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## Uncertainty in humidity measurements

*Publication of the EUROMET Workshop P758*

Martti Heinonen  
Mittatekniikan keskus

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## Foreword

In 2003, the EUROMET Humidity Expert Group decided to organise a workshop for harmonising the uncertainty evaluation methods used by the European national humidity standards laboratories. As the co-ordinator of the project, the Centre for Metrology and Accreditation (MIKES) looked for most suitable place and date for the event. Finally, it was decided to arrange the workshop in conjunction with the TEMPMEKO 2004 Conference in Dubrovnik on Monday 21 June 2004. This publication was decided to prepare on the basis of the presentations and discussions at the workshop to make the knowledge and experience share in this fruitful event available as widely as possible.

The workshop was arranged within the EUROMET project P758 as planned. 44 experts from 21 countries representing all continents attended the event. Presentations and live discussions dealt with uncertainty analysis methods when using primary and secondary humidity calibration systems. Attention was particularly paid to the contribution of devices under calibration.

All the practical arrangements of the workshop were carried out by the organisers of the conference, i.e. FSB. I want to express gratefulness to all involved and especially prof. Davor Zvizdic for their efforts which made the event possible. Furthermore, I want thank Stephanie Bell, Jan Nielsen, Jovan Bojkovski, Domen Hudoklin, Günter Scholz, Anders Kendtved and Vito Fernicola for their presentations and contribution to this publication.

Martti Heinonen  
Helsinki 20 September 2004



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# 1 Introduction

Today, increasing emphasis is put on the realistic uncertainty estimation in measurements. The main reason for traceable measurements and establishing measurement standard infrastructures is the need for measurement results that can be recognised by everybody throughout the world. This need can be satisfied only if uncertainties - i.e. the quality of the measurement result - are estimated in a realistic way according to widely recognised methods. This is especially important for national standards laboratories acting locally as the main sources of traceability for calibration laboratories etc.

To support global trade and prevent technical barriers national metrology institutes (NMI) from 38 countries signed the Mutual Recognition Arrangement (MRA) in 1999. Within this arrangement the NMIs officially recognise all the calibration services listed in the appendix C of the MRA. This appendix is often called CMC and is a database maintained by the BIPM. It includes measurement ranges and uncertainties of the highest level calibration services provided by the NMIs. All the services have been reviewed and accepted by all the MRA signatory organisations. The review and approval are carried out in the framework of regional metrology organisations (e.g. EUROMET in Europe) and the international metrology organisation CIPM.

To ensure smoothly progressing approval of CMCs, it is highly important that the methods to evaluate uncertainties are harmonised in some extent. Because the CMCs are for calibration services the stated uncertainties do not include only the components related to the measurement standards but also to the instruments under calibration. Here, "best available" instruments are considered.

The EUROMET Workshop on Uncertainty in Humidity Measurements provided a forum for discussions on the methods to estimate and calculate the uncertainty in humidity calibrations of different types. The objectives of the workshop were:

- harmonisation of the methods in applying the GUM (Guide to the Expression of Uncertainty in Measurement [1]) principles in humidity calibrations
- share knowledge and experience in estimating uncertainty.

The discussions dealt with the uncertainty of the reference value and the influence of the instrument under calibration when using:

- dew-point generator as a primary standard
- relative humidity generator as a primary standard
- humidity generator with a secondary standard
- climatic chamber with a secondary standard.

Especially, discussions on the performance of the "best available" instruments took place in the workshop. As a result of the discussions, common view on the matter was found.

This publication summarises the presentations as well as conclusions of discussions at the workshop.

## 2 Uncertainty in measurements and calibrations

Whenever we are presenting measurement results we are dealing with an estimate (that is often called a measurement result) and an assumption of its quality. In many cases, no direct indication on the quality is given, which makes the users of the results non-equal with respect to each other: If no uncertainty estimation is given and the user of a measurement result has no knowledge on the matters affecting the measurement, his view on the quality of the result is mainly based on the number of decimals or digits presented. On the other hand, a user with large metrological experience uses mainly his knowledge when considering the quality. Even in the latter case, the conclusions drawn from the result is partly based on a guess because the quality was judged without seeing the actual set-up and knowing all the facts available during the measurements. In humidity measurements particularly, the actual uncertainty is often several tens times larger than expected by a non-experienced user.

Obviously, a measurement result without a statement on the measurement uncertainty is incomplete and does not give information enough. We can present the needed information only if we have analysed our measurements and carried out an uncertainty estimation. The depth of the analysis depends on the target uncertainty level: A very rough estimation carried out by an experienced measurer in his/her mind may be good enough in some industrial or environmental applications. At the NMI level, however, a thorough analysis with proper mathematical methods must be used to obtain international recognition.

We must understand that we never know all parameters affecting measurement results. But we have to be able to identify and quantify the parameters contributing the results (i.e. estimate & uncertainty) significantly with respect to the target uncertainty level.

At the Workshop, Stephanie Bell (National Physical Laboratory, UK) presented the background, estimation and calculation of the measurement uncertainty. Her talk covered concepts of measurement uncertainty, approaches to evaluating uncertainty, spreadsheet model (template), generic sources/types of uncertainty, probability distributions, divisors/coverage factors, sensitivity coefficients, correlation, type A and type B evaluations of uncertainty and effective number of degrees of freedom. A short summary of her presentation is given below.

### 2.1 Some facts about measurement uncertainty

#### (“the Four Noble Truths”!)

- Every measurement is subject to some uncertainty.
- A measurement result is incomplete without a statement of the uncertainty.
- When you know the uncertainty in a measurement, then you can judge its fitness for purpose.
- Understanding measurement uncertainty is the first step to reducing it

## 2.2 Understanding the terminology

*uncertainty of measurement:*

Rigorous definition [2]:

parameter associated with the result of a measurement, that characterises the dispersion of the values that could reasonably be attributed to the measurand.

Simplified definition:

quantified doubt about the result of a measurement

### NOTES

1. The parameter may be, for example, a standard deviation, or the half-width of an interval having a stated level of confidence.
2. Uncertainty of measurement can comprise many components.
3. It is understood that the result of the measurement is the best estimate of the value of the measurand and that all components of uncertainty contribute to the dispersion.

## 2.3 Error versus uncertainty

It is important not to confuse the terms error and uncertainty:

- Error is the difference between the measured value and the “true value” of the thing being measured.
- Uncertainty is a quantification of the doubt about the measurement result.

In principle, errors can be known and corrected; but any error whose value we do not know is a source of uncertainty.

Because we never know exactly the actual value of an error or any other parameters affecting the measurement results, they all have uncertainties contributing to the combined uncertainty.

## 2.4 Approach to evaluating uncertainty of measurement:

### Input - formulation - evaluation

- *Inputs* to an uncertainty estimate are list/knowledge of sources of uncertainty in a measurement [model]
- *Formulation* of an uncertainty estimate - “defining the uncertainty calculation” (e.g. in the form of a spreadsheet)
- *Evaluation* - making a calculation (e.g. using the spreadsheet) to get a value of estimated uncertainty for a particular measurement under particular conditions



## 2.5 Eight main steps to evaluating uncertainty

### (homage to the GUM)

1. Decide what you need to find out from your measurements. What actual measurements and calculations are needed to produce the final result? Formulate a mathematical model (including components with an estimate of zero).
2. Carry out the measurements needed.
3. Estimate the uncertainty of each input quantity that feeds into the final result. Find relevant sensitivity coefficients using the mathematical model. Express all uncertainties in consistent terms
4. Decide whether the input quantities would be independent of each other. If you think not, then some extra calculations or information are needed (correlation).
5. Calculate the estimate of your measurement result (including any known corrections for things such as calibration).
6. Find the combined standard uncertainty from all the individual parts.
7. Express the uncertainty in terms of a size of the uncertainty interval, together with a coverage factor, and state a level of confidence.
8. Record the measurement result and the uncertainty, and state how you got both of these.

## 2.6 “Eight steps” to evaluating uncertainty of measurement

1. Think ahead
2. Measure\*
3. Estimate uncertainty components
4. (Consider correlation)
5. Calculate results (inc. known corrections)
6. Find the combined uncertainty
7. Express the result (confidence interval, confidence level coverage factor)
8. Document it

## 2.7 “Eight steps” in depth

### 2.7.1 Think ahead

- The measuring instrument - bias, drift, noise, etc.
- The condition being measured - which may not be stable.
- The measurement process - may be problematic
- Imported uncertainties - e.g. calibration uncertainty (But the uncertainty due to not calibrating is worse.)
- Operator skill
- Sampling issues
- The environment - temperature, air pressure, etc.
- ... and others...

### 2.7.2 Estimate uncertainty components

According to the basic statistics on sets of numbers, you can calculate from repeated measurements:

- an *average* or *mean* - to get a better estimate of the true value
- a *standard deviation* - to show the spread of the readings. This tells you something about the uncertainty of your result.

Figure 2.1 illustrates the mean value and standard deviation when studying a normally distributed population of numbers. Sample standard deviation  $s$  is an estimate of population standard deviation  $\sigma$ .

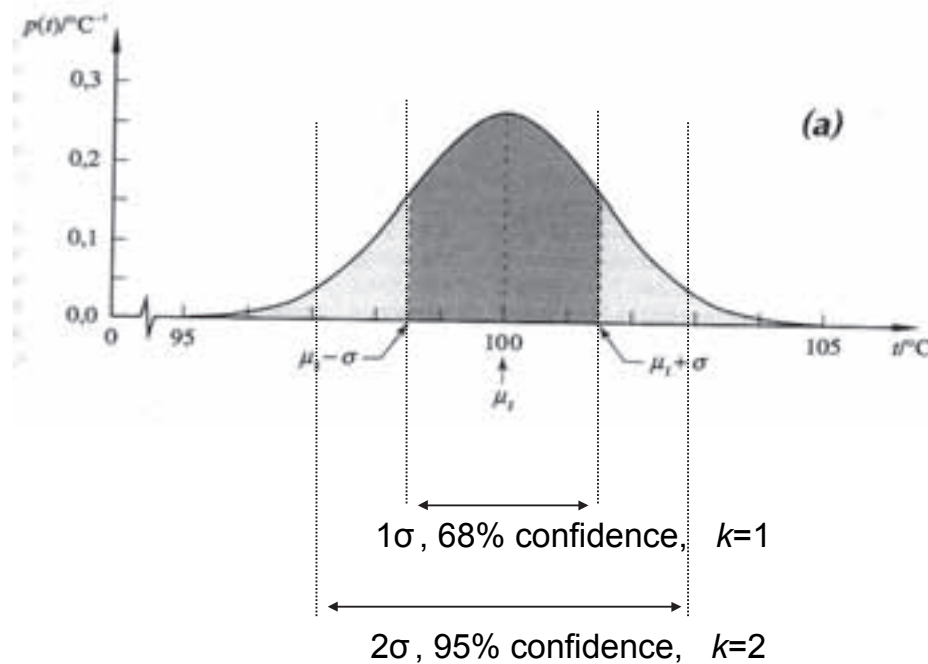


Figure 2.1 Probability distribution and the confidence levels

The two ways to evaluate individual uncertainty contributions are:

**Type A evaluations:**

uncertainty estimation using statistics (usually from repeated readings)

**Type B evaluations:**

uncertainty estimation from any other information, e.g. from:

- past experience of the measurements,
- from calibration certificates ,
- manufacturer's specifications,
- from calculations ,
- from published information and
- from common sense.

It worth noticing that these two methods do not correspond to the difference between random and systematic effects.

Usually, when using type A evaluation we assume to have normal (i.e Gaussian) probability distribution (fig. 2.2). Type B evaluations are often based on the assumption of a rectangular distribution (fig. 2.3).

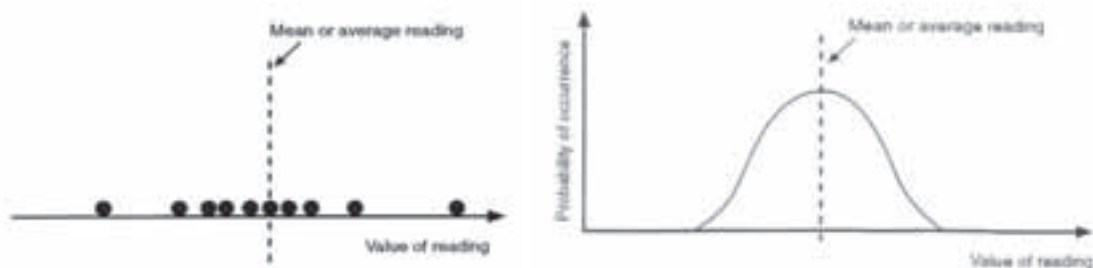


Figure 2.2 “Normal” or Gaussian distribution

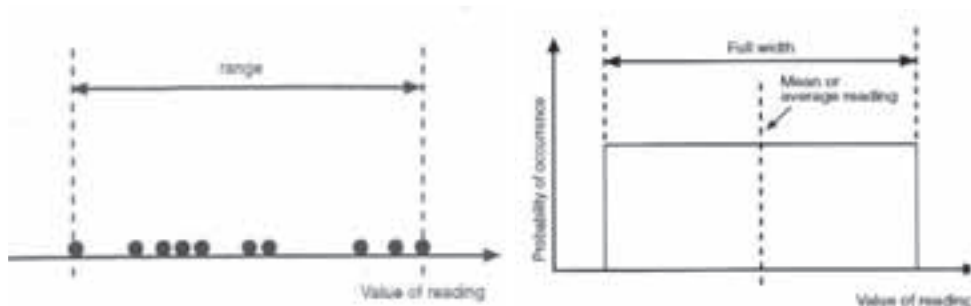


Figure 2.3 Uniform or rectangular distribution

### 2.7.3 Evaluating standard uncertainty

Uncertainties are expressed in terms of equivalent probability. The uncertainty of a mean value is called *standard uncertainty* ( $u$ ), which is derived in the following way:

For a Type A uncertainty evaluation:

$$u = \frac{s}{\sqrt{n}} \quad (2.1)$$

For a Type B evaluation of a rectangular distributed uncertainty:

$$u = \frac{\text{half - width}}{\sqrt{3}} \quad (2.2)$$

In a case of an asymmetric rectangular distribution (e.g. in some cases a pressure correction can be only on one side of the estimate), the Type B evaluation is obtained by dividing the full-width by the square root of 3.

