# THE EFFECT OF AIR TIGHTNESS ON RH BUFFERING AND CONTROL

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## *ABSTRACT*

It has been known for over thirty years that air exchange rate is fundamental to the hygrometric performance of display cases. However, the expense of commercial testing services and the unavailability of methods had severely limited testing. The availability of relatively inexpensive equipment and the use of simplified methods has resulted in at least a fifty fold increase in the number of air exchange rate measurements undertaken in the UK. Coupled with developments in measuring technologies for relative humidity, which has allowed more widespread and more accurate monitoring, a corpus of data now exists to assess the effect of different air exchange rates on RH buffering and control within display cases and storage enclosures. These results demonstrate that in most instances where attempts to control the hygrometric performance of enclosures has failed, air (or moisture) exchange is the key variable. The potential major drawback of tightly sealing showcases, besides cost and time, is the concentration of off-gassed products from objects, dressing or construction materials. The carboxylic acids are by far the most widely reported culprits of adverse effects on objects inside showcases and storage enclosures. Diffusion tube based measurements are ideal to determine carboxylic acid concentrations inside such enclosures and a body of such data has now been acquired. Methanoic acid emissions from paint have been shown to follow existing models. Ethanoic acid concentrations from MDF were found to increase dramatically at air exchange rates below 0.5.

## *INTRODUCTION*

Besides providing security for their contents, the most common conservation use for showcases is to protect against relative humidity fluctuations or to allow the display of artefacts in environments that are known to be aggressive. It has been known for over thirty years that air exchange rate, AER is fundamental to showcase performance in this area [1,2,3,4]. However, the expense of commercial testing and the unavailability of methods has severely limited testing. The development of affordable methods has allowed air exchange rates to be measured in a large number of showcases [5]. This, coupled with developments in measuring technologies for relative humidity, which have allowed more widespread and more accurate monitoring, has generated a corpus of data for assessing the effect of different air exchange rates on RH buffering and control within showcases and enclosures. Many institutions are using air exchange rate in the specification criteria for new showcases. Better knowledge of its effects can lead to better targeted, cheaper specifications.

The existing models for RH buffering and control capacity have been tested and their predictions compared to monitored data. A number of applications for calculating the performance of showcases and requirements for conditioning have been developed.

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## *METHODS*

Air exchange rate has been measured using carbon dioxide tracer gas decay following the broad method discussed in Calver et al [5]. All measurements were made with a Vaisala GMP70 data-loggers and probes. The probe was placed centrally on the base of the case and 5000 ppm of carbon dioxide injected. An initial measurement of the carbon dioxide concentration in the case before injection was made and subtracted from all subsequent readings. The air exchange rate was calculated, averaging over 72, 96 or 120 hour periods to account for diurnal effects.

Temperature and RH measurements were made with Meaco or Hanwell radiotelemetry systems, with either Rotronic Hygrostop or Vaisala Humicap probes, Hanwell Humbug dataloggers with Humicap probes, or Smartreader SR002 dataloggers. All sensors were calibrated annually with a three point RH calibration traceable to UK National Physics Laboratory standards via the UK National Accreditation Measurement Service. In all instances temperature and RH were measured in the room space as well as the enclosure.

Where the amount of buffer could be accurately measured, ie large amounts of silica gel in enclosures with relatively little other reactive hygroscopic material, the hygrometric half life was calculated using the formula developed by Thomson [2]. The interior RH was then modelled from the room RH by simple iteration. Since there is a lag in internal RH, using the initial RH as the starting point for the model means the results are influenced by earlier RH. Better experimental fits were obtained by allowing the initial RH to vary in 1% RH intervals, 5% above and below the initial measured internal RH. The modelled RHs were compared by eye and the 'best' initial RH selected. Thomson's model assumea isothermal conditions between the case and the room and instant equilibrium of the whole buffer mass with the immediately adjacent air. Modelling was also undertaken based on the formula developed by Tetrault and Weintraub, which accounts for non isothermal conditions [6].

For cases where the amount of buffer could not be accurately measured (constructed from wood or wood based materials), modelling was applied by varying the hygrometric half life. The best half life model was determined as that with the minimum root mean square deviation between the model and the measured RH inside the enclosure. Knowing the air exchange rate of the case, the mass of buffer per unit volume was then calculated from Thomson's equation.

