films of $CoCl_2$ only, with no PVP binder (NP). Curves in 4c are for the following films: (1) AB#11; (2) AB#13; (3) AB#14.



(c)

Fig. 4 (Cont'd) — These S-shaped curves are typical of the waveguide device response (Δmv) vs relative humidity (% RH). The thin films coated onto the surface of the waveguide are of three types: (a) Films prepared from homogeneous $CoCl_2$/PVP solutions (H). The curves in 4a are for the following films: (1) AB#1; (2) AB#12; (3) AB#10; and (4)AB#6. (b) Films of $CoCl_2$ covered with a second film of PVP (non-homogeneous, NH). Curves in 4b are for the following films: (1) AB#16; (2) AB#15. (c) Films of $CoCl_2$ only, with no PVP binder (NP). Curves in 4c are for the following films: (1) AB#11; (2) AB#13; (3) AB#14.

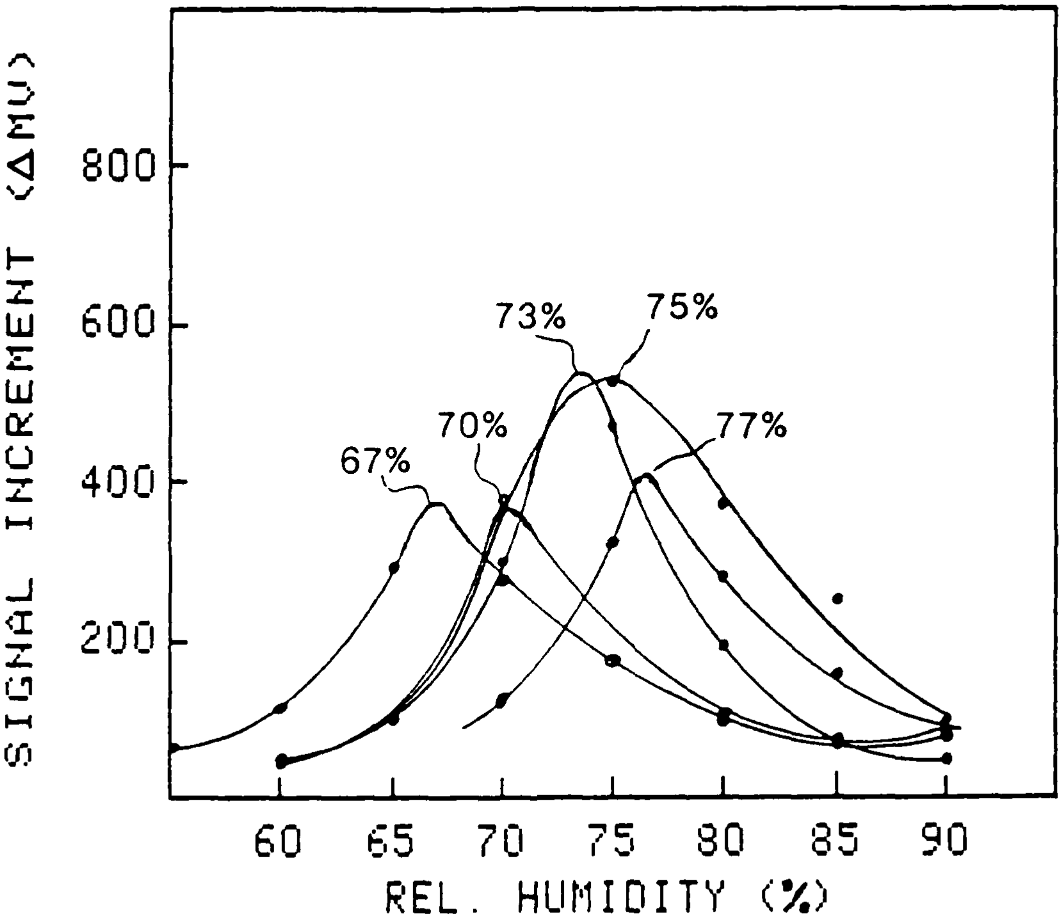


Fig. 5 — Examples of simple derivative curves used to determine inflection points. The details of individual film parameters and inflection points are given in Table 1.

