

ORGANISATION INTERNATIONALE DE MÉTROLOGIE LÉGALE



INTERNATIONAL RECOMMENDATION

The scale of relative humidity of air
certified against saturated salt solutions

Échelle d'humidité relative de l'air certifiée par rapport à des solutions saturées de sels

OIML R 121

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FOREWORD

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THE SCALE OF RELATIVE HUMIDITY OF AIR CERTIFIED AGAINST SATURATED SALT SOLUTIONS

1 Objet

The relative humidity scale certified with the help of saturated salt solutions is used in hygrometry in the relative humidity (RH) fixed points method. It is a subsidiary scale comprising a number of fixed points reproduced by secondary standards for humidity measurements.

The RH fixed points represent some specific RH values that are established at a certain temperature over saturated solutions of salts arising from the hygrostatic properties of such solutions.

This Recommendation specifies a set of selected saturated salt solutions whose RH values at a specific temperature correspond to fixed points (or scale marks) of the scale of relative humidity. Moreover, it indicates the conditions under which saturated solutions can be used as hygrostatic solutions.

The fixed points method is convenient, inexpensive and reproducible. It is often used for the calibration and checking of instruments that are generally used in industry and research laboratories to measure the relative humidity of air.

The use of hygrostatic solutions has also been described in ISO 483 [1], in IEC 260 [2], and in national standards [3, 4, 5].

The properties of the solutions and of the water vapor pressure over these solutions have been the subject of numerous studies in a great number of laboratories. The water vapor pressure associated with several saturated salt solutions has been most comprehensively reviewed by Lewis Greenspan, who has selected results on the basis of certain criteria and the concept of their statistical weight [6].

The data for most of the solutions have been selected from the set of values of function $U = f(t)$ (i.e. the temperature dependence of relative humidity) reported by Greenspan (1977). For sodium chloride, only the data over temperatures from 50 °C to 80 °C have been taken from Young (1967) upon verification that these agree with the values reported by Huang and Whetstone (1985) and with the earlier data by Arai (1976) and Vekker (1973). For lithium chloride, due to considerable discrepancies in the relevant literature, the RH values for the 5 °C to 20 °C range have been averaged from Greenspan (1977), Arai (1976), Acheson (1965), Wekker (1973) and Wexler (1954). The selection of the temperature range for which the RH values over saturated salt solutions should be given by this Recommendation has been made among those reported in the reference sources listed above.

The vapor pressure standards, including water, have been recommended by the International Union of Pure and Applied Chemistry (IUPAC) and described in the IUPAC Recommendation referred to in [19].

2 Units of measurement

The units of measurement to be used in calculations shall be those of the SI System and should conform with the International Document OIML D 2 *Legal units of measurement*.

- 2.1 The relative humidity of air as reproduced by hygrostatic solutions shall be expressed as percentages (%).
- 2.2 The temperature shall be expressed in degrees Celsius (°C).
- 2.3 The pressure shall be expressed in hectopascals (hPa).

3 Definitions

- 3.1 A hygrostatic solution is a saturated solution of specified salt which remains in thermodynamic equilibrium in the three-phase system at a specific temperature and pressure.
- 3.2 The physical quantity reproduced by a hygrostatic solution is the relative humidity of air over the saturated solution of the salt at given temperature and pressure.
- 3.3 The relative humidity U_w , with respect to water in moist air at pressure p and temperature t , is the ratio (expressed as a percentage) of the vapor mole fraction of water x_v to the vapor mole fraction of water x_{vw} which the air would contain if it were saturated with respect to water at the same pressure p and temperature t .

Accordingly:

$$U_w = 100 (x_v/x_{vw})_{p,t} = 100 (e'/e'_w)_{p,t}$$

where:

indices p and t indicate that each term is subject to identical conditions of pressure and temperature,

e' is the vapor pressure of water vapor in moist air,

e'_w is the saturation vapor pressure.