Carboxylic acid concentrations inside showcases were measured using diffusion tubes exposed for twenty eight days and analysis by ion chromatography [7]. Measurements were made every three months to account for the large seasonal variation in carboxylic acid concentrations in showcases containing wood products in naturally conditioned buildings. This is because large seasonal variations in temperature and RH dramatically influence carboxylic acid emissions from wood products and paints and the air exchange rates of showcases.

Since the major hygroscopic materials present in showcases exhibit hysteresis over part of the RH range found in buildings, their performance differs when the enclosure is drier or wetter than the room and when they are working at an RH below the hysteresis region or in it [8]. Hysteresis can have a dramatic effect on the buffering capacity of silica gels, with the $B_H$ value (defined in the appendix) in a limited RH interval being much less than expected from the sorption chart [8].

### *Silica gel as the only buffer in the enclosure, drier than outside, below hysteresis on the isotherm*

Archaeological iron can be amongst the least stable of materials and can rapidly deteriorate at RH levels above 16%. Many institutions use polypropylene boxes with silica gel to store archaeological iron. Since reliable low RH indicators are expensive and the volume of material is large, modelling the RH and hence the replacement time of the silica gel has been undertaken. Four models were tested and over thirty boxes in four different stores monitored over a period of two years. The Thomson and Tetrault and Weintraub models were found to give excellent results, with the Thomson model being computationally easier [9]. A web based application has been developed to allow other institutions to apply the model to their collections.

In order safely to display vulnerable archaeological metals in damp environments a standard showcase design incorporating silica gel has been developed and extensively tested with twelve cases in four different locations. An air exchange rate of 0.4 $day^{-1}$ was specified for these cases from calculation using the iteration of Thomson's equation described previously and RH and AER measurements of existing desktop showcase designs [10]. The designs were found to exceed the specification and managed to retain an RH close to 20% for over twelve months in environments of up to 90% RH. A representative case is shown in Figure 1. Both the Thomson and the Tetrault and Weintraub models gave excellent results. One would expect Thomson's model to begin to fail if there are

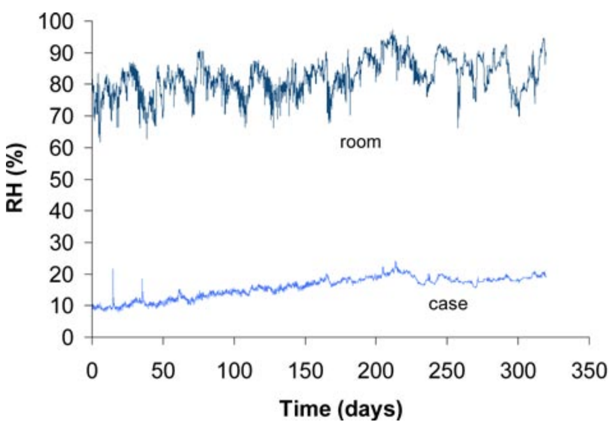


*Figure 1. Conditions inside standard 'EH1' showcase at Pevensey Castle. The RH is maintained close to 20% for eleven months.*

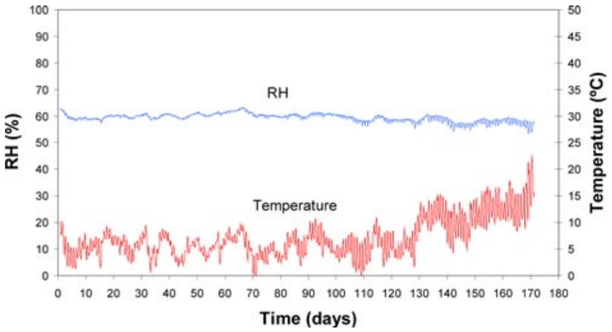


*Figure 2. Lullingstone coffin case. The RH is maintained within a 10% band by use of an airtight case and Prosorb.*

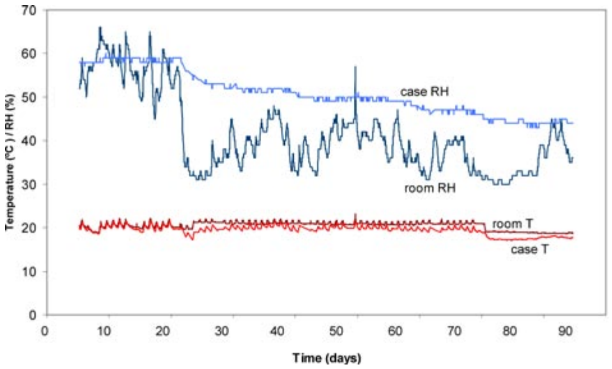


*Figure 3. Down House case. The RH is maintained above 40%, during the winter/spring heating period.*

