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A COMPARISON OF THREE EQUILIBRIUM RELATIVE HUMDITY MEASURING DEVICES

M.J. Snavely*, J.C. Price** and H.W. Jun**

* Searle Reseach and Development, 4901 Searle Parkway, Skokie, Illinois 60077, Correspondence

** University of Georgia, College of Pharmacy, Athens, Georgia 30260

ABSTRACT

Three different types of equilibrium relative humidity measuring devices, capable of measuring the equilibrium relative humidity of a hygroscopic sample, were compared. The devices were: 1) a Container Hygrometer Apparatus, 2) a Dew Point Apparatus and 3) a Digital Hygrometer Apparatus. The devices were tested for accuracy of relative humidity measurement by generating atmospheres of known relative humidity in the sample compartments of the devices. The Digital Hygrometer Apparatus was found to be the device of choice for routine measurements, as it had acceptable accuracy over a wide range of humidites, and was easy-to-use. This device was used to measure the equilibrium relative humidity of a mixed-sugar tablet diluent at two different moisture contents.

INTRODUCTION

It is common practice to study the interaction of water vapor with hygroscopic pharmaceuticals using classical isopiestic methodology;[1,2] i.e., the total water contents of the samples are measured after equilibration in different controlled humidity atmospheres, and a sorption isotherm is generated. Direct measurement of the equilibrium relative humidity of hygroscopic pharmaceuticals, although of value to the formulation scientist, has been rarely reported, possibly because suitable instrumentation has been unavailable, expensive or difficult to use. Such measurements have been used to study the influence of moisture on the stability of various foods.[2,4] Recent advances in humidity sensing technology, including lower equipment prices, have made it possible to make such measurements at reasonable costs and, with suitable choice of instrument, acceptable accuracy. This study compares three different types of humidity sensing devices.

EXPERIMENTAL

Temperature Measurement And Control

The humidity measuring instruments under study were maintained at 25 $\pm$ 0.2^{o}C by placing them in glass water circulation chambers insulated from external temperature changes by a styrofoam box. Instrument temperatures were measured with a Type K subminiature thermocouple probe connected to a Keithley Digital Thermometer (Model 871; Keithley Instruments; Cleveland, OH). The temperatures of the circulation chambers were controlled by a constant temperature circulation bath.

Humidity Measurement

Container Hygrometer Apparatus (Fig. 1)

This instrument (Model A-2507; Perfector Scientific; Atascadero, CA) contains a fiber type sensor with a dial readout. The hygrometer top fits tightly into an aluminum sample container. Sample relative humidities were read from the instrument dial. The manufacturer's specifications are: Range = 35 - 95% RH; Accuracy = ± 3% RH.

Dew Point Apparatus (Fig. 2)

This device, which was designed and constructed using component parts, consists of a highly polished sterling silver mirror mounted on a thermoelectric cooling module (Single Stage Cooling Module - Model 930-7; Borg Warner Thermoelectrics; Chicago, IL) which is in turn mounted on a heat sink. The top and base of the apparatus were built using clear plastic, and were made airtight by means of an o-ring seal. The temperature of the mirror was monitored using the above digital thermometer by embedding the thermometer probe into the mirror; the mirror was visually observed for dew (or frost) formation, at which time the temperature of the dew point was recorded. The process was repeated in triplicate, and the dew point temperatures averaged.

Digital Hygrometer Apparatus (Fig. 3)

The sensor for this instrument (LCD Hygrometer - Model 24-3309-50; Cole-Parmer Instruments; Chicago, IL) consists of a special capacitor whose capacitance changes predictably with humidity. The sensor probe was sealed internally and externally with silicone rubber sealant to ensure an airtight seal with the sample compartment top. The sample compartment

