An Experimental Verification of Saturated Salt Solution-Based Humidity Fixed Points

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The high instability and hysterisis of the relative humidity sensors currently available on the market render necessary simple and economic calibration methodologies that can be used as secondary or working standards. The chemical equilibrium-type systems based on saturated aqueous salt solutions, even though simple and economical, are not always metrologically satisfactory for calibration. They can, in fact, be unreliable, when some fundamental requirements are neglected; also, unacceptable discrepancies continue to exist in the equilibrium relative humidity reference data of saturated aqueous salt solutions furnished by both literature and standards. To highlight the factors that increase the reliability of calibrations with saturated aqueous salt solutions, the authors of this paper have redetermined the equilibrium relative humidity reference data of 11 saturated aqueous salt solutions at ambient pressure and temperature. The solutions chosen were the ones generally used as fixed points to obtain a relative humidity calibration scale.

KEY WORDS: moist air; relative humidity; saturated salts.

1. INTRODUCTION

The increased civil and industrial requirement for traceability requires the development of reliable, simple, and low-cost calibration methods. Regarding the calibration and checking of humidity sensors in test laboratories, it should be emphasized that, the use of both the precision humidity generator [1, 2] and gravimetric methods [3-5] as primary standards has been consolidated for some time. On the other hand, secondary calibration methods are still the subject of debate [6-8].

1423

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As with the methods used for calibrating temperature sensors, it is possible to group the secondary calibration methods into (a) comparison calibration methods and (b) fixed point calibration methods. The first method consists in continuously varying the humidity value by means of a generator, usually a climatic cell, and calibrating the sensor by comparison with a reference standard. This method has definite advantages, such as (i) high accuracy, (ii) the possibility of calibrating sensors which require continuous sampling (for example, psychrometers and most condensation sensors), and (iii) continuing the calibration under all thermodynamic conditions at atmospheric pressure. It does, however, present a series of disadvantages, such as suitable uniformity and stability only over a restricted humidity and temperature range unless customized, bulky, and highcost climatic cells are used [6].

Fixed-point calibration, instead, is based on chemical systems in equilibrium which allow a known and constant relative humidity value to be maintained in a sealed, reduced-dimension container. These systems use a solution in equilibrium with its own vapor phase in the presence of air at atmospheric pressure. Under these conditions, the moist air in the container is characterized by a relative humidity value dependent on the temperature used for each solution. This value is repeatable and reproducible and can be used to set up a fixed calibration point.

Among the chemical systems in equilibrium, it is possible to distinguish (i) titrated solutions (usually based on sulfuric acid or glycerine or other solutions that are less temperature dependent) and (ii) saturated aqueous salt solutions (usually a single salt or sometimes mixtures of two salts). The desired humidity value is obtained by varying, in the first case, the concentration of the solute and, in the second, the solute type. The principal advantage of these methods lies in the reduced setting-up costs; moreover, *a priori* knowledge of the reference data of the relative humidity of the solution makes using a further reference standard unnecessary and, also, gives a further economic advantage. However, these methods give rise to a number of inconveniences in calibrating the continuous sampling sensors, and thus their use is limited to calibrating hygrometers with an in situ probe. Furthermore, chemical-equilibrium systems have not been sufficiently characterised for so rigorous a use as calibrating sensors, despite their having long been used for materials testing. In particular, a reliable and repeatable calibration procedure has not yet been univocally defined, and above all, for the various solutions, there are still some discordances as to the reference data for the relative humidity at equilibrium.

The titrated solutions are inconvenient because they require an accurate titration to be carried out which has to be verified at the end of the test. Furthermore, compared to the saturated aqueous salt solutions,

they have a greater dependence on both the sources and the removals of humidity. Thus, saturated aqueous salt solutions represent a simple and economical alternative to both titrated solutions and to comparison calibration methods. On the other hand, for saturated aqueous salt solutions it is necessary to follow precise prescriptions in their preparation and use to avoid considerable uncertainties in setting up the fixed calibration point. These uncertainties can prove to be even greater than 5% relative humidity (RH) [10], which are values that are intolerable for calibration purposes, since relative hygrometers have a lower uncertainty [11]. Hence, it is opportune to emphasize that some aspects on the preparation and use of saturated aqueous salt solutions have been touched upon in many standards [12–18]. Furthermore, a number of recommendations on these aspects have been made in the literature [10, 19–21].