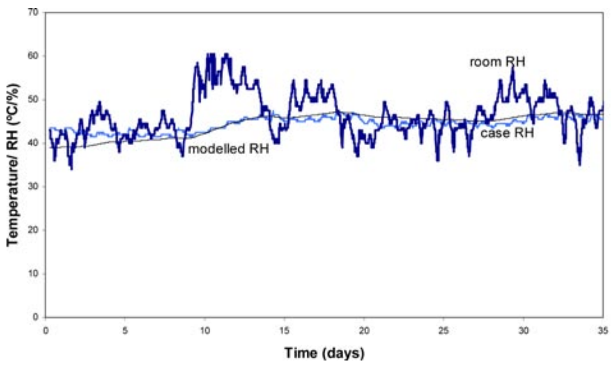


*Figure 4. Apsley House cases. Modelled and measured RH. The model correctly describes the general trend, but under-estimates short term RH variations.*

temperature differences between the showcase and the outer space. Since these cases are not internally lit and direct sunlight illumination of the cases has been intentionally excluded, the temperature difference is negligible (less than 0.5ºC).

*Silica gel as the only buffer in an enclosure, drier than outside, in hysteresis region on isotherm*

Both regular silica gel and then Prosorb have been used in a showcase containing a lead coffin and skeleton, displayed in a damp building. Initially the case fluctuated between 25 and 65% RH using normal silica gel, replaced with dry gel at six month intervals. Reducing the air exchange of the case and replacing the regular silica gel with Prosorb allowed much better control, 50-65%, and removed the dangerous low RHs when the silica gel was changed (figure 2).

*Silica gel as only buffer in enclosure, wetter than outside in the hysteresis region of isotherm.*

Three showcases displaying natural history collections in a house that is thermostatically heated for human comfort were found to have dangerously low RH throughout the winter and spring. Since their performance was inadequate, they were resealed. This reduced the air exchange rates from 4.5, 4.9 and 6.2 per day to 0.7, 0.6 and 0.8 per day, improving the cases' performance to acceptable levels, retaining an RH above 40% throughout the heating period (figure 3).

*Some hygroscopic materials, ambient RH*

It is difficult to estimate the amount of buffer available in a showcase constructed of wood. Not only is it difficult in retrospect to calculate how much wood is in the case, but the slow penetration of water vapour into wood means that it is likely that the whole thickness of the wood is not contributing to the buffering effect. This means that even knowing how much wood is present and its sorption curve will not necessarily give an accurate measure of the buffering potential. A series of ten nineteenth century showcases used to display silver has been investigated. The empirical, numerical approach described earlier has been used. The best fit half life was determined from the minimum square root variation. As can be seen in figure 4, the Thomson model gives a good overall fit, but underestimates the short term variations in humidity, particularly the daily variations driven by temperature changes. This is not unexpected, as wood responds slowly to changes in RH, with short term changes causing rapid equilibration at the surface of the wood, but longer term changes taking several days for deeper wood to respond [11]. The amount of buffer reacting, the B value in the model, therefore depends on the time scale of the RH changes and a single hygrometric half life as predicted from this approach would be inadequate.

*Silica gel and hygroscopic materials, ambient RH*

A series of measurements over three years on nine showcases with artsorb, has shown that cases with an air exchange rate above one per day were unable to maintain a 40% to 60% RH band over a period of ten months [12]. The placing of the artsorb within the display plinths in the cases means that all the densely displayed objects have to be removed to change it and the opening of the house means this is extremely difficult until the winter closed period.

### Mechanical control

In order successfully to control the RH inside a showcase or enclosure, a mechanical control system needs to be able to supply or remove water vapour to the air, faster than it is entering or leaving the showcase. The ingress or egress rate can be calculated from the air exchange rate and internal and external hygrometric parameters. Depending on the closeness of control required, one may need to consider the instantaneous rates, as these can vary significantly over the diurnal cycle.