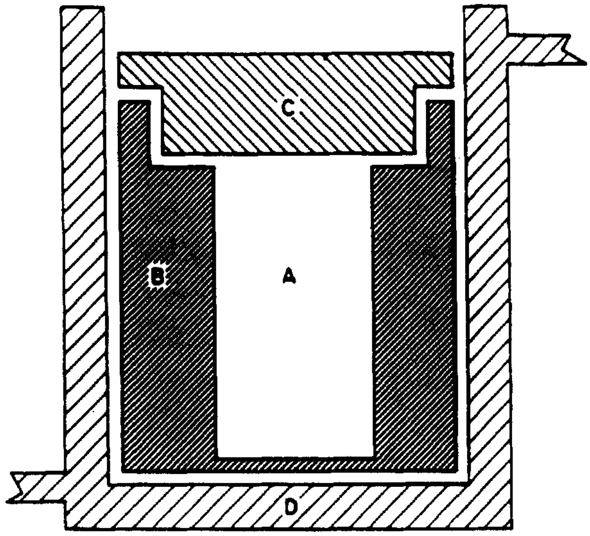

FIGURE 1

Container Hygrometer Apparatus. Key: A. Sample Compartment; B. Aluminum Base; C. Dial Type Hygrometer; D. Glass Circulation Chamber

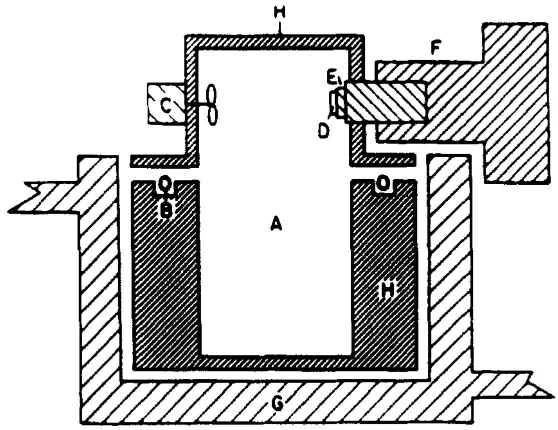

FIGURE 2

Dew Point Apparatus. Key: A. Sample Compartment; B. O-Ring Seal; C. Equilibration Fan; D. Mirror; E. Thermoelectric Cooling Module; F. Heat Sink; G. Glass Circulation Chamber; H. Plastic Top and Base

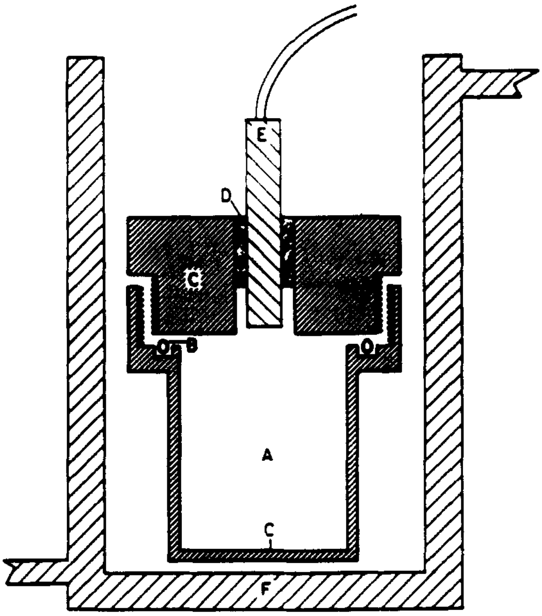

FIGURE 3

Digital Hygrometer Apparatus. Key: A. Sample Compartment; B. O-Ring Seal; C. Plastic Top and Base; D. Silicone Rubber Sealant; E. Digital Hygrometer Probe; F. Glass Circulation Chamber

consists of a plastic top and base hermetically sealed by an o-ring. Sample relative humidities were read from the instrument's digital readout. The manufacturer's specifications are: Range = 10 - 95% RH; Accuracy = ± 2% RH, ± 1 digit.

Instrument Calibration And Performance

Standard atmospheres of known relative humidities were generated in the sample compartments of the instruments by using the selected saturated salt solutions[2] listed in Table 1. The relative humidity of the sample compartments were monitored until

TABLE 1

Saturated Salt Solutions

Saturated Salt Solution	Relative Humidity at 25.0°C
Potassium Acetate	22.51
Magnesium Chloride	32.78
Magnesium Nitrate	52.89
Cobalt Chloride	64.92
Ammonium Chloride	78.57
Potassium Nitrate	93.58

equilibrium was achieved, as indicated by a change of less than one percent in the instrument reading over a 24 hour period. Humidities recorded from the Container Hygrometer and the Digital Hygrometer were obtained after calibrating the instruments at 53% RH. All measurements were repeated in triplicate and averaged.