To calibrate a relative hygrometer over its entire working range (generally, 10-95% RH), it is necessary to locate various saturated aqueous salt solutions that have different relative humidity values, thereby enabling the entire operating range of the calibration sensor to be covered. The great number of available solutions should allow different sets to be identified which satisfy the above-mentioned conditions. There are, however, some factors which condition this choice, such as

- (a) the repeatability and reproducibility of the solution used in setting up the fixed calibration point,
- (b) dependence on the influencing quantities (in particular on temperature),
- (c) the cost of the salt,
- (d) accurate knowledge of the relative humidity reference data for the saturated aqueous salt solution.

The solid-liquid phase diagrams for each saline solution [22] can give useful indications as to the choice of fixed calibration points. For example, the phase diagram of the $ZnCl_2$ salt solution shown in Fig. 1 [23] shows how the cryohydric point or, alternatively, some transition points of the hydrated crystals prove to be independent of temperature. These points, therefore, are points of great interest for calibration. The cryohydric temperatures for some of the saturated aqueous salt solutions and the corresponding relative humidity values are shown in Table I. From this table, it can be seen that the use of these thermodynamic points as fixed calibration points proves to be feasible only for values greater than 60% RH; in fact, lower relative humidity values should be obtained at temperatures of less than -50° C. On the other hand, it is absolutely necessary to avoid, since they are very unstable, the maximum points (M) of each hydrated crystal and the meta-stable conditions (dashed curve). The hypothesis of using the transition points of the hydrated crystals (Z) as fixed points should be evaluated analyzing the pressure-temperature curves case by case [23, 24] since there are thermodynamic conditions under which these points could prove to be unstable.

As an alternative to the transition points and to the cryohydric point, the fixed calibration point can be chosen in the area of the least dependence of relative humidity on temperature. In fact, if we assume, to a good approximation, that the influence of total pressure can be ignored, the temperature and consequent variation in solubility constitute the principal influencing factors of the calibration system. Therefore, a high derivative of the relative humidity compared to the temperature renders the calibration system noticeably dependent on the efficiency of the thermostatic system. In particular, since it is preferable, for obvious reasons, to operate near ambient temperature, the choice of the fixed calibration points can be made preferring the solutions that satisfy the conditions mentioned at precisely that temperature.

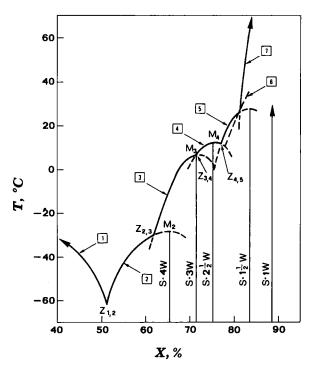


Fig. 1. The liquid-solid phase diagram of the $ZnCl_2$ salt solution [23].

| Salt | T _c (°C) | ф (% RH) |
|--------------------------------|---------------------|-------------|
| $Ba(NO_3)_2$ | -0.6 | 99.4 |
| K ₂ SO ₄ | - 1.5 | 98.6 |
| KNO3 | - 2.9 | 97.2 |
| $Sr(NO_3)_2$ | - 5.6 | 94.7 |
| ZnSO₄ | -6.6 | 93.8 |
| BaCl ₂ | -7.7 | 92.8 |
| KCI | -10.65 | 90.2 |
| KBr | -12.6 | 88.5 |
| NH₄CI | -15.4 | 86.1 |
| NaNO ₃ | -17.5 | 84.4 |
| КІ | -22.5 | 80.4 |
| $Ca(NO_3)_2$ | -27.9 | 76.3 |
| K_2SO_3 | -45.5 | 64.3 |
| CaCl ₂ | -51.5 | 60.7 |

Table I. Cryohydric Temperature T_c and Relative Humidity Values ϕ for Saturated Aqueous Salt Solutions

Finally, saturated aqueous salt solutions cannot be use without precise knowledge of the values of the relative humidity at the fixed points chosen as the reference ones for calibration. Unfortunately, the values of the relative humidity reported in the literature also differ from each other around 1-2% RH at 20°C (cf. Tables II and IV) and up to 3-4% RH at different temperatures [25].