### Circulating systems

A major new exhibition in the gatehouse at Kenilworth Castle required close environmental control for vulnerable loan material in a room with a known poor environment. The recent marketing of a close control, low maintenance circulated system for showcases, Miniclima EB08 and 09, appeared an ideal solution for this application. In order to prove the technology to lenders, a unit was placed in a showcase in the foyer of the English Heritage head office. Its performance was monitored over a year and found to be suitable. To expand the data set and define the showcase specification, air exchange rate measurements were undertaken on showcases at the Post Office Museum. This institution had Miniclima units installed three years ago (the earliest installation in the UK) and monitoring confirmed their performance. The required conditioning load was determined from a year of environmental monitoring data in the proposed exhibition space, and from loan conditions. Combined with the Post Office Museum data and foyer trials, this information was used to develop the showcase air exchange rate specification. After installation of the exhibition in April, the monitored data has been compared to the specification. The results are shown in Table 1. All of the cases except one performed as predicted. The tapestry case showed a series of short lived temperature and RH spikes around 4 pm every day over the late autumn. These coincided with infra-red illumination of the compartment containing the conditioning unit through a single white blind on one of the windows. This increased the compartment temperature, reducing the dehumidification capacity of the Peltier unit in the conditioning unit. Improving ventilation in this compartment by adding a fan drawing air into the compartment overcame this.

| Case | Air Exchange Rate ($day^{-1}$) | Volume ($m^3$) | Control range (%) | Percentage time within range |
|---|---|---|---|---|
| tapestry | 0.11 | 4.5 | 45-55 | 99.47 |
| paintings | 0.59 | 6 | 45-55 | 100 |
| manu-scripts | 0.86 | 0.67 | 50-60 | 100 |
| leather | 0.69 | 1.2 | 45-55 | 100 |

*Table 1. Performance of Cases Controlled by Miniclima Units*

The RH failure times for the showcases, meaning the period that they will retain acceptable RH conditions after the mechanical control device has failed, was calculated for different additions of Prosorb to the showcases. Within this time, the mechanical systems would need to be repaired or replaced or the objects would need to be removed to safe storage. For the Kenilworth exhibition, the remoteness of the site, lack of specialist staff and use of a foreign made conditioning system all mean that response time is likely to be relatively long. Therefore, 8kg/$m^3$ of Prosorb was incorporated into every showcase. In the event of a system failure this was calculated to provide a window of twenty days in which to respond, by repairing the control unit or moving the objects affected to safe storage, before the case climate would move outside the specified loan conditions.

When the loan of objects in one case finished they were replaced with low vulnerability stone artefacts. The Miniclima unit was turned off and the performance of the case compared to the model described above. Extremely good agreement was observed, as shown in Figure 5.

### Dehumidifiers

Ducted Munters dehumidifiers are used in showcases at Peveril Castle and in the Mesopotamia and Ancient Levant Galleries in the British Museum. These contain

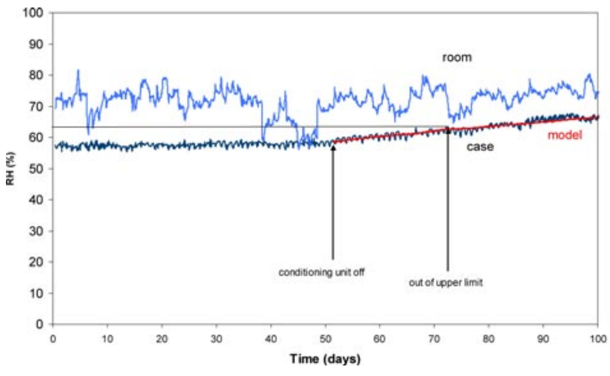


*Figure 5. Modelled and measured RH inside a showcase after the conditioning unit was switched off. Note the good agreement with the modelled failure time.*

| Construction | Glass | Glass | Perspex |
|---|---|---|---|
| Volume ($m^3$) | 2 | 2 | 0.5 |
| Air Exchange Rate ($day^{-1}$) | 20.46 | 6.52 | 4.09 |
| RH range (%) | Percentage of readings in RH range | | |
| <20 | 0.05 | 3.15 | 28.00 |
| 21-25 | 0.33 | 12.56 | 44.36 |
| 26-30 | 8.68 | 59.89 | 22.47 |
| 31-35 | 60.50 | 24.40 | 4.68 |
| 36-40 | 29.32 | 0.00 | 0.50 |
| 40-42 | 1.00 | 0.00 | 0.00 |
| 42-43 | 0.10 | 0.00 | 0.00 |

*Table 2. Performance of Cases Controlled with Dehumidifiers*

vulnerable archaeological copper alloys showing signs of bronze disease. The conditioning systems aim to keep the RH below 42%. The air exchange rates of the cases and the annual distribution of RH values are shown in Table 2. As can be seen cases with air exchange rates of 7, and below maintain RHs below 42% while the one with a higher AER just fails.