Other typical Type B evaluation is for normal distributed uncertainty (e.g. calibration uncertainty). In this case, the divisor equals to the coverage factor reported for the uncertainty.

### 2.7.4 Combining standard uncertainties

The combined uncertainty ( $u_c$ ) is derived by means of summation in quadrature:

$$u_c = \sqrt{\sum_i [c_i u(q_i)]^2} \quad (2.3)$$

where  $q_i$ ,  $c_i$  are an input quantity and its sensitivity coefficient (see chapter 2.7.7), respectively.

This rule applies where the result is found using addition / subtraction. Other versions of this rule apply

... for multiplication or division

... for more complicated functions

All uncertainties must be at same level of confidence (i.e. all are expressed as standard uncertainties).

### 2.7.5 Correlation

Equation (2.3) is valid only for non-correlating input quantities, i.e. for input quantities that are independent to each other. In many cases a quantity affect another one, which must be taken into account when combining the standard uncertainties. A typical example of correlated input quantities are shown in figure 2.4. When calibrating an instrument, the reading of the instrument (UUT) follows well the deviating reference value (Ref):

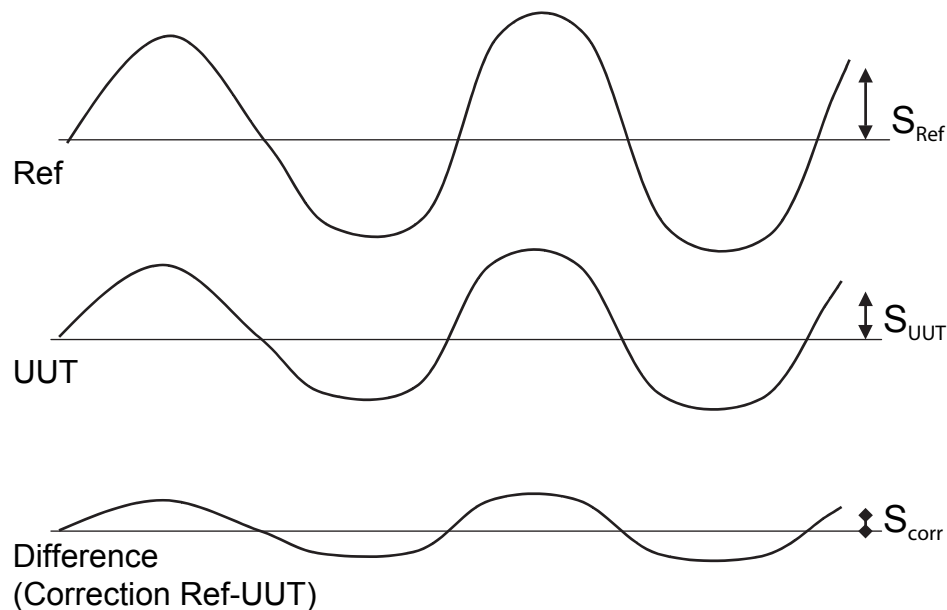


Figure 2.4 Illustration of correlation

Simple quadrature summation of independent standard deviations would suggest:

$$s_{diff}^2 = s_{ref}^2 + s_{UUT}^2 \quad (2.4)$$

but clearly  $s_{diff}$  is far smaller than the combination of the two others.

Because of the correlation, the deviation of the result of calibration (i.e. calibration correction for the UUT = Ref - UUT) is significantly smaller than in a case of non-correlated input quantities.

NOTE: The correlation may increase or decrease the deviation of the result.

The correlation is calculated using:

$$u(\bar{x}, \bar{y}) = \frac{1}{n(n-1)} \sum_{i=1}^n (x_i - \bar{x})(y_i - \bar{y}) \quad (2.5)$$

where  $\bar{x}$ ,  $\bar{y}$  are arithmetic means of the observed values  $x_i$ ,  $y_i$  respectively and  $n$  is the number of measurements. The correlation is taken into account in the uncertainty calculation in the following way:

$$\begin{aligned} u_c^2 &= \sum_i \sum_j c_i c_j u(q_i, q_j) \\ &= \sum_i [c_i u(q_i)]^2 + 2 \sum_i \sum_{j=i+1} c_i c_j u(q_i, q_j) \end{aligned} \quad (2.6)$$

Thus, the combined standard uncertainty in the presented example is (because  $c_{ref} = 1$  and  $c_{UUT} = -1$ ):

$$u_c = \sqrt{u_{ref}^2 + u_{UUT}^2 - 2u_{ref,UUT}} \quad (2.7)$$

Sometimes we know cause-and-effect relationship but sometimes not. If a positive correlation is ignored uncertainty tends to be overestimated. If a negative correlation is ignored uncertainty tends to be underestimated. But when can we safely ignore correlation?

**Answer:** when the covariance uncertainty is much smaller than component variances ( $s_{xy}^2 \ll \text{other } s^2$  and "other  $u$ ")

### 2.7.6 Calculation of results and a mathematical model

The method used for calculating measurement results are described with a *mathematical model*. The model should include all significant components affecting the result (i.e. the estimate and the uncertainty).

With the model, you should be able to calculate the result from the initial data. Thus, relations of all affecting components (incl. the components with different units and components with an estimate of zero) to the final result can be derived from the model.

The model may consist of a single equation or a set of equations. The uncertainty of the measurement result is calculated using the model according to the GUM [1].

### 2.7.7 Combined standard uncertainty: Spreadsheet model

Table 2.1 Calculation using a spreadsheet template

Symbol of the input quantity	Source of uncertainty	Value as the basis for uncertainty estimation	Probability distribution	Divisor	Sensitivity coefficient	Contribution to combined uncertainty	Degrees of freedom
	<i>One row for each input quantity contributing uncertainty</i>						
$u_c$	Combined standard uncertainty		Normal				
$U$	Expanded uncertainty		Normal ( $k=$ )				

The columns are:

- Symbol or reference for an input quantity
- Source of uncertainty:  
brief text description of each uncertainty
- Value as the basis for uncertainty estimation  
a number on which the uncertainty estimation is based. The estimate comes from whatever information you have, such as “worst case limits” or “standard deviation”.  
Units should be shown, e.g. °C, %rh.
- Probability distribution  
rectangular, normal, (or rarely others)
- Divisor  
factor to normalise a value to a standard uncertainty;  
Depends on the probability distribution.
- Sensitivity coefficient  
sensitivity coefficient expressing the effect of a small change in an input quantity to the measurement result. It can be obtained derivating the mathematical model  $F=F(q_0, \dots, q_N)$ :

$$c_i = \frac{\partial F}{\partial q_i} \quad (2.8)$$

The unit of the sensitivity coefficient equals to the unit of the measurement result divided by the unit of the input quantity.

NOTE: The sensitivity coefficient may differ from 1 although the units of the input quantity and the measurement result are the same (e.g. if two measurement standards are used simultaneously in calibration, the sensitivity coefficient of the readings of the standards is 0.5).

- Contribution to combined uncertainty  
standard uncertainty of the input quantity multiplied by the sensitivity coefficient, i.e. “the value as the basis for uncertainty estimation” / “Divisor” x “Sensitivity coefficient”
- Degrees of freedom  
an indication of the reliability of the uncertainty estimate (the uncertainty in the uncertainty!) - sometimes ignored! Even for rectangular distributions, the degrees of freedom is usually finite, sometimes even very small.

The rows are:

- Title row
- One row for each uncertainty
- One row for combined standard uncertainty,  $u_c$ , by summing “in quadrature” and taking square root, i.e.  $u_c = \sqrt{a^2 + b^2 + \dots}$

In a case of significantly correlated input quantities, the correlation is included in the calculation.

The final row shows the expanded uncertainty,  $U = k \cdot u_c$ . Normally, a coverage factor  $k = 2$  is used (giving a level of confidence of 95 percent, as long as the number of effective degrees of freedom  $\nu_{eff}$  is large). There are, however, cases where a dominating component with small number of actual degrees of freedom reduces the  $\nu_{eff}$  so much that a significantly larger coverage factor is needed to obtain the 95 % confidence level.

The expanded uncertainty is what finally should be reported.

### 2.7.8 How to express the measurement result

For reporting a measurement result:

- Write down the estimate and uncertainty of the measurement result, and state how you got both of these.
- Express the uncertainty in terms of a coverage factor together with a size of the uncertainty interval, and state a level of confidence.

### 2.7.9 Coverage factor and degrees of freedom

For expressing the uncertainty at a desired confidence level, you should work with standard uncertainties and then multiply up to the desired value of  $k$

$k = 1$  for a confidence level of approximately 68 %

$k = 2$  for a confidence level of approximately 95 %

$k = 3$  for a confidence level of approximately 99.7 %

These approximations hold true only if your combined uncertainty has “many degrees of freedom” (is based on many measurements, has many sources)

Because the sample standard deviation  $s$  is only an estimate of population standard deviation  $\sigma$ , we make an allowance for the unreliability of statistics on small samples in the following way:

- (weighting with Student’s t factor)
- using Welch-Satterthwaite equation when combining uncertainty components with different number of degrees of freedom ( $\nu_i$ ):

$$v_{eff} = \frac{u_c^4}{\sum_{i=1}^N \frac{u_i^4}{v_i}} \quad (2.9)$$

Number of degrees of freedom  $v_i$  of a standard deviation of  $n$  data is  $n - 1$ . For a worst-case estimate of limits of uncertainty is infinite ( $\infty$ ); which is less intuitive. ( $v_i = \infty$  only if there is no probability at all for a value outside the limits; this is actually never true in real life.)

Interestingly,  $v_i$  can tell us the uncertainty in the uncertainty estimation for the parameter  $q_i$ : [1]:

$$u_r(u(q_i)) = u_r(u_i) \approx 2(v_i)^{1/2} \quad (2.10)$$

- For  $v_i = 500$ ,  $u_r(u_i) \approx 9$  % of uncertainty estimate
- For  $v_i = 100$ ,  $u_r(u_i) \approx 20$  % of uncertainty estimate
- For  $v_i = 30$ ,  $u_r(u_i) \approx 37$  % of uncertainty estimate

Number of degrees of freedom of the combined uncertainty - i.e. number of effective degrees freedom - is calculated using the Welch-Satterthwaite equation.

- If the number of effective degrees of freedom is small the coverage factor must be larger than 2 ( $k > 2$ ) to obtain the 95 % confidence level.
- "Traditionally" we aim for  $v_{eff} > 30$ . In this way, we prevent the need for a further coverage factor analysis. (When  $v_{eff} > 30$  a coverage factor of 2.00 to 2.09 is needed to obtain the 95,45 % coverage probability.)

## 2.8 What is an "uncertainty budget" for?

- To find out what is the uncertainty in your measurement or process
- To demonstrate that you have considered it
- To identify the most important (largest) uncertainties so you can work to reduce them
- To "operate within your budget" (it is actually an "error budget" .... cf "uncertainty analysis")

## 2.9 What is not a measurement uncertainty?

- Mistakes are not uncertainties
- Tolerances are not uncertainties
- Accuracy (or rather inaccuracy) is not the same as uncertainty
- Statistical analysis is not the same as uncertainty analysis



### 3 Uncertainty budget for a dew-point generator

There are many parameters in use to describe humidity of a gas. The humidity, however, can be fully described with a single parameter (any of them) if the gas pressure and temperature are known. Many national humidity laboratories have chosen the dew-point temperature as the primary humidity parameter for practical reasons: As the realisation of a dew-point temperature scale, a dew-point generator provides a simple source of traceability in a wide range at good uncertainty level. (The same generator system may also contain a calibration chamber system providing possibility to realise the units of all other humidity quantities.) A special attention must be paid to the uncertainty analysis because it is the starting point for a complete traceability chain in hygrometry.