Greenspan [26] has collected experimental data available in literature for 28 saturated saline solutions at atmospheric pressure, evaluating the reference data of the most dependable relative humidity, processing them according to the measurement methodology used and to the uncertainty associated to it by each experimenter [9, 25, 27, 28]. Under calibration conditions in which it is necessary to operate at temperatures different from 20° C, the data currently available in the literature are less numerous and, as has already been said, often of low reliability. For these conditions, too, Greenspan [26], using the above-described methodology, collected reference data for the relative humidity ϕ of the saturated aqueous salt solutions shown in Table II, for the range, in general, between 0 and 100°C at intervals of 5°C, also providing an interpolating polynomial for each salt.

Despite the fact that the data processed by Greenspan are numerous and derive from different measurement methods, it is necessary to emphasize that these values

- (i) refer primarly to experiments carried out in the 1960s or even earlier and, consequently, using old measurement technologies and
- (ii) have not been systematically supported by later experimental verification; moreover when this verification has been attempted for a limited number of salts [10, 19, 29]. even though the relative humidity measurements are compatible with Greenspan's data, there are discrepancies for some salts.

Consequently, even if the calculations carried out by Greenspan have often been accepted by International Standards or Recommendations

| Salt | φ (% RH) | σ _φ (% RH) | <i>dφ/dT</i> (% RH °C ⁻¹ | |
|----------------------------------|-------------|--------------------------|--|--|
| CsF | 3.83 | + 1.10 | - 0.0942 | |
| LiBr | 6.61 | <u>+</u> 0.58 | -0.0487 | |
| ZnBr | 7.94 | ±0.49 | - 0.0434 | |
| кон | 9.32 | ±0.90 | -0.2438 | |
| SOH | 8.91 | ± 2.40 | -0.1323 | |
| LiCl | 11.31 | <u>+</u> 0.31 | -0.0004 | |
| CaBr | 18.50 | <u>+</u> 0.50 | -0.3705 | |
| LiI | 18.56 | ±0.16 | -0.2000 | |
| KCH ₃ CO ₂ | 23.11 | <u>+</u> 0.25 | -0.0889 | |
| KF | 30.85 | ±1.30 | -0.6337 | |
| MgCl ₂ | 33.07 | ±0.18 | -0.0516 | |
| NaI | 39.65 | ±0.59 | -0.2735 | |
| K ₂ CO ₃ | 43.16 | ±0.33 | 0.0015 | |
| $Mg(NO_3)_2$ | 54.38 | ±0.23 | -0.2982 | |
| NaBr | 59.14 | ±0.44 | -0.3121 | |
| CoCl ₂ | 64.92 | ± 3.50 | - 0.5969 | |
| KI | 69.90 | ±0.26 | -0.2114 | |
| SrCl ₂ | 72.52 | <u>+</u> 0.05 | -0.3272 | |
| NaNO ₃ | 75.36 | ±0.35 | -0.2211 | |
| NaCl | 75.47 | <u>+</u> 0.14 | -0.0322 | |
| NH₄Cl | 79.23 | ±0.44 | -0.1323 | |
| KBr | 81.67 | ±0.21 | -0.1723 | |
| $(NH_4)_4SO_4$ | 81.34 | ±0.31 | -0.0715 | |
| KCl | 85.11 | ±0.29 | -0.1574 | |
| $Sr(NO_3)_2$ | 86.89 | ±0.29 | -0.3660 | |
| KNO3 | 94.62 | ±0.66 | -0.1826 | |
| K ₂ SO ₄ | 97.59 | ±0.53 | -0.0591 | |
| $K_2 CrO_4^{a}$ | 97.88 | ±0.49 | -0.1737 | |

Table II. Greenspan Equilibrium Relative Humidity Values, Measurement Uncertainties σ_{ϕ} , and ϕ Gradient at 20°C

" At 25°C.

Humidity Fixed Points

[18, 20] as giving the reference data of the equilibrium relative humidity for saturated aqueous salt solutions, some of these values have been modified in consideration of the already mentioned discrepancies. For example, the OIML has modified the following.

- (i) The data for sodium chloride from 50 to 80°C have been replaced by those proposed by Young [30] and later verified by Huang and Whetstone [29], Arai et al. [31], and Vekker and Gershkowits [32],
- (ii) The data for lithium chloride between 5 and 20°C have been averaged on the data of Greenspan [26], Arai et al. [31], Acheson [9], Ueda [33], Vekker and Gershkowits [32], and Wexler and Hasegawa [25].