4 Conditions for use of the saturated salt solutions

4.1 General

A hygrostatic solution reproduces the value of relative humidity under the following conditions:

- a) if the total pressure of water vapor and air mixture in the gaseous space over the solution is near the standard pressure (101 325 Pa);
- b) if there is thermodynamic equilibrium between the solid, liquid (solution) and gas (air and water vapor mixture); and
- c) if the solution is used at a suitable temperature.

4.2 Temperature stability requirements

The relative humidity is highly temperature dependent. In addition to causing a hygrostatic effect, the hygrostatic solutions placed in the closed test cabinet cause a decrease in temperature dependence.

In a small or well ventilated test cabinet containing a salt with a large, free surface, the influence of slow temperature variations on the value of relative humidity will be reduced by the action of the salt solution.

However, provisions must be made to avoid both rapid temperature variations with time, taking into account the inertia of action of the salt solution, and temperature differences from one point to another in the working space.

In commercial hygrometers, the following is recommended:

- a) forced air circulation in hygrometric containers placed in a climatic chamber allowing temperature control (to $\pm 0.1\text{ }^{\circ}\text{C}$ or $\pm 0.2\text{ }^{\circ}\text{C}$);
- b) non-thermostated hygrometer of high thermal inertia, thermally insulated and operated in an environment of relatively stable temperature (variations of room temperature preferably less than $1\text{ }^{\circ}\text{C}$).

5 Hygrostatic solutions

5.1 The relative humidity scale certified against saturated solutions of salts, referred to as hygrostatic solutions, is made up of a set of 11 humidity fixed points (HFP), obtained with the use of saturated solutions of 11 salts. The numbers given to the HFPs denote the approximate nominal values of relative humidity at $20\text{ }^{\circ}\text{C}$.

The scale encompasses the relative humidity range from 2 % to 98.5 % and a temperature range from $5\text{ }^{\circ}\text{C}$ to $80\text{ }^{\circ}\text{C}$.

The scale is made up of the following salts:

HFP 4	Caesium Fluoride CsF	temp. from $15\text{ }^{\circ}\text{C}$ to $80\text{ }^{\circ}\text{C}$
HFP 7	Lithium Bromide LiBr	temp. from $5\text{ }^{\circ}\text{C}$ to $80\text{ }^{\circ}\text{C}$
HFP 12	Lithium Chloride LiCl	temp. from $5\text{ }^{\circ}\text{C}$ to $80\text{ }^{\circ}\text{C}$
HFP 23	Potassium Acetate CH_3COOK	temp. from $10\text{ }^{\circ}\text{C}$ to $30\text{ }^{\circ}\text{C}$
HFP 33	Magnesium Chloride MgCl_2	temp. from $5\text{ }^{\circ}\text{C}$ to $80\text{ }^{\circ}\text{C}$
HFP 43	Potassium Carbonate K_2CO_3	temp. from $5\text{ }^{\circ}\text{C}$ to $30\text{ }^{\circ}\text{C}$
HFP 59	Sodium Bromide NaBr	temp. from $5\text{ }^{\circ}\text{C}$ to $80\text{ }^{\circ}\text{C}$
HFP 70	Potassium Iodide KI	temp. from $5\text{ }^{\circ}\text{C}$ to $80\text{ }^{\circ}\text{C}$
HFP 75	Sodium Chloride NaCl	temp. from $5\text{ }^{\circ}\text{C}$ to $80\text{ }^{\circ}\text{C}$
HFP 85	Potassium Chloride KCl	temp. from $5\text{ }^{\circ}\text{C}$ to $80\text{ }^{\circ}\text{C}$
HFP 98	Potassium Sulfate K_2SO_4	temp. from $5\text{ }^{\circ}\text{C}$ to $50\text{ }^{\circ}\text{C}$

When the salt solutions that make up the HFP scale are used at temperatures above $40\text{ }^{\circ}\text{C}$, the risk of salt crystals settling on the surface rather than being immersed in the solution must be taken into account.