RESULTS AND DISCUSSION

The data obtained from the instrument performance experiments were evaluated by calculating the percent error as follows:

$$\% \text{ Error} = [(RH_E - RH_L)/RH_L] \times 100$$

where (RH_E) and (RH_L) are respectively the experimental and literature relative humidities; Fig. 4-6 are plots of the percent error *versus* RH. The experimental relative humidities for the Dew Point Apparatus were calculated *via* the definition of relative humidity; i.e., at a given temperature:

$$RH = (P/P_o) \times 100$$

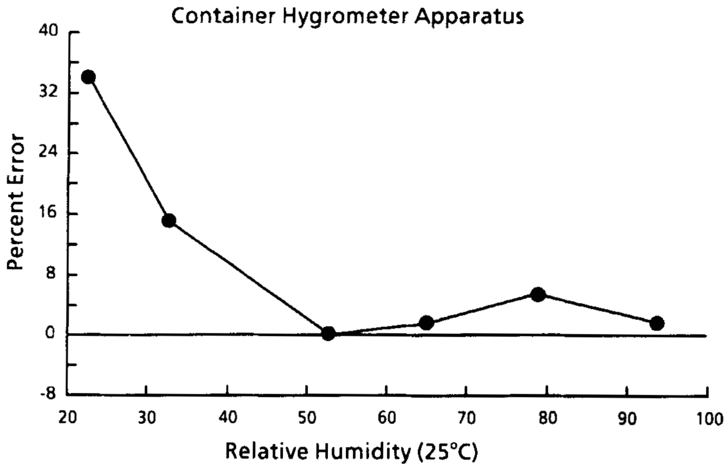

FIGURE 4

Percent error of indicated relative humidity reading at various relative humidites. Adjusted to zero error at 53 % RH.

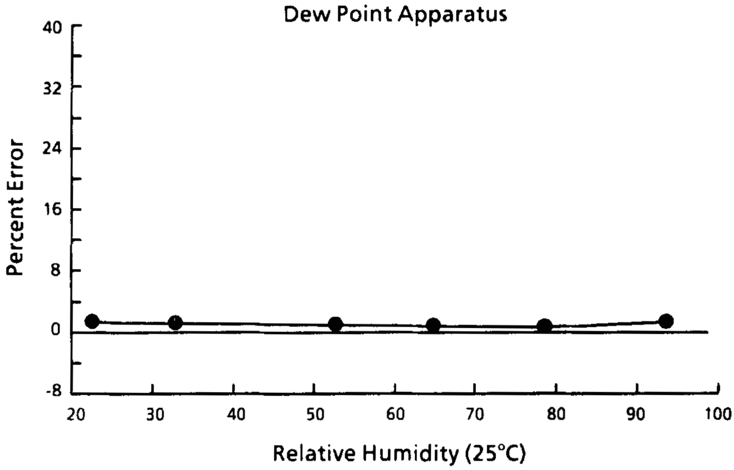

FIGURE 5

Percent error of indicated relative humidity calculated from measured dew point temperatures at various relative humidities.

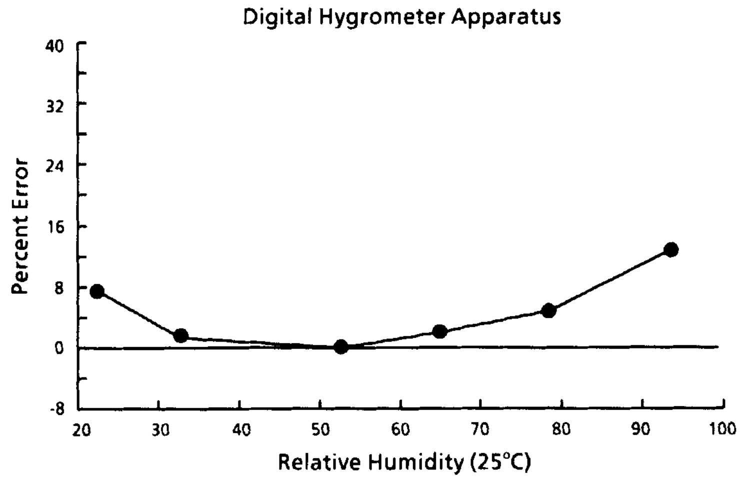

FIGURE 6

Percent error of indicated relative humidity reading at various relative humidites. Adjusted to zero error at 53 % RH.