The present authors have carried out an accurate experimental investigation of some of the saturated aqueous salt solutions indicated by Greenspan at the temperature of 20°C to investigate the relative humidity values. In particular, the saturated aqueous salt solutions investigated were the ones made up of the following salts: (1) lithium bromide, LiBr; (2) lithium chloride, LiCl; (3) potassium acetate, KCH₃CO₂; (4) magnesium chloride, MgCl₂; (5) potassium carbonate, K_2CO_3 ; (6) magnesium nitrate, Mg(NO₃)₂; (7) potassium iodide, KI; (8) sodium chloride, NaCl; (9) ammonium sulfate, (NH₄)₂SO₄; (10) potassium nitrate, KNO₃; and (11) potassium sulfate, K₂SO₄. These solutions were chosen since they were recommended either by OIML or by DIN as fixed points for forming a calibration scale of the relative humidity of moist air [21]. As can easily be seen, the relative humidity values of the chosen solutions uniformly cover the range between 7 and 98% RH, which is the characteristic range of relative hygrometers.

2. EXPERIMENTAL APPARATUS

The experimental apparatus used to verify the salt-solution fixed points was set up in such a way as to reproduce the real conditions of humidity sensor calibration based on salt solutions. In fact, for humidity sensor calibration, direct evaluation of air relative humidity at ambient temperature and pressure under a suitable enclosure is more meaningful than is indirect evaluation based on vapor partial pressure.

The experimental apparatus is shown in Fig. 2. An *in situ* chilled mirror dew-point hygrometer completely contained in the enclosure under test was installed. It covered a dew-point range from -40 to 60° C, with an

estimated reproducibility better than 0.15° C, and an air temperature range of -10 to $+60^{\circ}$ C, with an estimated reproducibility better than 0.05° C, with a coverage factor equal to 2. All the above uncertainties are estimated at the level of two standard deviations. The chilled mirror dew-point hygrometer was calibrated against the national primary standard humidity generator of the "G. Colonnetti" Institute of Metrology. (IMGC).

Two Pt100 four-terminal resistance thermometers, covered with Teflon, and an accurate data acquisition unit, with a 1-m°C resolution, were used. They covered a range of 0 to 50°C, with an estimated reproducibility of better than 0.05°C, and were calibrated with a Pt25 transfer standard directly traceable to national standards. Temperature measurements were carried out in such a way as to compare the solution and air temperatures and, consequently, to minimize the temperature gradient.

A high-performance liquid-bath thermostat coupled with a digital temperature controller IEEE-488 drive was used to establish a uniform temperature distribution in the enclosure under test. The bath flow chute assembly and motor stirrer ensure thorough water mixing, thereby giving excellent uniformity and stability. In a regulation range between -30 and 300° C the stability and uniformity of the thermostatic system are better

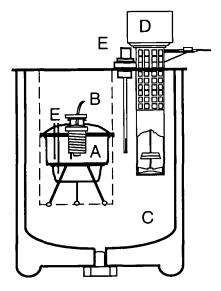


Fig. 2. Experimental apparatus: (A) enclosure; (B) dew-point hygrometer; (C) liquid-bath thermostat; (D) stirred; (E) thermometers.

| Salt | Mol H ₂ O | R _{sa} | R _{si} | R _U , CETIAT | R _U , IUPAC | R _U , Wzormat | R _U |
|----------------------------------|-------------------------|-----------------|-----------------|----------------------------|---------------------------|-----------------------------|----------------|
| LiBr | 1 | 174 | 881 | | | _ | 350 |
| LiCl | 1 | 80 | 72 | 140-180 | 130 | 360 | 200 |
| KCH ₃ CO ₂ | 1.5 | 255 | 1092 | _ | _ | | 500 |
| MgCl ₂ | 6 | 55 | 310 | _ | 200 | 400 | 500 |
| K ₂ CO ₃ | 2 | 111 | 196 | 180-220 | 135 | | 400 |
| $Mg(NO_3)_2$ | 6 | 74 | 279 | | - | 600 | 500 |
| KI | — | 143 | _ | | | | 300 |
| NaCl | _ | 36 | | 200-250 | 50 | 35 | 220 |
| $(NH_4)_2SO_4$ | _ | 76 | — | — | 100 | 80 | 100 |
| KNO3 | _ | 31 | _ | | 60 | 30 | 60 |
| K₂SO₄ | _ | 11 | | _ | — | 10 | 60 |

Table III. Salt-Water Ratio R at 20°C (g of Salt per 100 g of Water)^a

" R_{SA} , anhydrous salt saturation amount; R_{SI} , hydrated salt saturation amount; R_U , amount used.