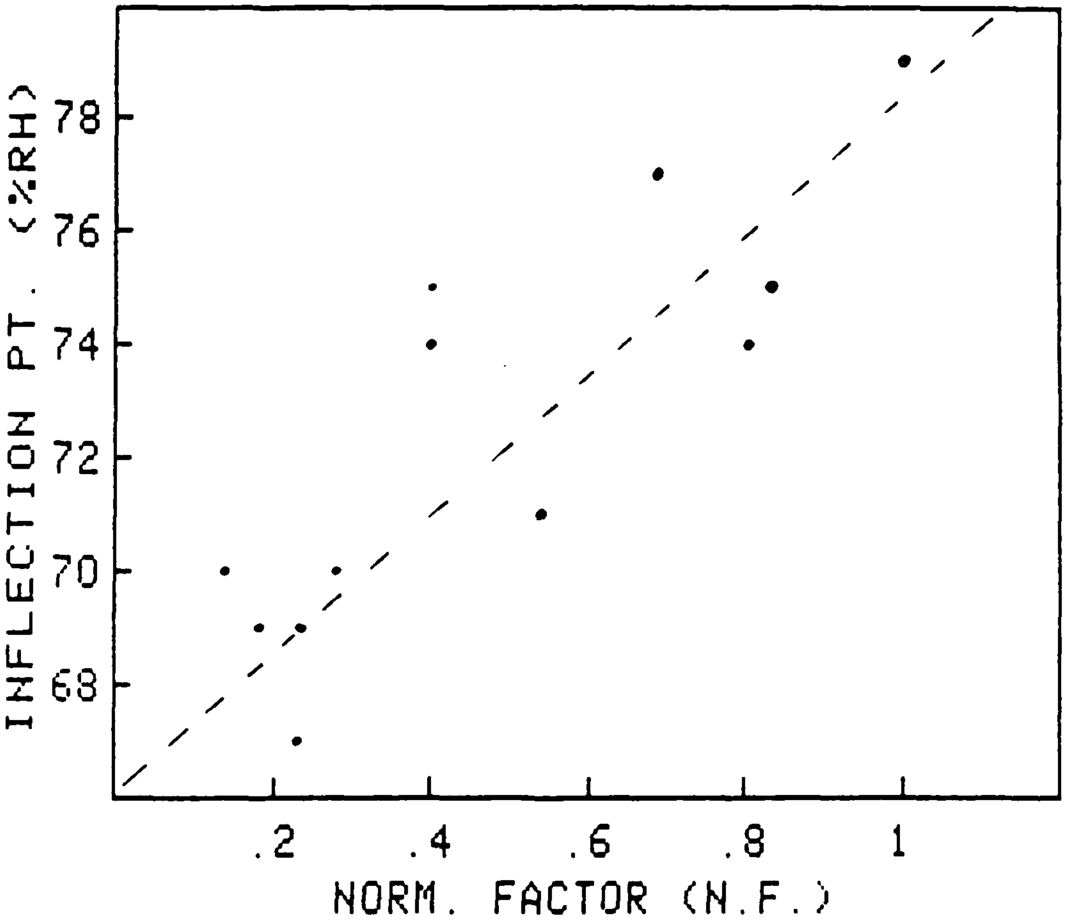
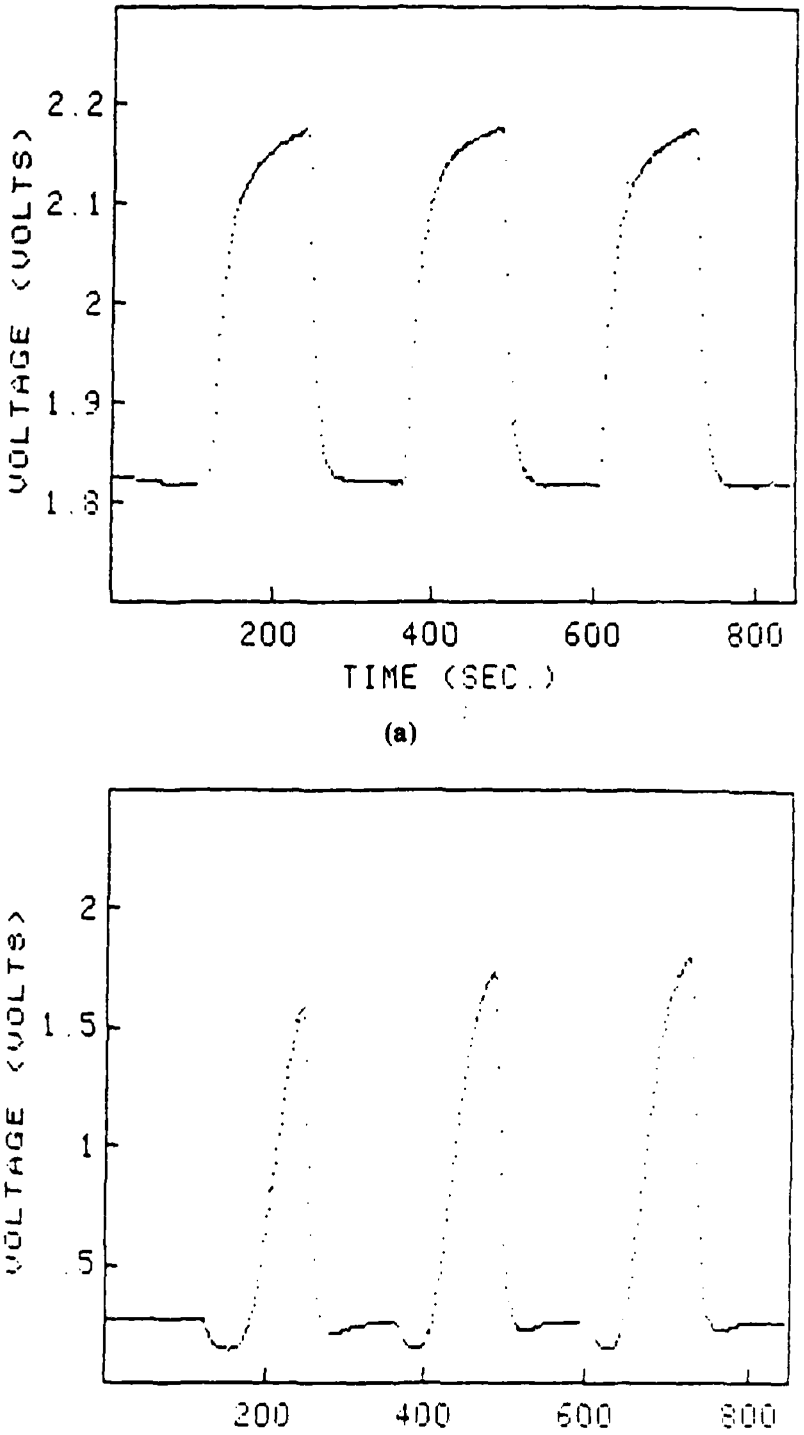


Fig. 6 — Plot of inflection points (% RH) vs normalization factor (N.F.). For details regarding the determination of the N.F., see text.



(a)

(b)

Fig. 7 — Response vs time curves for different film thicknesses: (a) thin film (AB#5), (b) thick film (DIP#1).

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