

Measurement of Indoor Relative Humidity Using a Passive Sampler for Water Vapour

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Abstract

As part of the energy and indoor climate survey recently carried out in Sweden (the ELIB study) a simple, inexpensive but reliable passive sampler for estimating monthly averages of relative humidity has been developed. The diffusion sampler consists of a 5 ml plastic tube prepared with lithium chloride monohydrate ($\text{LiCl} \cdot \text{H}_2\text{O}$) as trapping medium. After necessary calibration of this particular design of sampler the relative humidity can be calculated from the weight change of the sampler, the time of sampling and the average temperature during this period. The estimated accuracy of the method is better than $\pm 2\%$ RH up to 65% RH.

Introduction

The nation-wide energy and indoor climate survey recently conducted in Sweden, the so-called ELIB study (Norlén and Andersson, 1993), involved extensive investigations of some 1500 dwellings. One of the indoor climate factors included in the study was the relative humidity, measured as the average over one month. The magnitude of the field survey made the use of conventional humidity probes and data loggers inconceivable. In response to the need for much simpler and less expensive devices, attention was focused on the possibilities of employing a passive sampling technique.

Two categories of passive samplers for water vapour can be identified; one is based on the adsorption and desorption characteristics of hygroscopic materials, and the other on the diffusion of vapour through an orifice to a reference medium of known equilibrium vapour pressure. The former type was recently employed in a field survey comprising some 130 dwellings in Denmark (Nielsen, 1989; Bergsoe, 1990). Small blocks of beech wood were pre-conditioned at a known relative humidity and weighed before and after exposure. The difference in weight was then used to estimate the relative humidity with an uncertainty of $\pm 5\%$ RH using the sorption isotherm for beech wood. This type of device results in a kind of moving average with the significance of previous humidity conditions declining as the exposure continues.

As time-weighted averages over a whole month are useful and compatible with other variables measured in the ELIB study, the integrating type of sampler represented by the latter category above was chosen. Samplers based on this concept, using silica gel or concentrated sulphuric acid as trapping medium, were originally described by Palmes and Gunnison (1973), and more recently by Girman et al. (1986), who considered a modification employing molecular sieve. None of these devices was designed

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for exposures longer than approximately one week, partly because of the limited water absorption capacity of the trapping media being used. Another complication with silica gel and molecular sieve is the interference from, primarily, carbon dioxide. Especially under conditions of low humidity, errors in the observed weight gains would be unacceptable without correction.

In order to eliminate the inconveniences mentioned, lithium chloride monohydrate ($\text{LiCl} \cdot \text{H}_2\text{O}$) was in the present case chosen as the trapping medium. In equilibrium with its saturated solution this hydrate has a water vapour pressure corresponding to 11–13% RH within the range of temperatures prevalent in dwellings (Wexler, 1965; Gál, 1967). In addition, at each temperature the water vapour pressure remains virtually constant as long as the absorbed amount of water is kept below about 50% of the initial weight of the pure monohydrate (Hougen, 1954). As compared with other desiccants LiCl has an unusually high capacity to absorb water without any phase transformations. All these circumstances make lithium chloride monohydrate a suitable trapping medium in passive samplers for water vapour.

The purpose of this article is to describe and evaluate the moisture measuring device developed for the ELIB study. The results of the actual survey, however, were recently reported by Norlén and Andersson (1993) and Tolstoy (1993).

Theory

According to Fick's first law of diffusion, the sampling rate J in a diffusion tube is directly proportional to the difference in vapour pressure at the orifice of the tube and at the absorption medium at the bottom:

$$J = \frac{DA}{L}(c_0 - c_i) \quad (1)$$

where D = Diffusion coefficient of water vapour in air

A = Cross sectional area of the tube

L = Diffusion length of the tube

c_0 = Water vapour concentration of the ambient air

c_i = Water vapour concentration at the trapping medium interface.

In the present case, where the sampler is used for

measuring relative humidity, Equation 1 may be developed into the following expression:

$$\text{RH}_{\text{air}} = 100 \left(\frac{\Delta m L}{v_s D A t} \right) + \text{RH}_{\text{LiCl}} \quad (2)$$

where RH_{air} = Relative humidity of the ambient air

Δm = Weight gain (or loss) of the sampler

v_s = Average saturation water vapour concentration

t = Exposure time

RH_{LiCl} = Relative humidity at the trapping medium interface.