The core of a dew-point generator is the saturator. In principle, sample gas (often air) is in thermodynamic equilibrium with plain water or ice in the saturator. Thus, according to the definition the dew-point temperature of the gas in the saturator can simply be determined by measuring the saturator temperature (i.e. air temperature in the saturator). Due to the conservation of mass we can calculate the dew-point temperature of a gas sample drawn off from the saturator ( $t_d$ ) using the following equation:

$$\begin{cases} f(p_s, t_s)e_w(t_s) = x_{ws} p_s \\ f(p_d, t_d)e_w(t_d) = x_{wd} p_d \\ x_{ws} = x_{wd} \end{cases} \quad (3.1)$$

$$\Rightarrow f(p_d, t_d)e_w(t_d) = \frac{p_d}{p_s} f(p_s, t_s)e_w(t_s)$$

where:

- $e_w$  = saturation pressure of pure water vapour
- $f$  = enhancement factor
- $p_d, p_s$  = gas pressure in the outlet and saturator, respectively
- $t_s$  = saturator temperature
- $t_d$  = dew-point temperature of the gas in the outlet
- $x_{wd}, x_{ws}$  = mole fraction of water vapour in the outlet and saturator, respectively.

The equation holds if gas molecules (incl. water vapour molecules) are not absorbed/adsorbed or desorbed by the walls or dead spaces of the flow path between the saturator and the outlet. The equation shows that the saturator temperature and the pressure in the saturator and in the outlet are needed for determining the dew-point temperature outside the saturator.

In reality, there is no such saturator in which complete thermodynamic equilibrium is reached. Furthermore, referring to the previous chapter the saturator temperature nor the pressures cannot be measured with zero uncertainty. Finally, there is no tubing available in which gas molecules are not absorbed/adsorbed or desorbed. These three aspects of non-ideality form the basis for an uncertainty analysis of a dew-point

generator. They may include various components (i.e. input quantities) analysed in various ways.

In the past ten years many papers have been published describing uncertainty estimations for dew-point generators (e.g. [3 - 8]). The publications show that there are many ways to carry out the uncertainty analysis. One must, however, be careful that all significant components are included and estimated in a realistic way. Empirical evidence should be available for the major components.

At the Workshop, Jan Nielsen (NMI-VSL, The Netherlands) presented a method used for estimating the uncertainty of the dew-point temperature scale at NMI. A short summary of his presentation is given below. Further information can be found in his article published in *Metrologia* [9].

### 3.1 What is humidity?

Mostly, when measuring humidity we are determining the amount of water vapour in air or other gases. We measure it as:

- Water vapour pressure (Pa)
- Dew-point temperature (°C)
- Relative humidity (%rh)
- Volumetric concentration (ppm<sub>v</sub>)
- Absolute humidity (g/m<sup>3</sup>)
- etc.

In 1963 L. P. Harrison defined the *dew-point temperature* of moist air as follows [10]:  
The thermodynamic dew-point temperature  $t_d$  of moist air at pressure  $p$  and with mixing ratio  $r$  is the temperature at which moist air, saturated with respect to water at the given pressure, has a saturation mixing ratio  $r_w$  equal to the mixing ratio  $r$ .

Here  $r_w = r_w(p, t_d)$  is the mixing ratio of moist air saturated with respect to a plane surface of clean liquid water when the system consisting of the water and moist air is at a uniform temperature  $t_d$ , ... and the system is at a pressure  $p$  equal to that which exists in the given sample of moist air having the mixing ratio  $r$ .

### 3.2 Ideal primary realisation (1-P generator)

A single pressure generator (1-P) can be used as a primary realisation system for the dew-point temperature. An ideal system would fulfil the following requirements:

- plane surface of pure water in the saturator
- no net heat-exchange in the saturator and 100 % saturation
- no pressure drop
- no net mass transfer of water molecules between the sample gas and the tube walls (or surroundings of the tubing) in the tube connecting the saturator and a dew-point measuring instrument.

In such system, the saturator temperature is equal to the dew-point temperature of the sample gas and  $r_w = r$ .

### 3.3 Basis for an uncertainty budget

Evaluating the standard means that one has to investigate the difference of a practical standard from the ideal primary realisation. The uncertainty is then determined from the difference and the uncertainties in temperature and pressure measurements.

### 3.4 Example: NMI 1-P generator

As an example of a primary realisation for dew-point temperature, figure 3.1 shows a block diagram of the NMI dew-point generator. The operation of the generator is based on the single pressure method:

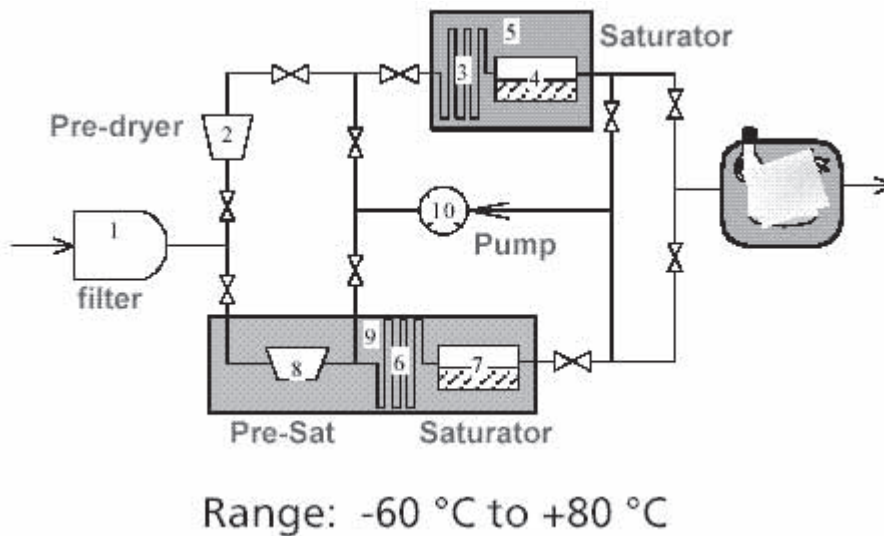


Figure 3.1 Block diagram of the NMI 1-P generator

#### 3.4.1 Efficiency and loading

*Definition:* the air must be fully saturated over a plane surface of water

The level of saturation is evaluated by efficiency and loading tests: A chilled mirror hygrometer was monitoring the output when changing the re-circulation flow-rate (fig. 3.2) and changing the purge flow-rate (fig. 3.3)

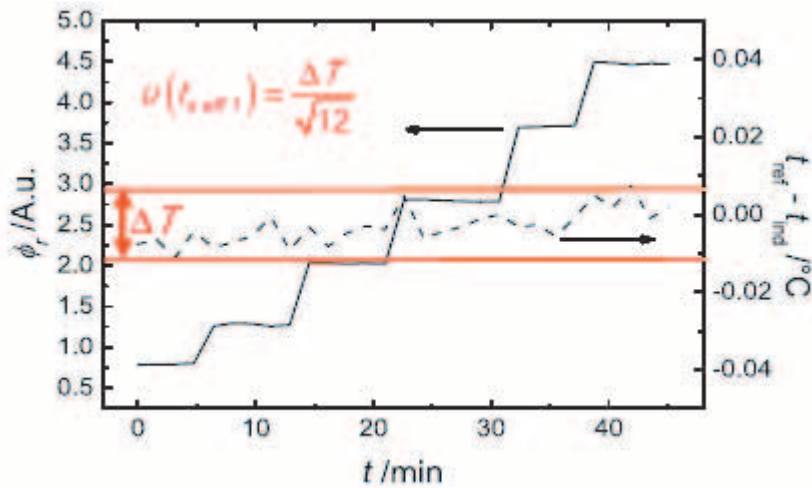


Figure 3.2 Difference between the reference dew-point temperature and the chilled mirror hygrometer reading (dashed line) while changing the re-circulation flow rate (black solid line).

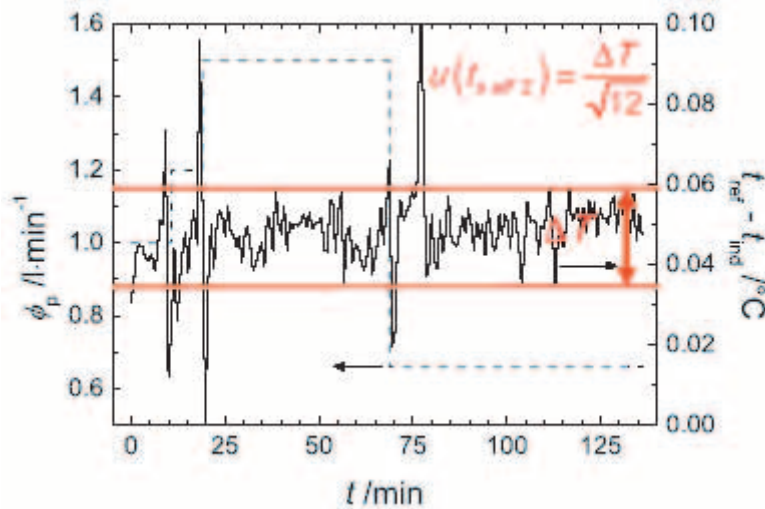


Figure 3.3 Difference between the reference dew-point temperature and the chilled mirror hygrometer reading (black solid line) while changing the purge flow rate (dashed line).

When combining these results we get the uncertainty due to the non-ideal saturation in the saturator as shown in figure 3.4:

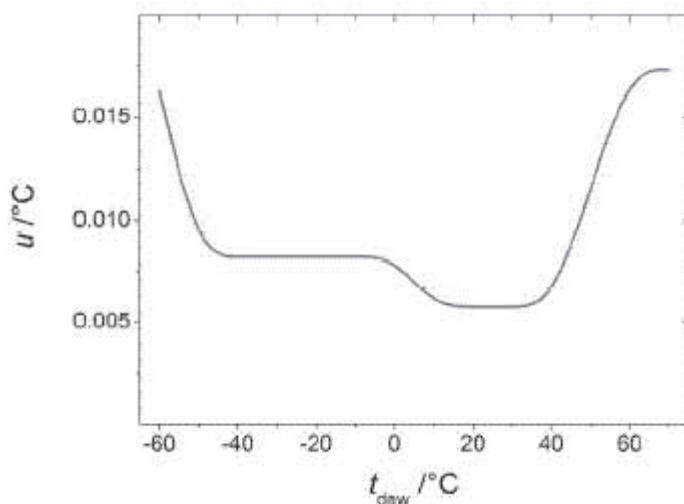


Figure 3.4 Uncertainty determined with the efficiency and loading tests for the NMi 1-P generator.

### 3.4.2 Contamination

*Definition:* The moist air is saturated with respect to a plane surface of clean liquid water.

To obtain a realisation close to the ideal one we:

- use of de-mineralized, filtered water
- check the water quality by comparing with an ICPMS a reference sample with a sample taken from the saturator after running the generator 1 week at  $-50\text{ }^\circ\text{C}$

You can find an example the water quality check in Table 3.1.

Table 3.1 Contamination (ICPMS)

Sample	Reference	Element
0.01 $\mu\text{g/g}$	< 0.01 $\mu\text{g/g}$	Cr
0.01 $\mu\text{g/g}$	< 0.01 $\mu\text{g/g}$	Cd
0.01 $\mu\text{g/g}$	< 0.01 $\mu\text{g/g}$	Ni
0.2 $\mu\text{g/g}$	< 0.01 $\mu\text{g/g}$	Cu
0.15 $\mu\text{g/g}$	< 0.01 $\mu\text{g/g}$	Pb
0.2 $\mu\text{g/g}$	0.2 $\mu\text{g/g}$	Ca
0.5 $\mu\text{g/g}$	0.2 $\mu\text{g/g}$	Si
3 $\mu\text{g/g}$	< 0.01 $\mu\text{g/g}$	Zn

Heat-exchangers

According to Raoult's law, the detected contaminations cause a depression of 0.2 mK in the dew-point temperature.

### 3.4.3 Temperature measurement

*Definition:* ...the system consisting of the water and moist air is at a uniform temperature...

The uncertainty of temperature measurement includes:

- calibration of sensor and indicator
- long-term stability, resolution
- Self-heat of sensor
- Stability and uniformity of saturator temperature

In our example, the contributions of the thermometer related components are summarised in figures 3.5 and 3.6. Measurement results shown in figure 3.7 illustrate the stability of the temperature in the saturator. The standard uncertainties due to the instability and non-uniformity of the saturator temperature are shown in figure 3.8.

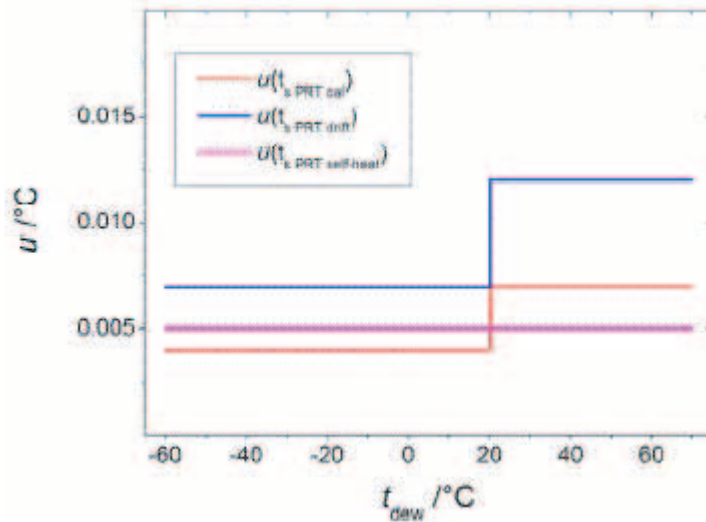


Figure 3.5 Uncertainty components related to the temperature sensor of the saturator.