^b Anhydrous salt.

' Hydrared salt.

than 0.01 and 0.02°C, respectively. In particular, the stability and uniformity estimated inside the enclosure were always better than 0.05°C.

The experimental apparatus was programmed and controlled by means of a personal computer and a proper procedure was implemented to completely automatize the measurement. The experimental tests were performed on 11 saturated salt solutions by using the preparation and test methodology described by Carotenuto and Dell'Isola [21]. In particular, a simple-geometry, low-volume (650-cm³) test enclosure with a hermetic seal was chosen. The salt-solution rates of the investigated solutions (reported in Table III) were chosen by providing a large solute excess. The volume of the air space per unit area of solution surface was less than 15:1 cm³ · cm⁻². This rate is less than the limit value recommended by ASTM [17] to minimize the transient time. Finally, twice-distilled water and salt for analysis were used.

3. EXPERIMENTAL RESULTS

The experimental analysis allows the following to be verified: (i) the equilibrium reference data in terms of relative humidity under standard conditions (ambient temperature $T_a = 20.0^{\circ}$ C, total pressure P = 101.3 kPa) and (ii) the preparation and test methodology.

On the basis of the experimental tests performed on the 11 fixed points, we determined the following quantities:

- (i) the relative humidity reference data,
- (ii) the repeatability, medium term stability, and reproducibility, and
- (iii) the transient time.

3.1. Reference Value of the Relative Humidity

The relative humidity in equilibrium with the saturated aqueous salt solution was calculated with the aid of [34]

$$\phi = \frac{f^{*}(P, T_{d}) p_{vs}(T_{d})}{f(P, T_{a}) p_{vs}(T_{a})}$$
(1)

where T_d is the dew-point temperature; f and f^* are the enhancement factors, which were evaluated, at temperatures T_a and T_d , respectively, by means of the relationship of Hyland and Wexler [35]; and p_{vs} is the water-saturated vapor pressure, which was evaluated with the aid of the relationship of Hyland and Wexler [36].

The results obtained and the uncertainties estimated in terms of dewpoint temperature with a coverage factor k equal to 1 are shown in Table IV. The uncertainties can be attributed, in accordance with the ISO Guide [37], to the following.

| Salt | T _d result (°C) | φ (% RH) | σ _A (% RH) | σ _в (% RH) | | φ(% RH) | | | |
|----------------------------------|-------------------------------|-------------|--------------------------|--------------------------|-------------|---------------------|---------------------------------|-------------------|--|
| | | | | | σ (% RH) | Greenspan [26] | Wyzykowska- Szerszen [19] | Cretinon [10] | |
| LiBr | -17.17 ± 0.36 | 6.83 | 0.21 | 0.05 | 0.22 | 6.61 ± 0.58 | <u> </u> | _ | |
| LiCl | -11.41 ± 0.20 | 10.95 | 0.17 | 0.07 | 0.19 | 11.31 ± 0.31 | 12.6 ± 1.0 | 10.9 <u>+</u> 0.6 | |
| KCH ₁ CO ₂ | -1.44 ± 0.11 | 23.52 | 0.19 | 0.14 | 0.24 | 23.11 ± 0.25 | _ | _ | |
| MgCl ₂ | 3.10 ± 0.08 | 32.64 | 0.18 | 0.19 | 0.26 | 33.07 ± 0.18 | 33.6 ± 1.2 | <u> </u> | |
| K,CO, | 7.21 ± 0.06 | 43.45 | 0.17 | 0.24 | 0.29 | 43.16 ± 0.33 | _ | 43.9 ± 0.5 | |
| $Mg(NO_3)_2$ | 10.49 ± 0.06 | 54.25 | 0.20 | 0.29 | 0.35 | 54.38 ± 0.23 | 56.2 ± 2.2 | _ | |
| кі | 14.27 ± 0.06 | 69.56 | 0.25 | 0.35 | 0.43 | 69.90 <u>+</u> 0.26 | _ | — . | |
| NaCl | 15.59 ± 0.06 | 75.76 | 0.27 | 0.38 | 0.47 | 75.47 ± 0.14 | 76.2 ± 1.7 | 75.2 ± 0.3 | |
| $(NH_4)_2SO_4$ | 16.57 ± 0.05 | 80.64 | 0.27 | 0.40 | 0.48 | 81.34 ± 0.31 | 81.3 ± 1.0 | _ | |
| KNO, | 18.99 ± 0.07 | 93.89 | 0.40 | 0.46 | 0.61 | 94.62 ± 0.66 | 95.0 <u>+</u> 1.7 | _ | |
| K₂SO₄ | 19.73 ± 0.06 | 98.33 | 0.38 | 0.48 | 0.62 | 97.59 <u>+</u> 0.53 | 98.9 <u>+</u> 1.3 | - | |