The instantaneous dehumidification requirement for a series of showcases displaying human bones in a wet church was calculated from the specified air exchange rates of the cases, their volumes, the measured temperatures and relative humidities in the church and the desired RH of less than 65%. The results are shown as figure 6. The required dehumidification load is well below the capacity of the unit selected (minimum of 110g/$m^3$ over the measured temperature range).

### *Limitations of this approach*

The Thomson model works reasonably well provided there is no significant temperature difference between the enclosure and the room. If there are significant differences, because of internal lighting or sunlight, then that approach will break down. Modelling using the Weintraub and Tetrault equation in these conditions would require an estimate of

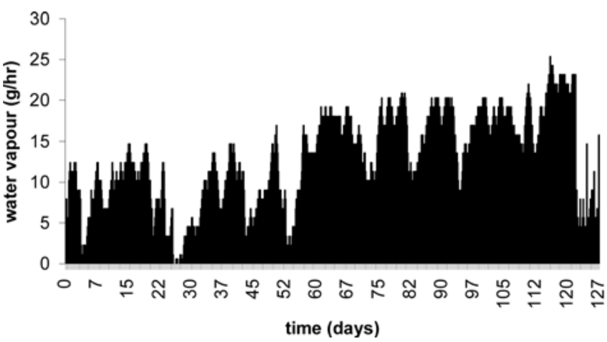


*Figure 6. Modelled instantaneous dehumification load at St Peter's Church, Barton. The required water vapour removal rate is below 30g/hr.*

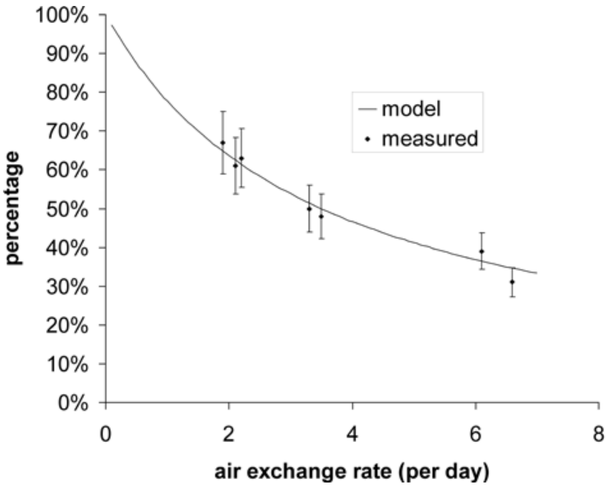


*Figure 7. Methanoic acid concentrations inside painted cases at Kenwood House. Concentrations are expressed as a percentage of the equilibrium concentration expected inside a perfectly sealed enclosure. The line is the modelled concentration from Meyer and Hermanns [15].*

the internal temperature, which is not a trivial exercise. The temperature differences will be strongly varying with time, due to lighting during opening hours and sunlight heating being a function of room and window geometry, orientation and time of the year. This would require intimate knowledge of crack and hole location and dimensions [13], which is unlikely to be readily available and in many instances can be extremely difficult to determine.

### *Methanoic (formic) acid emission from paint*

Application of an unsuitable paint to the inside of a series of wooden cases caused dramatic corrosion of jewellery solder. A series of carboxylic acid measurements confirmed that emission of methanoic acid was causing the corrosion, which had been identified as a lead methanoate by x-ray diffraction. A series of refits to increase the air exchange rate was undertaken on four cases to reduce the concentration. A case with similar initial concentration was measured as a control through out this work. Methanoic acid emission from paints is likely to be a strong function of temperature and a control was needed to quantify this effect [14]. The series of concentrations and air exchange rates allowed testing of the Meyer and Hermanns model [15].