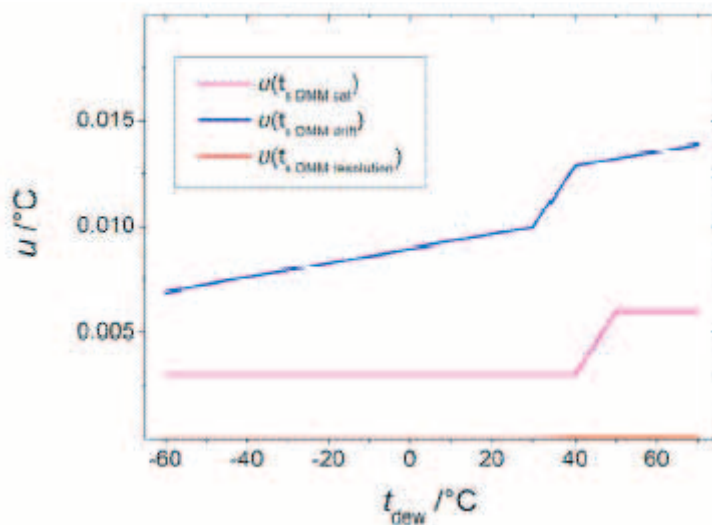


Figure 3.6 Uncertainty components related to the temperature indicator used in the saturator temperature measurements.

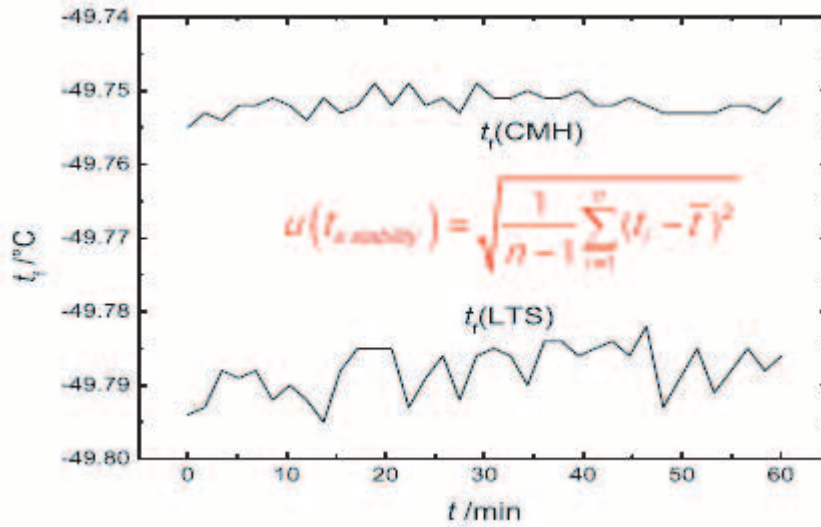


Figure 3.7 An example showing stability of the saturator temperature.

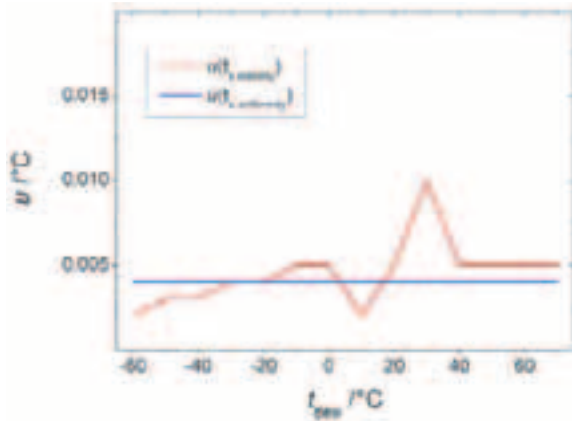


Figure 3.8 Standard uncertainties due to the non-ideal stability and uniformity of the saturator temperature.

### 3.4.4 Pressure drop

*Definition:* ... and the system is at a pressure  $p$  equal to that which exists in the given sample of moist air...

Air pressure is measured routinely with a calibrated barometer connected to the inlet of the saturator. In normal operation the pressure difference between the saturator and the instrument under calibration is  $< 100$  Pa.

The uncertainty estimation related to the pressure drop includes the contributions due to

- variation over time
- no correction is applied to the reference dew-point temperature value.

The estimated contribution to the overall combined standard uncertainty is shown in figure 3.9.

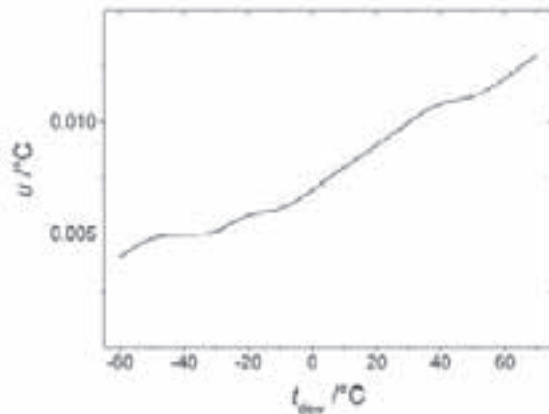


Figure 3.9 Standard uncertainty due to the pressure drop between the saturator and the hygrometer under calibration.

### 3.4.5 Time response and adsorption/desorption

*Definition:* ... has a saturation mixing ratio  $r_w$  equal to the mixing ratio  $r$ .

We prevent any mass transfer between sample air and ambient air the by keeping the system closed. This is verified with leak tests ( $< 5 \cdot 10^{-9}$  mbar·l·s<sup>-1</sup>@0.5 bar He). Furthermore, desorption effects are checked by time dependent tests (see figure 3.10.). In this way, we ensure that  $r$  is conserved in the system.

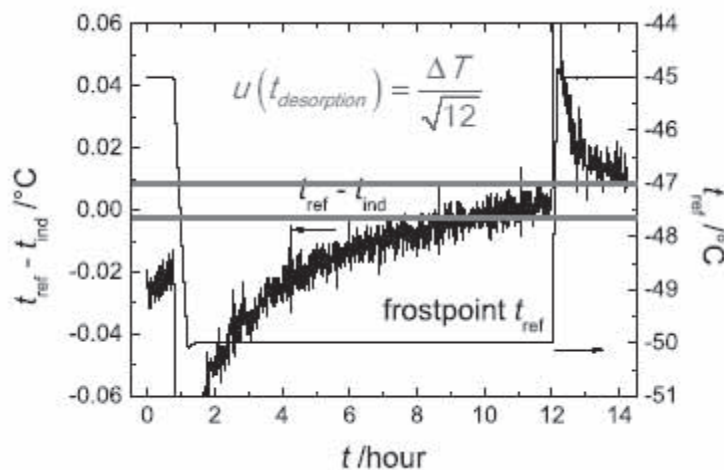


Figure 3.10 Standard uncertainty due to the pressure drop between the saturator and the hygrometer under calibration.

### 3.4.6 Summary

By combining the results presented above it was concluded that the expanded uncertainty of the dew-point temperature scale realised with the NMI 1-P generator is between 0.03 °C and 0.07 °C as shown in figure 3.11.



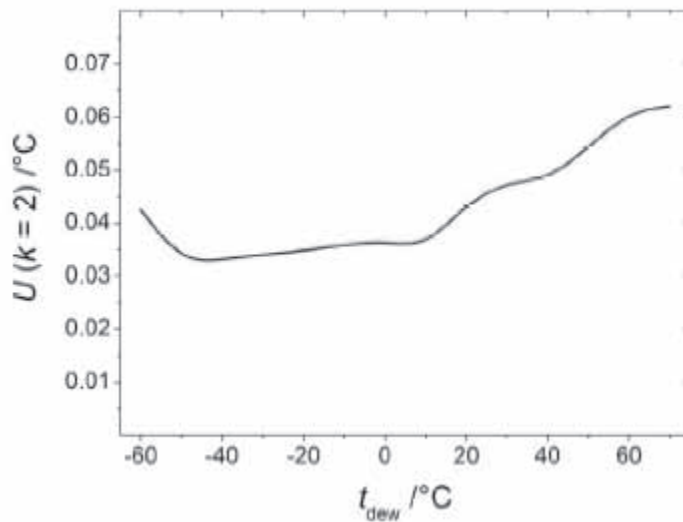


Figure 3.11 Expanded uncertainty ( $k=2$ ) of the dew-point temperature scale realized with the NMI 1-P generator.

### 3.5 Conclusion

When carrying out an uncertainty analysis for a dew-point generator, one actually establishes probability limits for the difference to an ideal generator (= the definition).

As a part of the analysis, uncertainty components are assessed by tests involving monitoring with a “real” hygrometer. Therefore, CMC/BMC data is limited by the performance of the available hygrometer and other instrumentation.

## 4 Uncertainty in calibrations with a secondary standard

Many national standards laboratories have chosen to maintain a secondary standard as their primary reference for humidity measurements. In this way, a significant amount of resources needed for developing and maintaining a primary standard is saved and all resources available can be focused in the service for customers. The traceability to a primary humidity standard is realised by calibrating the secondary standard(s) at another national standards laboratory. Usually, the traceability link is formed in terms of dew-point temperature because chilled mirror hygrometers are most stable instruments (in long term) available for humidity measurements in the needed range. Secondary calibration systems are also used for routine calibrations in most of the laboratories maintaining primary standards.

Instrumentation varies greatly in the laboratories using secondary standards. Some laboratories use equipment similar to the primary standard generators to form the controlled environment (or humidity controlled sample gas). Many laboratories use climatic chambers initially designed for industrial applications. Also other kinds of test benches are in use. Temperature and pressure measurements are carried out using

many kinds of instruments. Despite the variety in instrumentation the principles and main components in the uncertainty estimation are the same.

At the Workshop, Jovan Bojkovski and Domen Hudoklin (MIRS/FE-LMK, Slovenia) presented sources of uncertainty in calibrations, practical methods to quantify the components, validation, uncertainty related to the reference standard and the calibration equipment. A short summary of their presentation is given below.

## 4.1 Secondary calibration

Calibration is a process determining the difference in the value of a measuring device to a measurement standard. The result of a calibration can be a calibration correction (value of the standard - value of the device), calibration coefficient (e.g. sometimes relevant when calibrating psychrometers), characteristic curve (e.g. for a humidity transmitter, giving an equation to convert analog signal to the units of relevant humidity quantity), etc. The calibration result includes always measurement uncertainty that is derived from all relevant uncertainty components.

Calibration is done in a stable humidity environment using a calibrated reference dew-point hygrometer. In relative humidity (RH) calibrations, also a calibrated thermometer is needed. The reference dew-point hygrometer is calibrated against a primary standard (two pressure generator, single pressure generator, ...). The thermometer is calibrated either by comparison in a secondary thermometry laboratory or at fixed points.

## 4.2 Humidity “generator”

In a secondary calibration system, the role of a humidity generator is to produce a stable and homogeneous humidity environment. The actual value of the humidity is measured with a reference dew-point meter.

Several types of humidity “generators” (two pressure, single pressure, mixed flow, climatic chamber, ...) are in use in secondary calibration facilities.

## 4.3 Reference standards

Usually, a chilled mirror hygrometer is used as the reference standard for humidity. The traceability is established by calibrating it against a primary dew-point generator. Also RH hygrometers or psychrometers are used as the humidity standards, but the uncertainty is then typically larger.

Thermometers of different types are used as the reference standard for temperature measurement can be, e.g.:

- thermometer which is a part of the reference dew-point meter
- resistance thermometer ((S)PRT, thermistor) with measuring device (bridge, multimeter)
- other temperature measuring devices.