Thus, provided that the sampling characteristics of the tube are known from calibration tests, the relative humidity can be calculated from only three variables which are readily obtained, namely:

- the weight change of the sampler,
- the time of sampling, and
- the average temperature during this period (which in turn gives v_s).

Experimental

The passive sampler developed consists of a 5 ml polypropylene tube with screw closure of high-density polyethylene (Nalgene Cryovial). The overall length of the tube is 85 mm and the inner diameter is 9.7 mm.

The preparation of ($\text{LiCl} \cdot \text{H}_2\text{O}$) was made by dissolving anhydrous LiCl in water at 90°C until saturation and then letting the solution cool down to room temperature. This procedure ensures that the desired hydrate be formed and also maximizes the exchange of monohydrate. The excess salt solution was then separated from the monohydrate crystals by filtering with a filter pump. The pure monohydrate was stored in an airtight jar.

The sampler was prepared by placing about 1.5 g of ($\text{LiCl} \cdot \text{H}_2\text{O}$) at the bottom of the tube. A glass fibre filter disc was inserted and pressed against the salt hydrate crystals. The apparent diffusion length varied slightly from tube to tube but was typically 58 mm. The initial weight of each sampler without closure was about 4.5 g. Weighing of the samplers was made with a precision of 0.01 mg.

The sampler in its final modification, as used in

the ELIB study, is shown in Figure 1. In this case, two glass fibre filters were inserted into the tube, one close to the salt hydrate and another closer to the orifice of the tube. The reason for this will be further dealt with below. Also seen in the figure is the simple holder, made from corrugated cardboard, used to mount the sampler on the walls of the studied dwellings.

Calibration of the diffusion sampler was performed in 1.5 l polyethylene jars prepared with different salt hydrates representing relative humidities in the range 11 to 79% RH. Constant temperatures, 15, 20 and 25 °C, were maintained by keeping the jars in a climatic cabinet during testing. Six samplers were tested in parallel in each jar and at each temperature. The exposure time was 3 weeks or longer. A Protimeter DP989M dew point meter was used to continuously monitor the relative humidity and temperature in one jar at a time. The accuracy of the dew point meter is $\pm 1\%$ RH according to the manufacturer. The initial tests, however, which were performed at 20 °C, employed a Rotronic MP-100 humidity-temperature probe with an estimated accuracy of $\pm 2\%$ RH.

In principle, the sampling rate $\frac{\Delta m}{t}$ together with tabulated values for the diffusion coefficient D as a function of the temperature could be used in Equation 2 to calculate RH_{air} . However, this procedure turned out to provide insufficient accuracy when attempting to predict the relative humidities used as references during the calibration tests. Instead, the quantity DA in Equation 2 was fitted to the measured data by linear regression using the temperature as independent variable. In this way, any

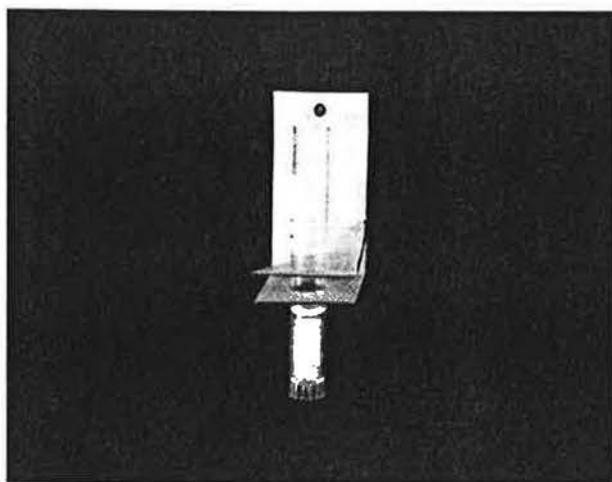


Fig. 1 The passive sampler for water vapour used in the ELIB study.

unknown calibration constant should be taken care of automatically.

As a final test, measurements with the calibrated sampler described were carried out in laboratory air for one month. Six samplers were tested in parallel while monitoring the relative humidity and temperature with the dew point meter connected to a data logger. Intermittent weighings and readings made it possible to compare the obtained values also after shorter intervals.