 Table IV.
 Comparison Between Relative Humidity Reference Values and Experimental Results at 20°C

- (i) Type A, σ_A uncertainties are estimated statistically and essentially connected to the repeatability and to the reproducibility of the saline solutions, to the repeatability of the measurements, T_d and T_a , and to the uniformity and the stability of the test systems,
- (ii) Type B, $\sigma_{\rm B}$ uncertainties are essentially connected to the uncertainty of the reference quantity, to the calibration correction, and to the interaction between the instrument under test and the solution itself. These uncertainties were estimated on the basis of the dew-point and air temperature uncertainties of the experimental apparatus.

The total uncertainty σ is evaluated as

$$\sigma = \sqrt{\sigma_{\rm A}^2 + \sigma_{\rm B}^2} \tag{2}$$

To evaluate the uncertainty on the basis of ϕ it is necessary to use the law of propagation of errors [38], where the pressure error is neglected:

$$\sigma_{\phi} = \sqrt{\left[\left(\frac{\partial\phi(P, T_{a}, T_{d})}{\partial T_{a}}\right)_{T_{d}}\sigma_{T_{a}}\right]^{2} + \left[\left(\frac{\partial\phi(P, T_{a}, T_{d})}{\partial T_{d}}\right)_{T_{a}}\sigma_{T_{d}}\right]^{2}}$$
(3)

Consequently, the overall measurement uncertainties regarding ϕ are σ_{ϕ} are functions of the thermodynamic conditions.

For each salt in Table IV the uncertainties in terms of relative humidity are shown. These values are included in the range between 0.19 and 0.62% RH with a coverage factor k equal to 1. The high repeatability and reproducibility of the solutions under test conditions render the total uncertainty σ essentially dependent on σ_B for high values of ϕ . In particular, for near-saturation conditions, this uncertainty can give rise to measurements of low reliability. On the other hand, for low values of ϕ , the uncertainty σ_B can be assumed to be practically negligible and the uncertainty σ proves in practice to coincide with σ_A .

3.2. Repeatability, Reproducibility, and Medium-Term Stability of Saturated Salt Solutions

For each saturated aqueous salt solution we determined

- (i) repeatabilty and reproducibility tests and
- (ii) medium-term stability tests.

The repeatability tests were carried out starting with equilibrium conditions at 20°C and disturbing the system by means of the container aperture. This gives rise both to a modest-sized thermal disturbance and to a hygrometric disturbance equal to the difference between the relative humidity of the solution and the laboratory. The reproducibility tests were carried out. by preparing the solution *ex novo* with the same proportions. For each test carried out, a high repeatability and reproducibility of the solution were obtained, with the measured ϕ values and the standard deviations proving perfectly compatible with those expected (cfr. Table IV). These tests were repeated 6 months from preparation on the solution

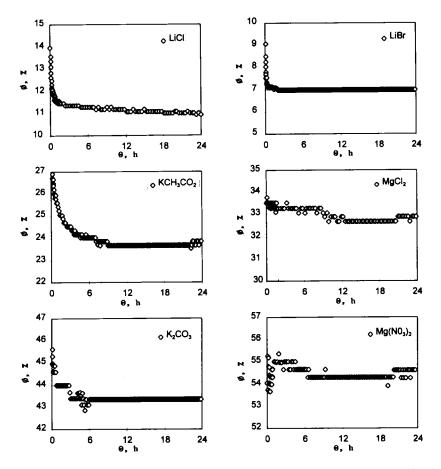


Fig. 3. Thermodynamic transient of the relative humidity of the saturated aqueous salt solutions investigated.