## 4.4 Measurement methods

The measurement method used for a particular calibration depends on the hygrometer under calibration (RH/absolute humidity/dew-point temp....) and the required conditions of the calibration:

- Parallel/serial sampling (calibrations in terms of dew-point temperature, mixing ratio, ...)
- Measurement of gas temperature (calibrations in terms of RH, absolute humidity, ...)
- Measurement of gas pressure (psychrometers, calibrations at high pressures, ...)
- Potential pressure drops
- Leakage, adsorption/desorption in sampling system
- Type of gas

## 4.5 Calibration with a secondary standard

Typical measurement configurations for dew-point and relative humidity calibrations are illustrated with the schematic diagrams in figures 4.1 and 4.2:

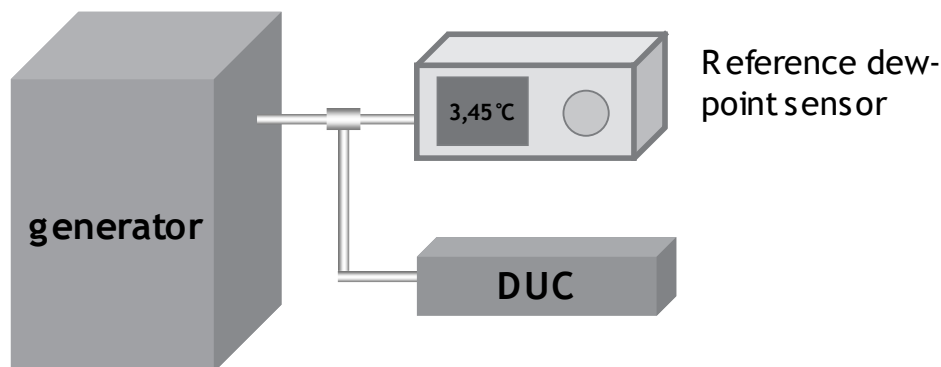


Figure 4.1 Set-up for dew-point calibration (Device under calibration - DUC- is a dew-point meter)

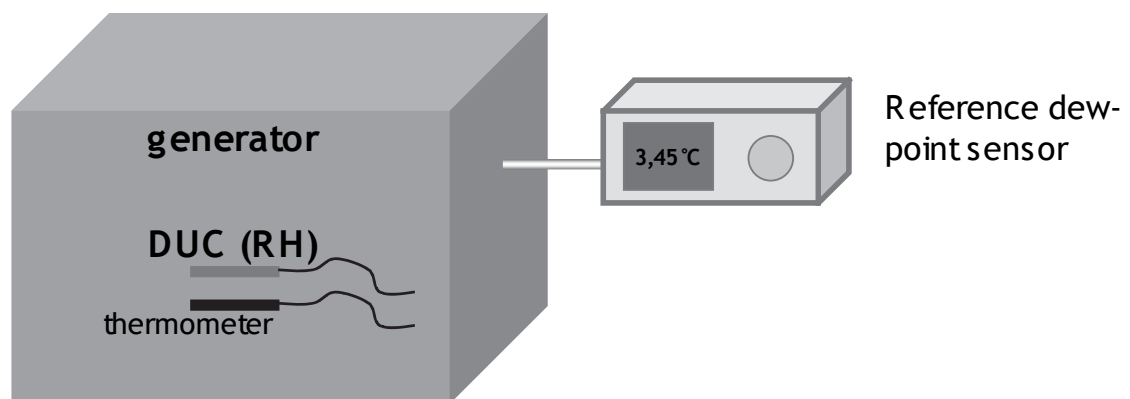


Figure 4.2 Set-up for RH calibration (DUC is a RH hygrometer)

## 4.6 Sources of uncertainty

Consequently, this would result in the following sources of uncertainty:

- due to generation of humidity
- due to uncertainty of reference standard
- due to DUC
- due to calibration method and ambient conditions

It is worth noticing that the correlation between the reference values and the DUC readings may be significant. The humidity in a climatic chamber often oscillates significantly (when compared with the uncertainty of the reference) which directly causes oscillation in the DUC readings. This can be taken into account by calculating the corresponding covariance (see chapter 2.7.5).

## 4.7 Uncertainty of humidity generation

The reference value (RV) is measured by a calibrated dew-point sensor; so only the deviations from the measured RV need to be characterised. The major uncertainty contributions are therefore:

- instability of generated humidity:
  - contributed by:
    - instability of dew-point temperature
    - instability of temperature (RH calibrations)
    - instability of pressure (two-pressure systems)
  - typically less significant component (but may be significant e.g. in RH calibrations in a climatic chamber)
  - instability can be measured during the calibration with stable reference humidity/temperature standard
  - standard uncertainty due to instability is taken as a combination of standard deviation of both dew-point and temperature
- inhomogeneity of generated humidity
  - almost insignificant in dew-point calibrations (if the inlet of the sampling tube of standard and DUC are in parallel and close to each other)
  - problems, if the reference standard and DUC as dew-point meter are sampling in serial (pressure drop, contamination,...)
  - in RH calibrations: large influence of temperature on relative humidity => inhomogeneity can be very significant.
  - Therefore the **temperature inhomogeneity needs to be quantified** in a RH calibration system.
- pressure difference between the reference and the DUC
- uncertainty of measurement device, used for evaluation.

## 4.8 Studying inhomogeneity in RH calibrations

Table 4.1 shows an example of the effect of humidity differences in the measurement chamber of a real calibration system. In this case, the combined expanded uncertainty ( $k = 2$ ) is contributed by the inhomogeneity up to 4.3 %rh.

Table 4.1 An example demonstrating the effect of inhomogeneity on the uncertainty of RH.

Temp: RH	-10 °C	0 °C	10 °C	20 °C	30 °C	40 °C	50 °C	70 °C
10 %rh	0.46	0.28	0.18	0.09	0.07	0.13	0,20	0.32
50 %rh	2.49	1.35	0.87	0.48	0.29	1.20	0.76	1.15
95 %rh (84%rh, 90%rh)	4.23	2.40	1.65	0.91	0.57	0.94	0.84	0.85
$U_{max, k=2}$	4.3	2.4	1.7	1.0	0.6	1.2	0.9	1.2

Typically, the standard uncertainties of RH due to the temperature inhomogeneity are from 0,1%rh to several %rh. The inhomogeneity can be reduced if a smaller calibration space is used or appointed (3 to 4 times smaller or more). An example of the reduced calibration volume is shown in figures below (fig. 4.3).

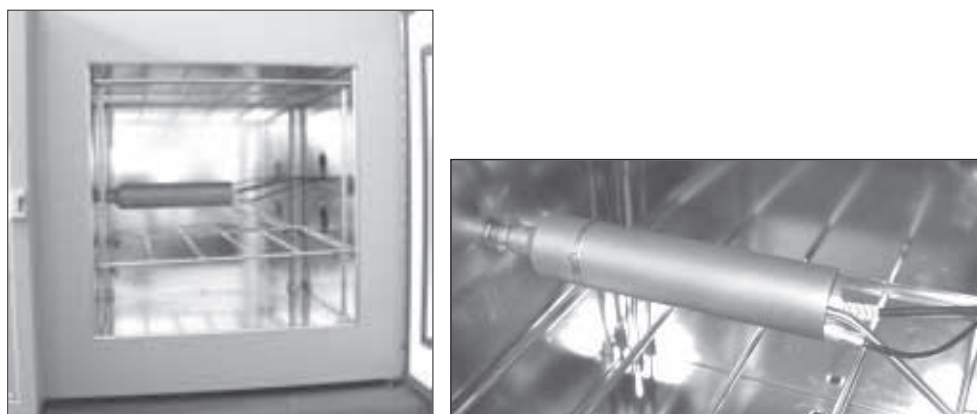


Figure 4.3 An example of significantly reduced measurement space.

Temperature gradients can be evaluated previous to calibration - less expensive possibility - or each time during the calibration (the set of thermometers has to be used all the time). The latter one is better, because the influence of DUC can also be determined, but more expensive (thermometers, bridge, scanner, PC...).

Often, it is most practical to combine the methods: Carry out separately a full test of temperature gradients and monitor continuously the gradients with e.g. two temperature sensors.

To evaluate inhomogeneity, thermometers are typically placed in the corners of the calibration area and one in the geometrical centre:

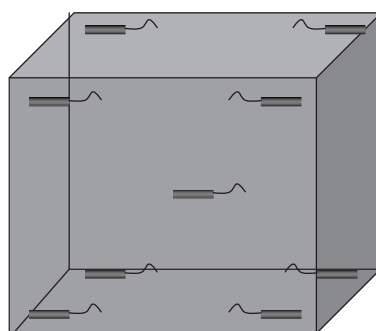


Figure 4.4 Arrangement of thermometers for testing the inhomogeneity

## 4.9 Uncertainty of reference standard

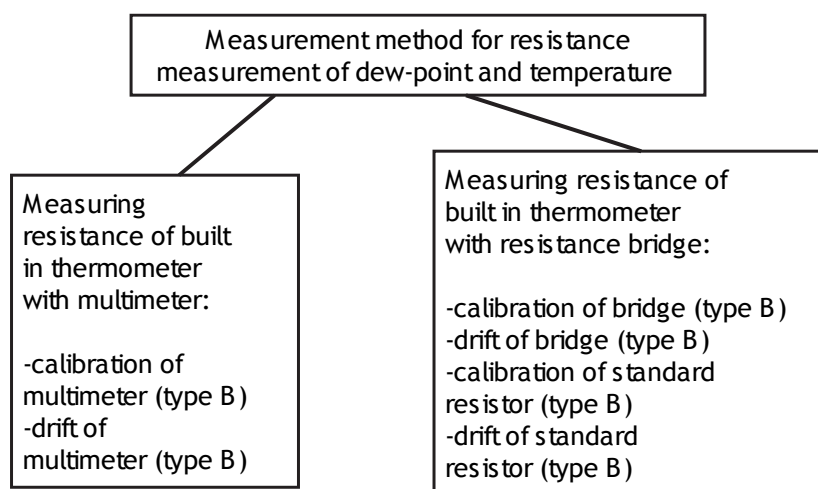
The uncertainty of reference standard depends naturally on the type of standard used. In general the following uncertainty contributions are to be determined:

- instability of the readings of the reference standard
- uncertainty, taken from the calibration certificate (dew-point standard & temperature standard)
- drift of the reference standard
- resolution (if not included in certificate) or actual sensitivity (if greater than the resolution or if analog signal or PRT resistance is used for determining the reading of the reference standard)
- uncertainty of calculation of relative humidity from air temperature and dew-point temperature (equations for saturation pressure of water vapour and enhancement factor)
- uncertainty of electrical measurement (bridge, multimeter,...) if relevant

In RH calibrations, if the reference is a dew-point sensor, then the temperature and dew-point contributions have to be considered separately:

$$u_c(RH_{ref}) = \sqrt{\left(\frac{\partial RH_{ref}}{\partial t_d} u(t_d)\right)^2 + \left(\frac{\partial RH_{ref}}{\partial t_c} u(t_c)\right)^2} \quad (4.1)$$

If the value of the measurement standard is obtained through a resistance measurement, the components to be taken into account should include at least:



NOTE: It has been observed that the resistance measurement method (AC, DC, etc.) may affect significantly the results when measuring the resistance of PRTs in chilled mirror hygrometers

If the value of the measurement standard is obtained by recording the display or digital output reading, the calibration uncertainty and drift include also the uncertainty due to electrical measurement in the hygrometer/thermometer. In this case, the thermometer should be calibrated as a single instrument (i.e. indicator unit and the probes).

## 4.10 Sources of uncertainty of DUC

The uncertainty of DUC readings depends on its type. In general, the following uncertainty contributions are to be determined:

- instability of DUC readings
- resolution or actual sensitivity (if greater than the resolution or if analog signal is used for determining the DUC reading)
- hysteresis
- the influence of DUC to calibration environment (self-heat, humidification - psychrometer)
- uncertainty of electrical measurements and devices (DMM, bridge, resistor,...; if relevant)
- drift (to be added by the end user)

## 4.11 Other sources of uncertainty

To be considered when calibrating hygrometers:

- uncertainty due to curve fit (if relevant)

Note: Usually, the uncertainty of curve fitting is contributed by uncertainties due to interpolation between the calibration points (non-linearity), hysteresis and differences of the fit to the estimates of the actual measurement results at the measurement points. If the number of measurement points is small (as it usually is), there are only small number of degrees of freedom related to those first two components. Therefore, if the standard uncertainties due to hysteresis and/or non-linearity are large compared with other components, the number of effective degrees of freedom of the final measurement result may be small. In this case, the proper value for the coverage factor should be calculated to obtain 95 % confidence level ( $k > 2$ ).

- leakage (stem of the sensor, cables)
- contamination (salts, oil, dirt)
- reproducibility

To be taken into account by users:

- different gas type used in calibration (nitrogen, air)
- difference between calibration measurement range and actual range (temperature, pressure,...)

Note: Calibration should always cover the whole humidity and temperature range of actual measurements. But it is not always clear how many points at minimum is needed to cover a range.

## 5 The uncertainty component related to the instrument under calibration

When carrying out the calculations to support CMC or BMC claims also the effect of the instrument under calibration must be taken into account. It has been agreed that the estimation of this effect should be based on the characteristics of the best available instrument [11,12]. One of the main objectives of the Workshop was to find a common view on this component at different calibration service categories. Discussions dealt with chilled mirror hygrometers, impedance RH hygrometers and psychrometers.

### 5.1 Chilled mirror dew-point hygrometers

Previous chapter reveals how important role chilled mirror hygrometers have in establishing traceability in hygrometry. Although commercial instruments today have features which make them easier to use, they still are sometimes quite tricky and need experienced operator to obtain a good uncertainty level. Despite the relatively similar specifications stated by the manufacturers, there are clear differences between different instruments. Also, many laboratories use older models that may have poorer characteristics than the updated models.

The operation of a chilled mirror hygrometer is based on maintaining zero net mass transfer between condensed phase and vapour phase of water and determining the temperature of the condensed phase. The condensed layer is initially formed by cooling a mirror surface below the dew-point temperature of the sample gas. The layer may consist of water droplets or ice crystals but mostly the initial condensate consists of droplets (at least down to  $-40\text{ }^{\circ}\text{C}$ ). In the range below  $0\text{ }^{\circ}\text{C}$ , phase transitions between solid and liquid phase and also within solid phase (changes in surface energy) occur affecting significantly the hygrometer reading. Also, metastable phases can be observed for a relatively long time. All phase transitions are sensitive to disturbances and contamination.

Although almost zero net mass transfer of water molecules can be obtained in a hygrometer at a stable situation, there is a significant heat transfer across the phase boundary (i.e. surface of the condensed layer). All types of heat transfer mechanisms (conduction, convection and radiation) between the mirror, condensed layer, gas and their environment affect the measurements.