In all the calibration tests only one filter disc was inserted in the tube. This disc primarily has the function of keeping the salt crystals in a fixed position at the bottom of the tube. During the initial stage of moisture up-take, the volume of the salt crystals and the saturated LiCl solution formed will be smaller than that of the original pure monohydrate. This can be related to the difficulty of compacting the fresh salt crystals at the bottom of the tube. When moisture is taken up by the salt crystals their morphology will change and the air between the crystals will gradually be replaced by the saturated salt solution, which results in a denser structure. After this stage the volume will increase with increasing moisture up-take and eventually exceed the original volume defined by the position of the glass fibre disc. There are two implications of the salt solution penetrating the glass fibre disc and not remaining at a fixed volume. First, the risk of salt solution leakage while handling the sampler and, secondly, the gradual change in diffusion length during exposure.

To diminish the risk of salt solution leakage and also, possibly, to minimize air convection in the tube, it might be necessary to introduce more filter discs mounted closer to the tube orifice. To this end, the influence of up to 8 filters in the same diffusion tube has been studied at 79% RH, 20 °C for about 3 weeks.

The second implication mentioned above should initially lead to a decreasing sampling rate and then, when the volume starts to increase, an increasing sampling rate. On the other hand, since the monohydrate is consumed during measurement, the sampler will eventually contain only the saturated LiCl solution. When this happens the sampling rate should gradually decrease as the equilibrium vapour pressure is no longer constant. To get an idea of the magnitude of the decreased trapping efficiency, two extremes of sampler were prepared. One was of the ordinary type with pure monohydrate while the other was prepared only with saturated LiCl solu-

tion. The test was conducted in laboratory air for more than 3 weeks using six parallels of each type.

From a practical point of view, samplers may have to be prepared and weighed several weeks, or even months, before the actual exposure period begins, i.e. when the screw closure is removed. Since the permeability of water vapour in most plastics is not negligible, the initial weight of the sampler may change during storage. In order to study the magnitude of this effect, six samplers with the screw closures on were stored in laboratory air for about six months. The gradual weight change was checked on various occasions during this period.

Results

The mean sampling rate during approximately three weeks is shown in Figure 2. Each data point represents the mean value of six samplers. The highest standard deviation observed among these data was 0.023 mg/h, a quantity that is too small to illustrate in Figure 2. The sampling rate is always zero when the relative humidity of the ambient air is the same as that maintained by the salt hydrate, i.e. in this case about 11% RH irrespective of temperature. The sampling rate seems to be a linear function of the relative humidity at all three temperatures up to about 70% RH. The only deviation observed is at 20°C and 79% RH where the sampling rate has decreased in relation to the other conditions. This indicates that the rate determining step no longer is the diffusion of water vapour in air but is governed by the efficiency of the trapping medium interface to absorb the water vapour.

The linear regression analysis of DA as depending variable made use of the sampling rates obtained at 15 and 25°C. The data at 20°C were not included

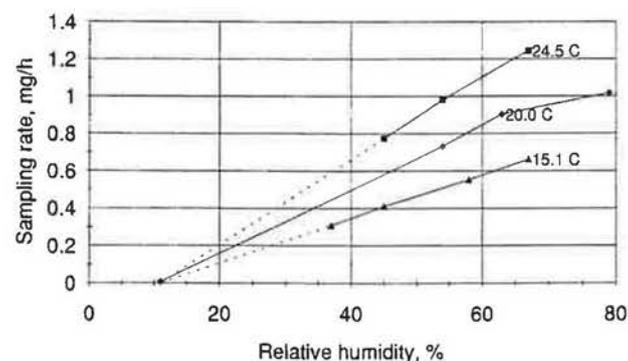


Fig. 2 Mean sampling rate of six diffusion samplers during three weeks as a function of the relative humidity at 15, 20 and 25°C, respectively.

since the reference values for the relative humidity were considered less accurate. In total, 42 observations were used in the regression analysis, yielding the following expression for DA, where 'T' is the temperature in °C:

$$DA = (1.231 + 0.01656 \cdot T) \cdot 10^{-9} \quad (\text{m}^4/\text{s}) \quad (3)$$

The coefficient of variation obtained for DA was 1.77%. After inserting the expression for DA in Equation 2 it was possible to estimate the reference RH-values used in the calibration. A comparison of the values calculated in this way, and the actual reference values is made in Figure 3.