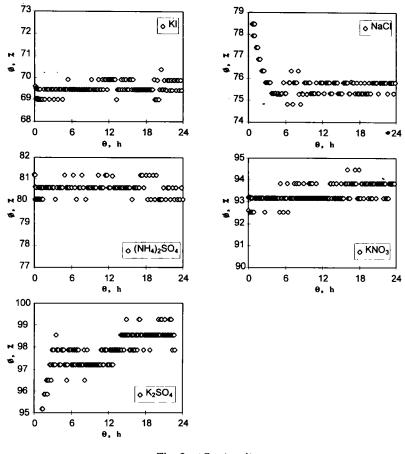


Fig. 3 (Continued)

stored at ambient temperature. Even in this case the results showed a high stability, in agreement with the experiments carried out by Cretinon and Meringoux [8].

3.3. Thermodynamic Transient

Figure 3 shows, for each saturated aqueous salt solution investigated, a trend that is typical of the thermodynamic transient of the relative humidity of the saturated aqueous salt solutions investigated upon closure of the container. The illustrations do not highlight the initial transient phase, since they have no influence on the considerations made hereinafter. From the examination of Fig. 3 it emerges that for ϕ to diverge from equilibrium conditions at a lower uncertainty than the one estimated, it is necessary on average to wait for an average time of more than 12 h. Lower equilibrium times, for example, about 6 h, can lead to errors of around 1-2% RH. Particular attention should be also be given to the preparation of the saline solution. In fact, in this case the duration of the thermodynamic transients before reaching steady-state equilibrium conditions are of the order of 48-72 h.

4. CONCLUSIONS

Comparison of the results obtained with those estimated by Greenspan [26] and later verified by Cretinon [10] and Wyzykoska-Szerszen [19] give rise to the following considerations.

- (a) For all the solutions the measured values of ϕ at equilibrium turn out to be compatible with the values reported by Greenspan and used by OIML [18], with a coverage factor of k = 2.
- (b) The salts LiBr, K_2CO_3 , Mg(NO₃), KI, and NaCl are very highly compatible (k < 1) with the values furnished by Greenspan.
- (c) The salts LiCl, KCH_3CO_2 , $MgCl_2$, and $(NH_4)_2SO_4$, even though compatible with the results of Greenspan, present a deviation higher than for the above-mentioned salts.
- (d) In the case of LiCl and K_2CO_3 verified by CETIAT [10], obtained with measurement method similar to that used by the authors, there is a greater correspondence with the values measured by the authors.
- (e) In the case of LiCl, $MgCl_2$, $Mg(NO_3)_2$, NaCl, $(NH_4)_2SO_4$, KNO_3 , and K_2SO_4 verified by Wzormat [18], there is, instead, a greater disagreement with the values measured by the authors, probably due to a greater dispersion of the experimental results.
- (f) The results concerning KNO_3 and K_2SO_4 merit separate discussion. In the authors' view, the poor agreement of these measurements with Greenspan's results is due to the lower reliability of the hygrometers at dew point for high humidity values.

From a methodological point of view, it is interesting to note the following.

(a) If calibrations are carried out with these solutions and a thermostatic system comparable to the one used, it is possible to maintain the same levels of uncertainty as ones used for commercially available climatic chambers,

Humidity Fixed Points

(b) It is necessary to wait about 12 h for a system of dimensions similar to those of the system used if one does not wish to tolerate further uncertainties due to an imperfect steady state.

These results confirm that, using a thermostatic system and observing a scrupulous method in preparing and using the solutions, values that are repeatable, reproducible, and stable over time can be obtained. The discrepancy between the measured values of ϕ and those obtained by Greenspan for some of the salts investigated, as well as the relevant disagreement between the various standard sources, suggest that further research on the salts tested be carried out.

This investigation should also be extended to all salts normally used in calibration so the latter are not affected by consistent deviations in the calibration.

NOMENCLATURE

- ϕ Relative humidity, % RH.
- σ_{ϕ} Relative humidity uncertainty, % RH
- σ_A Type A uncertainty
- $\sigma_{\rm B}$ Type B uncertainty
- σ Total uncertainty
- σ_{T_a} Ambient temperature uncertainty, °C
- σ_{T_d} Dew-point temperature uncertainty, °C
- f Enhencement factor
- k Coverage factor
- P Total pressure, Pa
- p_{vs} Water saturated vapor pressure, Pa
- *R* Salt-Water ratio, g of salt per 100 g of water
- $T_{\rm a}$ Ambient temperature, °C
- $T_{\rm c}$ Cryhydric temperature, °C
- $T_{\rm d}$ Dew-point temperature, °C
- x Composition, %

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