Because of the phase transitions and non-equilibrium state on the mirror, results of different quality are often obtained by different inexperienced operators. On the other hand, an experienced operator can achieve with the best available instruments reproducible results with a good uncertainty.

At the Workshop, Günter Scholz (PTB, Germany) presented his experience on chilled mirror hygrometers. A short summary is given below.



### 5.1.1 Dew-point measurement - Definition of task:

When measuring the dew-point temperature, we determine the temperature  $t_d$  defined by

$$e = x_w p = e_w(t_d) \cdot f_{gas}(p, t_d) \quad (5.1)$$

for a gas (at pressure  $p$ ) with the water vapour mole fraction  $x_w$ . The enhancement factor  $f$  is different for different gases.

$t_d$  is not the temperature of the gas but a parameter defining the equilibrium condition for the gas and liquid/solid water surface at the pressure  $p$ . Thus, the dew-point temperature is a similar parameter as the melting-point or boiling-point temperature.

$t_d$  cannot be measured with a thermometer only, but with a special device called a dew-point hygrometer.

### 5.1.2 Dew-point hygrometer

Dew-point hygrometers are not simple measuring instruments, but devices which produce and measure the measurand  $t_d$  in simplified ways.

Dew point is produced with a cooling system combined with a system for observation of dew formation. In modern dew-point hygrometers there is normally a control system for the stabilization of a condensate layer on a smooth and clean metallic surface. Thus, net mass transfer of water between the gas and condensate is reduced to about zero by controlling the surface temperature. Because of the cooling method, thermal equilibrium is not reached.

Dew-point temperature is measured with a thermometer (sensor) fixed as near as possible to the condensate layer (point of equilibrium). Normally a miniaturised PRT sensor is used as the sensor.

### 5.1.3 Errors in the temperature measurement:

Indication of temperature measured by the sensor is affected by the following errors:

- Error in resistance measurement
- Error in the resistance-temperature conversion function of the sensor. Normally a DIN formulation is used for PRTs but actual functions for real sensors differ from the DIN standard.
- Temperature difference between the point of temperature measurement and the surface of the condensate (the real point of equilibrium). The difference is caused by heat transfer through the condensate and mirror, heat transfer between the mirror and the surrounding body, heat produced by the sensor etc.

### 5.1.4 Error of realisation of dew point

Stability in time of indication of the mirror temperature is not a measure for uncertainty of dew-point temperature.

The question is: Are there different stable mirror temperatures possible for one and the same value of water vapour pressure, if repeated independent measurements are made at the same conditions?

The answer is yes. There are differences possible due to the Kelvin effect ( $\leq 0.01$  K) and the Raoult effect ( $\leq 0.05$  K or larger for trace humidity). Furthermore, empirical results indicate possibility to have different types of ice condensate (with different surface energy). Inhomogeneous thickness of condensate and differences in the emissivity of the condensate/mirror surface may cause differences in repeated measurements.

The effect of the errors may be greater than the instability of the control circuit. Calibrations of dew-point hygrometers at a high metrological level should include independent repeated measurements. The mean value of them gives a better estimation of the real value of dew-point temperature.

When interpreting the result of a dew-point temperature measurement, one have to take into account the effect of the pressure difference between the dew-point cell and the point of interest. When calculating values of other humidity parameters the real gas behaviour should be take into account.

## 5.2 Impedance RH hygrometers

Most of the relative humidity hygrometers in use today are of impedance-type (e.g. capacitive sensors). Most of the national standards laboratories calibrate also these instruments for customers. The characteristics of impedance RH hygrometers depend in great extent on its history of operation (RH and temperature range, contamination, thermal shocks etc.).

The core of the hygrometers is usually a thin polymer layer between electrodes. Once water molecules penetrate in the porous polymer the impedance of the system changes because of the polar nature of the molecules. The bonding of water molecules - and thus their mobility - depends on the molecular structure of the polymer, other gas molecules penetrated, temperature etc. Because surface phenomena may often be irreversible and slow, impedance sensors are often relatively unstable in long-term. This holds especially if the sensor is exposed to greatly varying temperature and very high humidity.

At the Workshop, Vito Fernicola (IMGC, Italy) gave a presentation on the impedance-type hygrometers. A short summary of his presentation is given below. Empirical data on characteristics of hygrometers of this type can be found e.g. in [13].

### 5.2.1 Sources of uncertainty when calibrating impedance RH hygrometers

The uncertainty of a calibration is contributed by the uncertainty of the reference value (i.e. uncertainty sources related to the measurement standard and calibration equipment) and uncertainty sources related to the instrument under calibration.

Characteristics of RH hygrometers considered here include:

- repeatability
- resolution
- short-term stability
- hysteresis
- temperature dependence

- non-linearity/interpolation error is taken into account if calibration curve or function is reported (in other cases the user should estimate the effect and take into account)
  - stem temperature effects
  - self-heating
  - ambient temperature changes affecting the display unit
  - contamination
  - air flow rate and direction (usually omitted)
- long-term stability is usually added by the user of the hygrometer

### 5.2.2 Temperature dependence, hysteresis

Figure 5.1 demonstrates the temperature dependence of an impedance hygrometer. Another example is in figure 5.2. It shows also the non-linearity and hysteresis of the instrument.

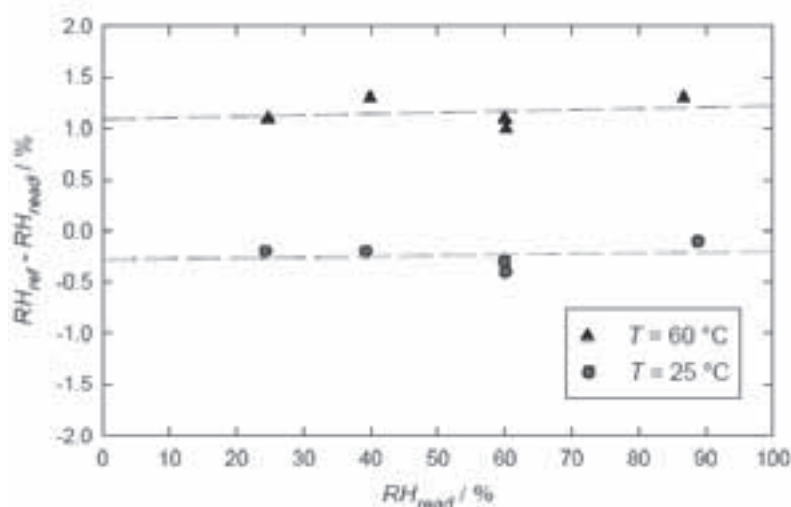


Figure 5.1 Temperature dependence of the calibration correction ( $RH_{ref} - RH_{read}$ ) of a capacitive hygrometer.

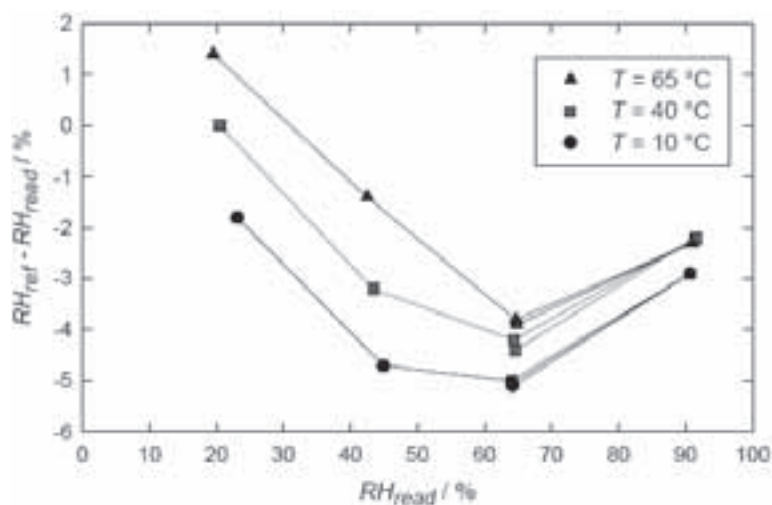


Figure 5.2 Temperature dependence, linearity and hysteresis of a capacitive hygrometer.

Temperature coefficients are used for describing quantitatively the temperature dependence. Coefficients of five capacitive sensors are shown in figure 5.3 [13]. It shows significant variations in both sign and magnitude of the coefficients.

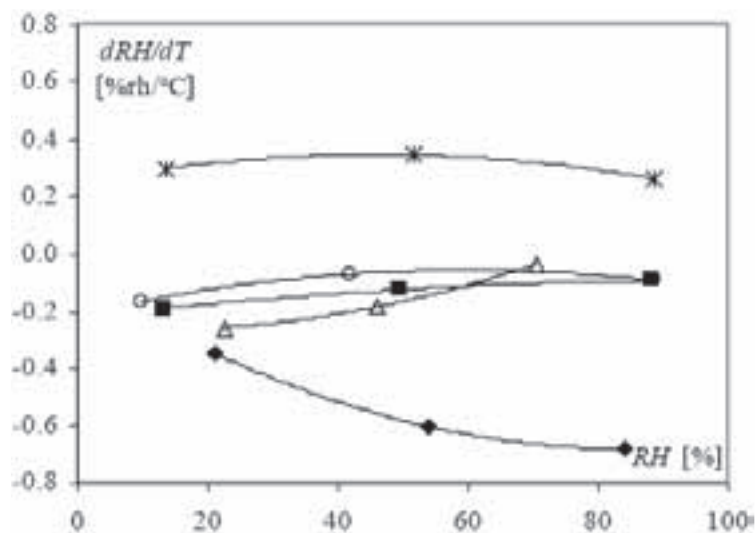


Figure 5.3 Temperature coefficients of five capacitive hygrometers.

### 5.2.3 Non-linearity/interpolation error

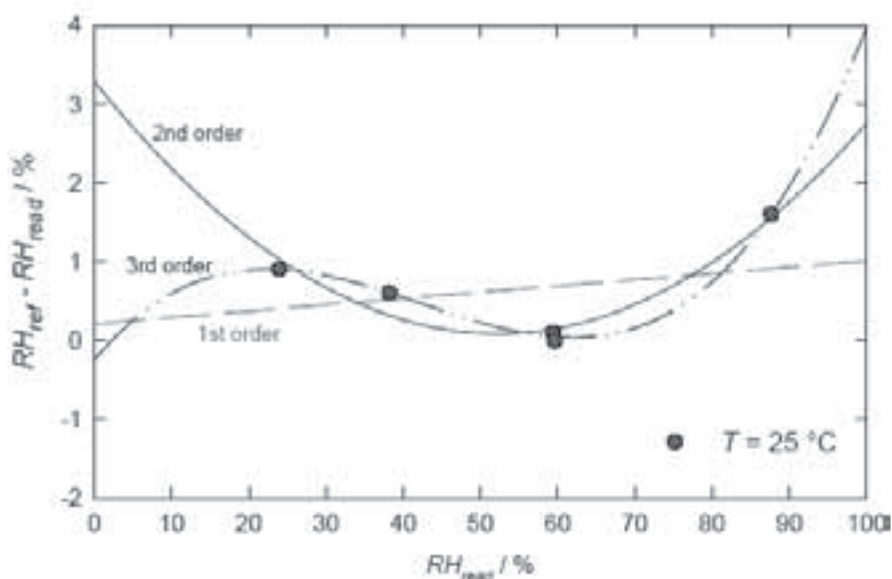


Figure 5.4 Polynomial fittings to calibration results.

Figure 5.4 above demonstrates difficulties in interpreting measurement results. If we carry out measurements only at e.g. four points, the information on the actual characteristic curve (i.e. calibration curve) is very limited. We usually decrease the uncertainty at the points by repeating the measurements but increasing the number of measurement points is often too expensive for the customers. We can improve the

quality of a polynomial fitting by increasing its order but the information on the non-linearity cannot be gained in this way.

The uncertainty of a fitting curve is contributed by a fitting error (difference between the fitting and actual measurement results at the measurement points) and an interpolation error (difference between the fitting and actual characteristic curve between the measurement points). It is worth noticing that the number of degrees of freedom related to the uncertainty of the interpolation error is usually very small. In the case of the 3rd order polynomial in the figure, the number is 1! Fig. 5.4 shows also that curve extrapolation outside the calibration range is polynomial-dependent and thus should be avoided.

#### 5.2.4 Stem temperature etc.

In some calibration systems, the hygrometer probe under calibration is partially immersed in a chamber in which the temperature is different from ambient temperature. The temperature difference induces a heat flow along the probe. Heat flows in the probe cover and in the electronics in it. As a result, thermal conditions in the chamber are disturbed. Also, the temperature of the polymer and temperature sensors of the probe may differ from the surrounding temperature. The effect depends on the temperature difference and the flow rate of air surrounding the probe.

An example of stem effect is shown in figure 5.5. The results were obtained by J. Lovell-Smith et al. [14].