As a matter of curiosity, the diffusion coefficient D can be obtained by dividing Equation 3 with the cross sectional area

$$A = \pi \cdot \left(\frac{9.7 \cdot 10^{-3}}{2} \right)^2 = 7.4 \cdot 10^{-5} (\text{m}^2):$$

$$D = (16.7 + 0.224 \cdot T) \cdot 10^{-6} \quad (\text{m}^2/\text{s}) \quad (4)$$

This expression gives a slightly lower value for D at room temperature and shows a stronger temperature dependence than is found in standard tables and handbooks. It should be pointed out, however,

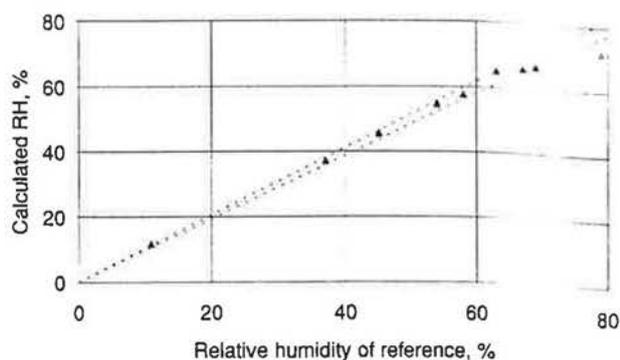


Fig. 3 RH-values calculated from Equation 2 after calibration compared with the measured reference values. The dotted lines represent the estimated standard deviation, $s_{RH} = 0.03 \cdot RH_{ref}$.

Table 1 Average RH-values at different times obtained from six diffusion samplers in comparison with average dew point meter values. Total exposure time is one month.

%RH for	Exposure time, hours					
	90	167	262	332	548	740
Diffusion samplers	42.2	39.7	34.7	35.0	36.1	36.4
Dew point meter	43.0	40.2	35.4	35.6	36.4	36.4
Difference	-0.6	-0.5	-0.7	-0.6	-0.3	±0.0

Table 2. Influence on sampling rate of glass fibre filters inserted into the diffusion tube. Exposure made at 79% RH, 20°C for three weeks.

	Number of filters					
	0	1	2	2	4	8
Sampling rate, mg/h	1.043	1.062	1.036	1.063	1.032	1.021
Relative difference, %	-	1.8	-0.7	1.9	-1.1	-2.1

that this study was neither meant to determine D nor has involved adequate methodology to do so.

The results of the one-month test of six samplers in the laboratory air are shown in Table 1. According to the dew point meter the relative humidity varied between 16 and 49% during the entire test period of one month. The standard deviation of the calculated RH-values for the six samplers was $\pm 0.2\%$ RH or less at all checkpoints.

The comparison of pure monohydrate and saturated LiCl-solution as trapping medium was performed during three weeks when the relative humidity varied in the range 15–27% RH and the temperature was between 25 and 27°C. The average sampling rate of six ordinary samplers resulted in 0.234 ± 0.005 mg/h while that of the samplers with saturated solution was 0.197 ± 0.003 mg/h, a decrease of about 16%. In this case the corresponding RH-values were 20.6 and 19.1% RH.

The influence of glass fibre filters can be studied in Table 2 where the sampling rates and their relative difference are compared for different numbers of filters. No significant difference can be seen in these values, which shows that the filters can be used without reservation. As a consequence of this result, the samplers used in the ELIB study were prepared with two filters, as shown in Figure 1.

The weight change during six months of storage in laboratory air ($\sim 35\%$ RH, $\sim 25^\circ\text{C}$) was $+6.45 \pm 0.06$ mg. This increase in weight will introduce an error in the final RH-estimate which is in the order of $+0.5\%$ RH, see Table 3.

Table 3 Sensitivity analysis of RH_{air} using Equation 2. The exposure time $t = 744$ h. The weight gain Δm varies with the RH-level.

Variable	Reference	input error	$\Delta\text{RH}_{\text{air}}$ at level		
			20% RH	40% RH	60% RH
L	58 mm	-1 mm	-0.1	-0.5	-0.9
T	20	+0.5°C	-0.3	-1.0	-1.7
Δm	varies	+5 mg	+0.4	+0.4	+0.4

Discussion

The results presented indicate that the passive sampler developed can be used to estimate average indoor relative humidities, or even absolute humidities, for exposure times of up to about one month. Absolute humidities are needed, e.g., when the moisture production in a dwelling is to be estimated, see Tolstoy (1993). For most other aspects of moisture which may be related to the indoor climate, the relative humidity is the most relevant quantity to consider.