The measured methanoic acid concentrations ratioed against the equilibrium concentrations, determined from the control case concentrations and air exchange rates, are shown in figure 7. As can be seen, the concentrations fall well onto the predicted values.

A set of showcases at the British Museum constructed over the past twelve years using similar designs and materials was selected to give a range of air exchange rates. Cases without objects that could be sources of carboxylic acids were selected and the surface area of an internal source, Moistop sealed MDF base and back boards, was measured [16]. All other materials in the showcases had undergone and passed accelerated corrosion tests with lead, indicating an extremely low emission rate of carboxylic acids.

The air exchange rates, and ethanoic acid concentrations are shown in Figure 8. Summer measurements are significantly higher as both temperature and RH increase the emission rate from wood products [17]. The acid concentration increases dramatically when the AER drops below 0.5. This result has important ramifications for showcase design. However the geometry of a showcase may affect this relationship. All the showcases investigated here were approximately 2m high, 0.5 to 1m deep and 2 to 4 m wide, with 'pull and slide' doors as the front face.

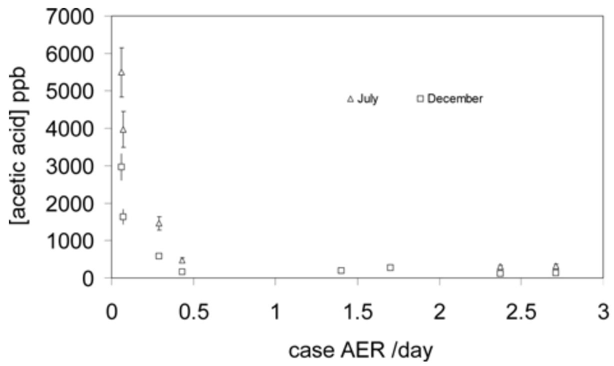


*Figure 8. Ethanoic acid concentrations in a series of cases at the British Museum. Concentrations increase sharply when AER drops below 0.5 per day. Summer concentrations are higher, because higher temperature and RH increase the emission rate from medium density fibreboard.*

## CONCLUSIONS

As expected the absolute importance of air exchange rate on an enclosure's ability to buffer or have the RH controlled within it, has been confirmed. The equations developed by Thomson and Tetrault and Weintraub have been verified and shown to have significant potential to predict the internal environment of enclosures from climate data for rooms and parameters for the enclosures. The predictions are not comprehensive; empirical methods are required when the amount and type of buffering material is not known (wooden carcasses). Surprisingly, the Weintraub and Tetrault equation does not appear to give better results, even when lighting causes internal temperature gains of up to 2ºC. The Thomson equation is computationally easier. The data can be used to design enclosure air exchange rate specifications which, coupled with rigorous testing and refitting as necessary, will provide 'guaranteed' internal environments. Of course, changes in room environments and other effects such as infra-red radiation through blinds will affect the internal RH.

Carboxylic acid concentrations increase as the air exchange rate decreases. The Meyer and Hermanns model appears to hold well for methanoic acid emission from paint. However an extremely interesting non linear effect for ethanoic acid in showcases of a particular geometry and construction type has been observed. For this geometry the concentration increases dramatically when the air exchange rate drops below 0.5 per day. If this behaviour is general then it has very important implications for showcase air exchange rate specifications and mitigation of ethanoic acid concentration and its adverse effects on artefacts.

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## *Appendix*

Thomson introduced the concept of hygrometric half life, which while a simplification of reality has provided beneficial insights for many years [2].

$$t_{1/2} = \frac{4\,MB}{N}$$

where t ½ is the hygrometric half life (days)
M is the loading of absorbent in the chamber (kg/m$^3$)
B is the specific moisture reservoir of silica gel (kg/kg per 1%RH)
N is air exchange rate (day$^{-1}$)

Weintraub and Tetrault developed an equation to determine the amount of silica gel required to buffer to a given RH fluctuation, which can be modified to estimate the time taken to reach a given RH [8].

$$t_{RH} = \frac{M_H FB}{C_{eq} DN}$$

where $t_{RH}$ is time to reach a specifed RH (days)
F is targeted range of RH fluctuation (%)
$M_H$ is specific moisture reservoir corrected for hysteresis (no units)
B is loading of absorbent in chamber (kg/m$^3$)
$C_{eq}$ is equilibrium concentration of water vapour (g/m$^3$)
D is decimal difference between external RH and chamber (no units)

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