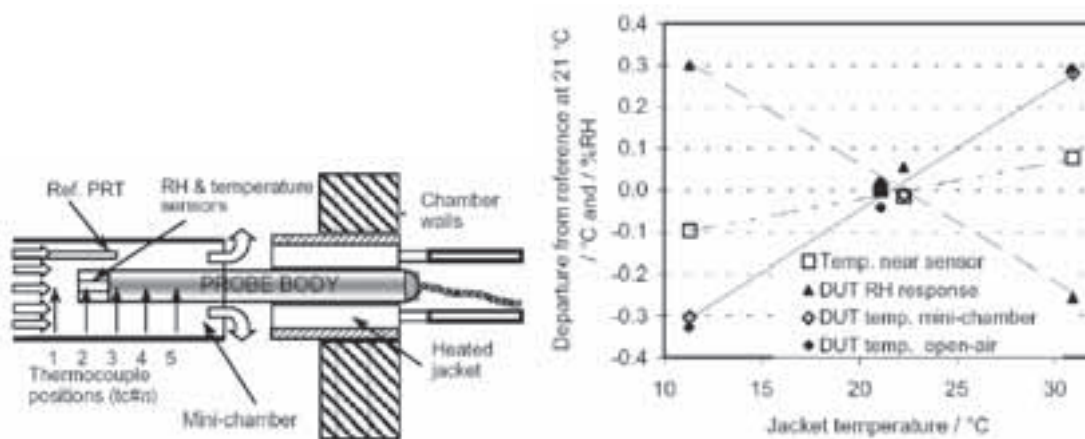


Figure 5.5 J. Lovell-Smith et al. studied the stem effect using the set-up on the left. The diagram on the right summarizes their results. [14]

#### 5.2.5 Contamination

Various gases affect polymer sensors. As an example, acetone vapour caused a drift of several percents in the investigations of Leppänen et al. [15] as shown in figure 5.6.

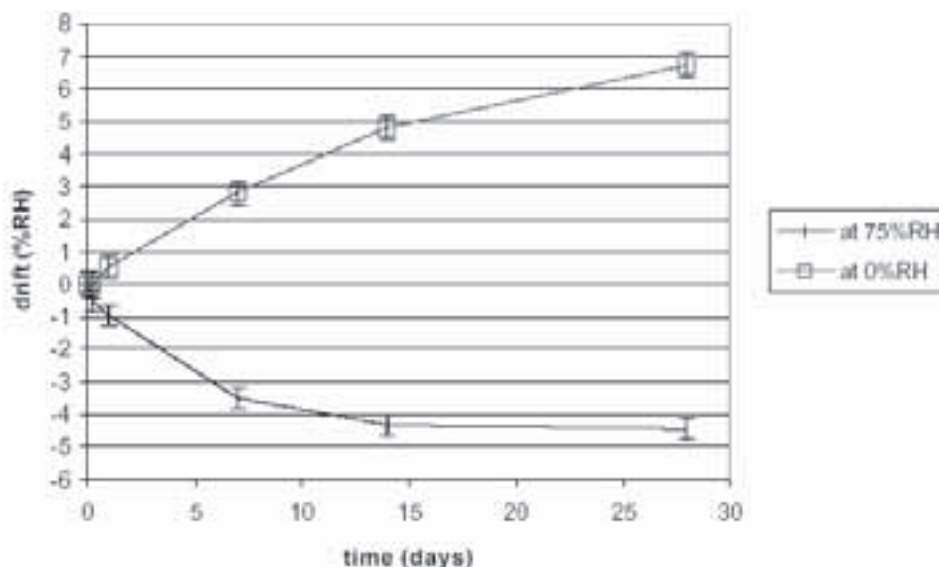


Figure 5.6 Drift caused for 6 sensors by exposure to 1800 ppm of acetone vapour [15].

Usually the effect of contamination, i.e. chemical interference, is not taken into account when estimating calibration uncertainty. It must be, however, kept in mind to use clean air (or other calibration gas) in the calibration system.

### 5.2.6 Long-term drift

Impedance RH hygrometers suffer usually from a significant long-term drift. The drift is often greater than 1 %rh/year. An example is given in figure 5.7.

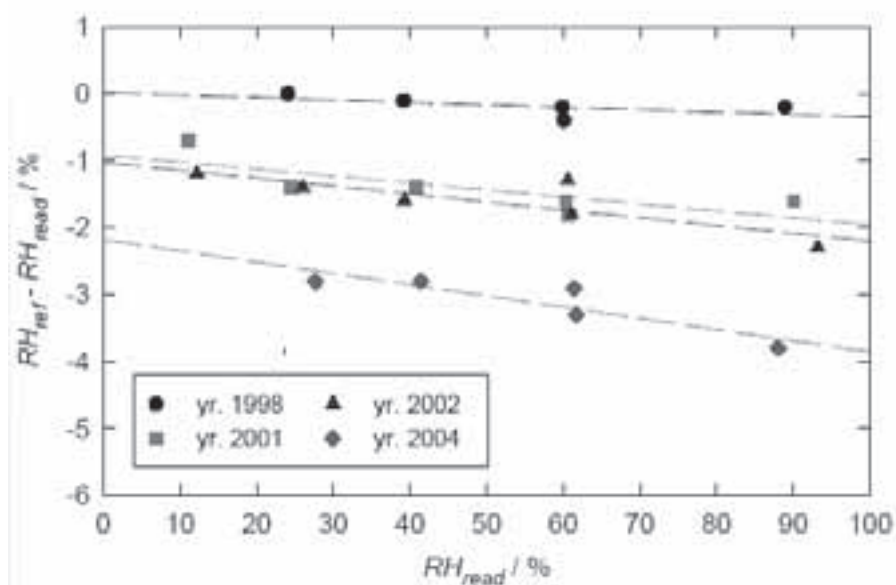


Figure 5.7 Long-term drift of a capacitive hygrometer.

### 5.2.7 Effect on the combined uncertainty

Tables 5.1 shows an example of the effect of an impedance hygrometer on the combined expanded uncertainty

Table 5.1 Effect of the hygrometer on the calibration uncertainty.

Quantity	Estimate (%rh)	Standard uncert. (%rh)	Probability distribution	Sens. coeff.	Contribution (%rh)
Reference RH	50.0	0.21	Normal	1	0.21
Readings of HUC <sup>1)</sup>	50.8	0.03	Normal	-1	0.03
Resolution of HUC <sup>1)</sup>	0	0.029	Rectangular	-1	0.029
Reproduc. of HUC <sup>1)</sup>	0	0.29	Rectangular	-1	0.29
Comb. std. unc.					0.36
Expanded unc. ( $k=2$ )					0.72

<sup>1)</sup> HUC = hygrometer under calibration

## 5.3 Psychrometers

Psychrometers (often referred to as dry/wet bulb psychrometers) form a special category of relative humidity hygrometers because the principle of operation is based on well-known relations of thermodynamics and because it changes the ambient humidity. Due to the solid theoretical basis psychrometers have been used as reference instruments e.g. in meteorological measurements for many years. When performing a calibration of a psychrometer in terms of relative humidity, special requirements are needed for the calibration system: First of all the instrument needs a significant air flow through it and secondly the water evaporating from the wick affects the surrounding humidity. It has been shown that calibration of the psychrometer thermometers alone is not sufficient for reliable humidity measurements.

If we consider a thermometer covered by a wet wick (see figure 5.8) at steady-state conditions, the evaporative heat flux ( $q_e$ ) can be described as:

$$\begin{aligned} q_e &= \dot{m}_e h_L \\ \dot{m}_e &= k_c (x_w - x_d) \end{aligned} \quad (5.2)$$

where  $h_L$ ,  $k_c$ ,  $x_w$  and  $x_d$  are the latent heat of vaporization, mass transfer coefficient, mole fraction of water vapour in the saturated air at the wick temperature ( $t_w$ ) and mole fraction of water vapour in the ambient air, respectively.

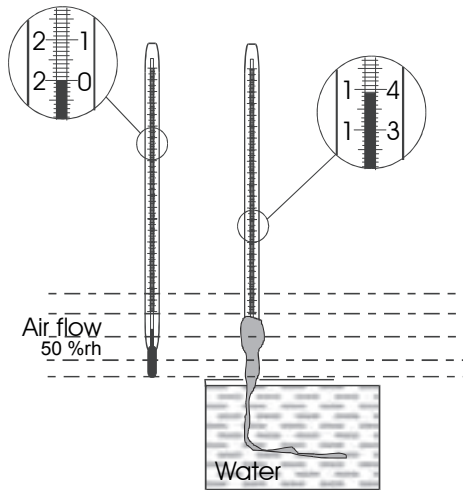


Figure 5.8 Principle of operation of a psychrometer. Evaporating water cools the thermometer covered by a wick.

On the other hand, the heat flux ( $q_t$ ) from ambient air to the wick is:

$$q_t = h_c (t_a - t_w) \quad (5.3)$$

where  $h_c$ ,  $t_w$  and  $t_a$  are heat transfer coefficient, wick temperature and ambient air temperature, respectively. If we assume that the radiation heat transfer is negligible (for simplicity, we also omit here other effects related to the non-ideality of the set-up and air as a gas mixture), conservation of energy implicates that  $q_e = q_t$ . Thus, we get:

$$h_L k_c (x_w - x_d) = \frac{h_L k_c}{p} (e_w - e_d) = h_c (t_a - t_w) \Rightarrow e_d = -\frac{h_c p}{h_L k_c} (t_a - t_w) + e_w \quad (5.4)$$

where  $e_d$  and  $e_w$  are the partial water vapour pressures in ambient air and on the wick. If we assume that  $h_c$ ,  $h_L$  and  $k_c$  are independent of temperature and pressure, we can write:

$$\frac{h_c}{h_L k_c} = A \quad (5.5)$$

$A$  is a constant related to the thermodynamic properties of humid air as well as the specific geometry of the psychrometer and the air flow through it. Thus, we can write for the relative humidity:

$$RH = \frac{e_d}{e_{ds}} \cdot 100 \text{ %rh} = \frac{f(p, t_w) e_{ws}(t_w) - A \cdot p \cdot (t_a - t_w)}{f(p, t_a) e_{ws}(t_a)} \cdot 100 \text{ %rh} \quad (5.6)$$

where  $f$ ,  $e_{ds}$  and  $e_{ws}$  are the enhancement factor, the maximum water vapour pressure at the ambient temperature and the saturation pressure of pure water vapour, respectively. This equation is well-known and widely used among users of psychrometers. The numerical value of  $A$  can be determined by calibrating the instrument although a conventional value is often used. It's worth noticing, however, that real psychrometers differ from the ideal case more or less. Therefore, in many cases a sufficient accuracy is not achieved simply by determining the  $A$  value.



Today, one of the most important applications for psychrometers is climatic testing, e.g. testing of electronics. Because tests are performed in extreme conditions, impedance-type sensors are not stable enough. On the other hand, tests need air flow which is sufficient also for a psychrometer. Furthermore, the humidifying effect does not disturb significantly and water supply is easily available in these test chambers due to the humidity control.

At the Workshop, Anders Kentved (DELTA, Denmark) gave a presentation on uncertainty sources related to psychrometers. A short summary of his presentation is given below.

### 5.3.1 Background

Psychrometers provide reliable method to measure relative humidity during climatic testing of electronics. In these tests, typical test conditions are:

10 %rh - 97 %rh at 15 °C - 85 °C

The required tolerance level is typically  $< \pm 2\text{-}3\text{ %rh}$ .

At DELTA, psychrometers are calibrated by comparison in climatic chamber using a dew-point hygrometer and thermometers:

Capability:

10 %rh - 97 %rh at 15 °C - 85 °C

Uncertainty within  $\pm 1\text{ %rh}$  ( $k=2$ ) for the entire range

(3 psychrometers calibrated in parallel)

### 5.3.2 Determination of relative humidity

Figure 5.9 illustrates the dependence of wet-bulb temperature on air temperature (dry bulb) and relative humidity.

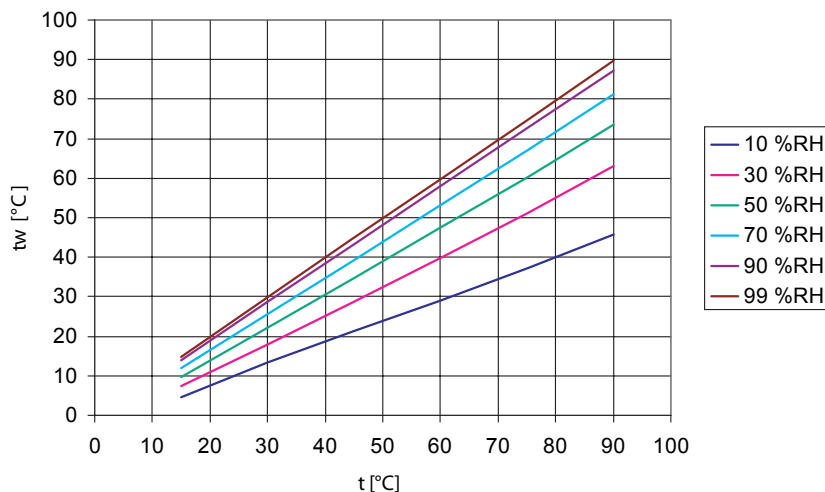


Figure 5.9 Psychrometric chart.

In many cases, the approximation for the combined heat and mass transfer coefficient in equation (5.5) leads to relatively large errors when operating in a large measurement range. This problem is sometimes solved using the following approximation:

$$\frac{h_c}{h_L k_c} \approx A(1 + B t_w) \quad (5.7)$$

or:

$$\frac{h_c p}{h_L k_c} \approx A(1 + B t_w) \cdot [p - f(p, t_w) e_{ws}(t_w)] \quad (5.8)$$

where  $A$  and  $B$  are constants.