The accuracy of the present method depends on several factors. To begin with, the error in the initial calibration of the method should be reflected in the coefficient of variation obtained for the quantity DA in the regression analysis. Further, when the methods is used in practice the variance of RH_{air} according to Equation 2 may be expressed in a simplified form as:

$$s_{\text{RH}_{\text{air}}}^2 = \text{RH}_{\text{air}}^2 \cdot \left(\frac{s_L^2}{L^2} + \frac{s_{v_s}^2}{v_s^2} + \frac{s_{DA}^2}{(DA)^2} \right) \quad (5)$$

The errors in Δm and t can be neglected in this context. Assuming that $s_L/L = 1/58$, $s_{v_s}/v_s = 0.3/17.28$ and using the coefficient of variation from the regression analysis $s_{DA}/DA = 0.0177$, the total variance may be estimated to $s_{\text{RH}_{\text{air}}}^2 = \text{RH}_{\text{air}}^2 \cdot 9.1 \cdot 10^{-4}$. Consequently, the standard error can be written as $s_{\text{RH}_{\text{air}}} = \text{RH}_{\text{air}} \cdot 0.03$.

This estimate is valid as long as the relative humidity stays below about 65% RH and the temperature keeps within the approximate range 15–25°C. The one-month test performed in laboratory air may be regarded as a strong indication of the validity of the error estimate made previously.

One error which has been neglected in the previous analysis has to do with the non-linear dependence of the saturation water vapour concentration on temperature. Since v_s is calculated from the average temperature over the whole measuring period,

this procedure will always underestimate the true average of v_s . Thus, the simplification made can be expressed in the following way, where n denotes an arbitrary number of samples taken during the measuring period:

$$v_s = v_s \left(\sum_n \frac{T_n}{n} \right) \leq \sum_n \frac{v_{sn}(T_n)}{n} \quad (6)$$

As an extreme example, assume that the temperature is 18°C for 2 weeks and 22°C for 2 weeks, which will result in an average of 20°C over 4 weeks. The left side of Equation 6 will then be 17.28 g/m³, whereas the right side will be (15.36 + 19.41)/2 = 17.39 g/m³. The relative difference between these two values is 0.6%. In practice, the temperature distribution around the average is very narrow which makes the error in v_s much lower than shown in the above calculation.

During exposure of the sampler, the gradual increase in diffusion length from 58 to typically 63 mm followed by a decrease down to, say, 52 mm at the end of the exposure, will cause corresponding changes in the sampling rate. These variations can be seen in the results presented in Table 1. This dynamic effect is included in the original calibration and need not be corrected for specifically. The essential thing is to measure the initial diffusion length as accurately as possible. Improvements of the design of the sampler can, of course, be made to eliminate the uncertainty which is related to the varying diffusion length.

Additional errors may be introduced when the method is being used under actual field conditions. Such errors could be due to e.g. draughty conditions, temperature differences between the diffusion sampler and the temperature sensor, lack of discipline and consistency while performing all steps in the measurement procedure, etc. From a strictly physical point of view, however, the temperature measurement and the variation in diffusion length will be the most important sources of error. The influence of these factors on the final result is best illustrated by varying them one by one using Equation 2. The result of this analysis is shown in Table 3. Also, the significance of the weight increase during storage of the sampler, typically 1 mg per month at 35% RH, can be studied in Table 3. Obviously, the sampler may be stored for several months before a repeated weighing would be necessary.

If the measuring period is one month, the sam-

pling rate must be lower than 1 mg/h to avoid complete dissolution of the salt hydrate. This corresponds in Figure 2 to a relative humidity below 55% RH and a temperature below 25°C. Consequently, as far as Scandinavian conditions are concerned, a decreased trapping efficiency will not occur very often, and if so, only for a very short period of time. The maximum magnitude of this effect at 65% RH and 25°C can be estimated at about -2% RH, based on the 16% lower sampling rate observed for the saturated solution. If the method described should be considered for conditions outside the ones specified here, there are several possibilities of modifying the sampler to meet the various demands that may arise.

Conclusions

A simple and inexpensive diffusion sampler for water vapour has been developed and tried out. Using lithium chloride monohydrate as trapping medium, the sampler estimates monthly averages of the indoor relative humidity of up to about 65% RH at temperatures between 15 and 25°C. However, the validity of the sampler can probably be extended outside this temperature range. The accuracy of the method after calibration is better than ±3% of the obtained value, i.e. better than ±2% RH at 65% RH. The sampler described was successfully used in the energy and indoor climate survey recently carried out in Sweden, (the ELIB study), which involved extensive investigations of some 1500 dwellings.

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