where (P) is the water vapor pressure of the sample and (P_o) is the vapor pressure of pure water. Sample water vapor pressures were determined by measuring the dew point temperature of the sample vapor, and obtaining the saturated water vapor pressure for the dew point temperature from standard water vapor pressure tables;[3] (P_o) was also obtained from these tables. The results of these studies are summarized as follows:

1) The Container Hygrometer Apparatus measurements (Fig. 4) differ from the literature values reported for the saturated solutions by 1.5 to 34.2%. Measurements made within the manufacturer's specifications, 35 - 95% RH, had a maximum error of 5.4%. Studies done with the hygrometer top in a controlled relative humidity atmosphere at 25°C and 33% RH showed only a 4.5%

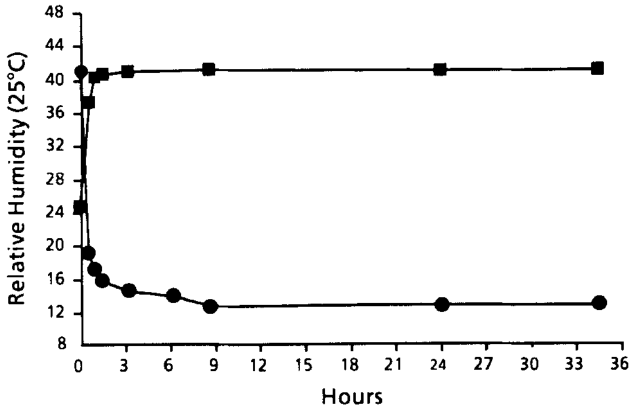

FIGURE 7

Relative humidity of Emdex at two moisture contents as a function of time. Key: ● = 1 % moisture; ■ = 8 % moisture

error compared to 15% for the Container Hygrometer Apparatus, indicating that the seal between the top and the base was not airtight.

2) The Dew Point Apparatus results (Fig. 5) differed from literature reports by only 0.6 - 1.3%. Thus, the instrument showed good accuracy over a wide range of humidities. Although the device has the disadvantage of requiring manual operation, it does provide direct water vapor pressure measurements and is likely to maintain it's accuracy for a sustained period of time. Therefore, the apparatus is useful in the calibration of other instruments. Instruments with automatic dew point sensors are commercially available.

3) The Digital Hygrometer Apparatus results (Fig. 6) differed from literature values by a maximum of

12.7%. Under the conditions of the study, the instrument's accuracy was considered to be acceptable between relative humidities of 33 - 53%. The device has the advantage of digital display of relative humidities, requiring only that the humidites be read from the digital readout.

Fig. 7 is a plot of the relative humidities, as measured by the Digital Hygrometer Apparatus, of Emdex^R (Edward Mendell Co., Carmel, NY) at two different water contents as a function of time. Emdex^R is a mixed-sugar direct compression tablet diluent. From Fig. 7 it can be seen that, at 25^{o}C, the equilibrium relative humidity of the 1% moisture sample is approximately 14%, while the equilibrium relative humidity of the 8% moisture sample is approximately 41%. Equilibrium relative humidity data obtained in such a manner is useful in determining the optimum relative humidity of the manufacturing environment of hygroscopic pharmaceuticals. Such measurements may also find use in studying the stability of hydrolabile drugs in the presence of moisture containing excipients. Furthermore, the instrumentation reported here is capable of measuring sample relative humidities at different temperatures, which may be useful in analyzing the results of accelerated stability studies.

CONCLUSION

Three devices capable of measuring the equilibrium relative humidity of hygroscopic samples were tested. Of the three, the Dew Point Apparatus was the most accurate, but required the most time and attentiveness to read. The Digital Hygrometer Apparatus was easy-to-read, and had reasonable accuracy over a wide range. All three instruments should be adjusted for minimum error using a suitable standard in the humidity range of interest. The Digital Hygrometer Apparatus was used to measure the relative humidities of two Emdex^{R} samples, with different total water contents, as a function of time.

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