Figures 5.10 and 5.11 illustrate the effect of uncertainty in temperature and pressure measurements on combined uncertainty. Analytical expressions for the sensitivity coefficients can be derived from equation (5.6) by derivating.

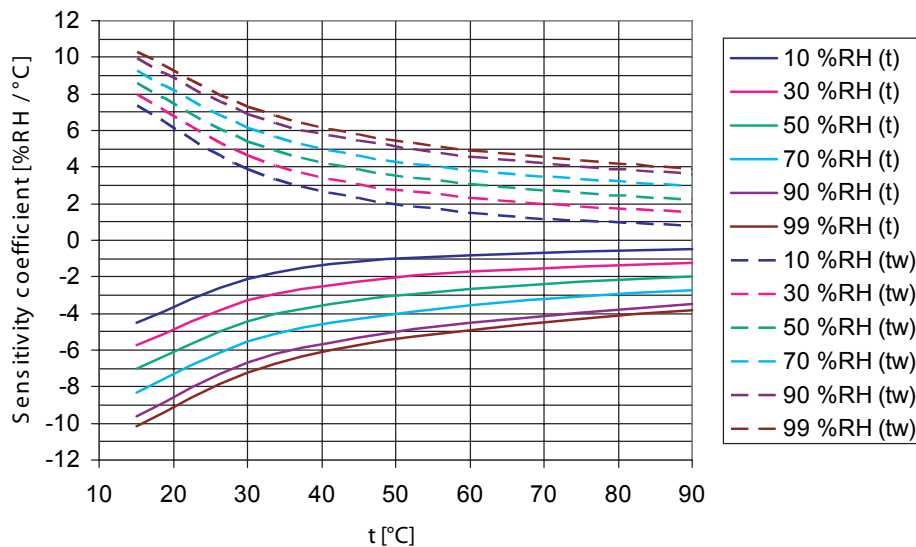


Figure 5.10 Sensitivity coefficient for wet (tw) and dry (t) bulb temperatures.

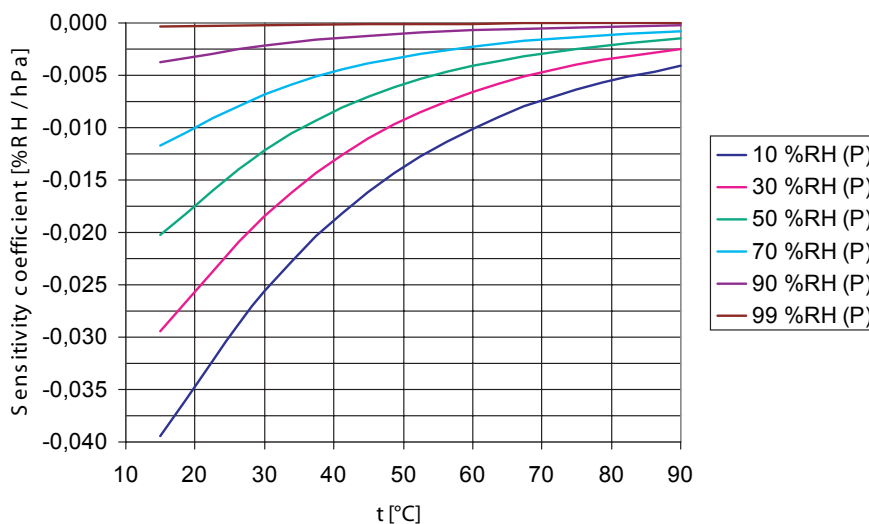


Figure 5.11 Sensitivity coefficient for air pressure.

### 5.3.3 Uncertainty contributions when calibrating psychrometers

Most significant uncertainty components related to psychrometers under calibration are (with typical values):

- Uncertainty of reference temperature measurement in calibration chamber
- typical increase of uncertainty due to psychrometers:  $\pm 20$  mK (stability in time)
- Uncertainty of reference dew-point measurements in calibration chamber
- typical increase of uncertainty due to psychrometers:  $\pm 20$  mK (stability in time)
- Resolution of psychrometer temperature measurement, typically:  $\pm 10$  mK to  $\pm 100$  mK
- Stability (short term) of psychrometer temperature measurement, typically:  $\pm 10$  mK
- Readings of psychrometer, typically:  $\pm 0.1$  %rh
- Reproducibility of psychrometer, typically:  $\pm 0.2$  %rh to  $\pm 0.5$  %rh (if caused by contamination of wick, typically:  $+0.2$  %rh to  $+0.5$  %rh)

There are several components whose contributions are often overlooked:

- Uncertainty of reference temperature measurement in calibration chamber - typical increase of uncertainty due to psychrometers:  $\pm 100$  mK (stability in calibration space)
- Changes in atmospheric pressure ( $p$ ) during calibration can cause uncertainty of psychrometer reading up to  $\pm 1$  %rh - measure atmospheric pressure during calibration!
- Psychrometers are very non-linear, uncertainty calculation is valid only for the specific calibration point (temperature, relative humidity)
- Readings of mercury-in-glass thermometers, typically:  $\pm 50$  mK
- Improper fitting of psychrometer wick, typically:  $\pm 0.5$  %rh to  $\pm 1.0$  %rh

The numerical values here represent a typical case.

An example of uncertainty calculation for a psychrometer calibration is given in table 5.2. As the result, the calibration correction to be applied to the RH indication is  $(1.4 \pm 0.7)$  %rh. The uncertainty is given at the 95 % confidence level.

Table 5.2 Uncertainty for a calibration of an electropsychrometer at 70 %rh and 30 °C.

<i>i</i>	Contribution, $X_i$	Estimate, $x_i$	Standard uncertainty, $u(x_i)$	Distribution	Sensitivity coefficient, $c_i$	Uncertainty $u_i(RH)$
1	Reference temperature	30,10 °C	0,029 °C	Normal	-4,0 %rh/°C	0,12 %rh
2	Reference dew-point temperature	24,09 °C	0,071 °C	Normal	4,2 %rh/°C	0,30 %rh
		$\Rightarrow RH_{ref} =$	70,3 %rh			0,32 %rh
3	Resolution of dry-bulb temp. (psychrom.)	0 °C	0,01 °C	Rectangular	-5,6 %rh/°C	0,06 %rh
4	Stability of dry-bulb temp. (psychrom.)	0 °C	0,01 °C	Rectangular	-5,6 %rh/°C	0,06 %rh
5	Resolution of wet-bulb temp. (psychrom.)	0 °C	0,01 °C	Rectangular	6,1 %rh/°C	0,06 %rh
6	Stability of wet-bulb temp. (psychrom.)	0 °C	0,01 °C	Rectangular	6,1 %rh/°C	0,06 %rh
7	Readings of the psychrometer	68,9 %rh	0,06 %rh	Rectangular	1	0,06 %rh
8	Reproducibility of the psychrometer	0 %rh	0,12 %rh	Rectangular	1	0,12 %rh
		$\Rightarrow RH_{ind} =$	68,9 %rh			0,17 %rh
Combined uncertainty:						0,36 %rh
Correction to be applied to the Psychrometer reading: $RH_{ref} - RH_{ind} =$		1,4 %rh	Expanded uncertainty:			0,7 %rh

### 5.3.4 Uncertainty contributions when measuring with a psychrometer

Most significant uncertainty components related to use of psychrometers (with typical values):

- Long term stability - drift of thermometers and measuring electronics, typically:  $\pm 0,5$  %rh to  $\pm 1.0$  %rh
- Thermal drift of measuring electronics during use at high or low temperatures - correlated and cancel out to some extent, typically  $\pm 0.2$  %rh to  $\pm 0.5$  %rh
- Uncertainty of readings from psychrometric charts (if relevant)
- Changes in atmospheric pressure ( $p$ ) during measurements cause uncertainty of the psychrometer reading up to  $\pm 1$  %rh - correction possible if the pressure is known
- Improper fitting of psychrometer wick, typically:  $\pm 0.5$  %rh to  $\pm 1.0$  %rh
- Contamination of the psychrometer wick - don't re-use the wick, change it!

### 5.3.5 Typical calibration curve

As an example, figure 5.12 shows calibration curves for an electropsychrometer.

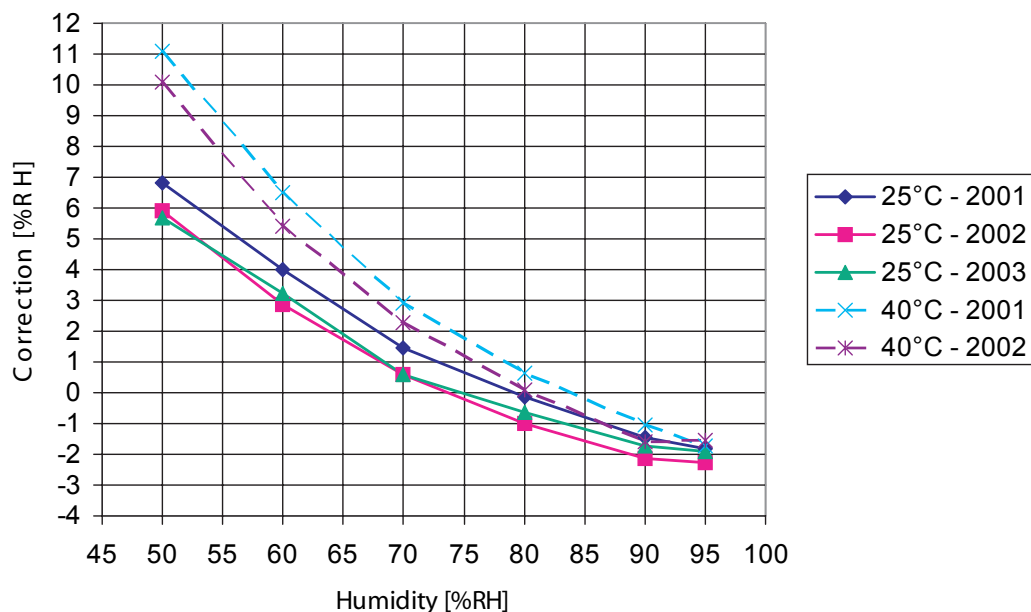


Figure 5.12 Calibration curves (without uncertainties) for a DELTA electropsychrometer EP02

### 5.3.6 Conclusions on psychrometers

- Psychrometers increase the uncertainty of reference temperature measurement in calibration chambers. This is due to the power dissipated in the psychrometer fan and evaporation of cooled air/water vapour from wet bulb.
- Psychrometers increase the uncertainty of reference dew-point measurement in calibration chambers because of water evaporation from wet bulb.
- The influence of a psychrometer on calibration uncertainty depends significantly on the size of the calibration chamber, air flow in the chamber and the location of reference thermometer probes in the chamber.
- The calibration measurement capability could be based on a small psychrometer capable of stable and high resolution temperature measurement.

## 6 Discussion

Discussions at the Workshop showed that humidity experts have a common view on the contribution of hygrometers of different kinds to the calibration uncertainty. It was agreed that smallest contributions of chilled mirror hygrometers and impedance RH hygrometers are typically 0.02 °C and 0.3 %rh to 0.5 %rh, respectively.

Some laboratories report a calibration curve (or calibration function) as the calibration result. In this case, the linearity (especially with RH hygrometers) may significantly affect the achievable uncertainty. When reporting results obtained at discrete points, the end user has to estimate the effect of linearity. In some laboratories, all the calibration points are measured twice (in both ascending and descending order) in RH calibrations to include the hysteresis effect of impedance RH sensors. Also, conventions to cover the whole temperature range needed by the user differed slightly from laboratory to another. It was agreed that 'ideal' calibrations cannot be performed due to practical limitations: One must compromise between the coverage of the calibration and - on the other hand - the time and money needed for the work and the technical/practical limitations of customers (automation systems, various calibration intervals and procedures, flexible calibration scopes etc.)

It is highly important that the calibration method and conditions are well described in the calibration certificate. Also, the uncertainty components related to the instrument under calibration should be stated.

Temperature gradients along RH probes under calibration should be kept at minimum. Thus, a partial immersion of the probes into a thermally controlled test chamber is not recommended. Homogeneity of both temperature and water vapour pressure is very important to achieve best uncertainty in RH calibrations.

## 7 Conclusion

The Workshop presentations covered all key aspects of the uncertainty estimation in humidity measurements at national standards level. Discussions indicated that the objectives of the Workshop were achieved. The event and this publication support the efforts being focused in the international mutual recognition of national humidity standards. Furthermore, the outcomes of this co-operative project will be benefited by all new humidity laboratories when developing and validating new calibration facilities.

In future, co-operation is needed in finding agreed methods to review CMC humidity entries and in providing training to new experts and laboratories in the field. For the CMC review process, discussions and procedures are needed especially with relative humidity entries and, e.g. status of chilled mirror based RH measuring systems as items to be calibrated.

Also, it would be worth studying further the use of numerical methods (Monte Carlo simulation) in uncertainty estimations (see e.g. [16]). This is recommendable because of strongly non-linear equations and mathematical models in hygrometry.

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