The potassium iodide solution must be free of potassium iodate KIO_3 and must be stored in a dark place.

5.2 The temperature dependence of relative humidity of air over the saturated salt solutions is presented in Table 1. The HFP values in Table 1 are given every 5 °C for a temperature range of 5 °C to 80 °C (except for the HFP 98 values known up to 50 °C and HFP 43 and HFP 23 values known up to 30 °C).

Table 1 provides the following data for each saturated salt solution over the temperature range:

- HFP values, i.e. the relative humidity values over the saturated salt solutions, at the specified temperature points,
- ΔHFP_D values, i.e. the uncertainties with which the HFP values are known (these values can be considered as equivalent to expanded uncertainties calculated with $k = 2$).

Under ideal conditions, the accuracy of the sources generated by this practice is equal to the uncertainty figures associated with each source value, as stated in Table 1.

6 Device for the reproduction of the relative humidity scale certified against saturated salt solutions

6.1 The hygrostatic salt solution shall be placed in a sealed measuring vessel (hygrostat) of a suitable shape and capacity to accommodate the hygrometer being examined.

6.2 The hygrostat shall be made of a corrosion-resistant non-hygroscopic material. It shall be of a simple form permitting easy cleaning.

6.3 The measuring vessel (hygrostat) of a capacity V and surface area of its walls S , shall have the lowest possible V/S ratio. The free surface of the solution shall always be as large as possible.

Without air circulation the height of the container shall not exceed the smallest dimension of the free surface of the solution. In containers with air circulation this height may reach 1.5 times the smallest dimension of the free surface. Container head-space volume shall be no larger than necessary to contain a stored item.

6.4 The thermostated hygrostat shall be equipped with a temperature control system that will maintain the stability of temperature and temperature gradients inside the measuring space within the limits ± 0.1 °C over temperatures from 5 °C to 50 °C, and within ± 0.2 °C over temperatures from 50 °C to 80 °C.

The non-thermostated hygrostat shall have its measuring space insulated from the surroundings. This insulation shall be adequate to reduce the influence of external temperature variations (preferably not exceeding ± 1 °C) to a sufficiently low rate within the measuring space so as to be fully compensated by the action of the hygrostatic solution.

Thermostated as well as non-thermostated hygrometers shall be equipped with a device for measuring the temperature of the air over the solution, and that of the solution with an expanded uncertainty, calculated with $k = 2$, less than 0.1 °C.

7 Procedure for preparing a hygrometric solution

7.1 The hygrometric solution is prepared from an analytical-reagent grade salt and pure (distilled or deionized) water. In certain cases, if the purity of the salt is unknown, it should be purified by crystallization from distilled or deionized water prior to its use in the preparation of the hygrometric solution.

Saturated salt solutions may be prepared using either anhydrous or hydrated reagents, which are often preferred to anhydrous forms for their solvent characteristics.

7.2 The salt shall be dissolved in water in such a proportion that 30 % to 90 % of the weighed sample remains undissolved. Consequently, a weighed sample for the solution shall be heavier (by 30 %) than the one corresponding to the solubility limit at a given temperature.

7.3 In order to obtain a homogeneous salt solution, the salt crystals shall be added to water of a much higher temperature than that required; the solution shall then be cooled down.

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Table 1
Equilibrium relative humidity values for selected saturated aqueous salt solutions

Relative humidity %											
t °C	HFP 4 Caesium Fluoride (7)	HFP 7 Lithium Bromide (7)	HFP 12 Lithium Chloride (7)	HFP 23 Potassium Acetate (7)	HFP 33 Magnesium Chloride (7)	HFP 43 Potassium Carbonate (7)	HFP 59 Sodium Bromide (7)	HFP 70 Potassium Iodide (7)	HFP 75 Sodium Chloride (8)	HFP 85 Potassium Chloride (7)	HFP 98 Potassium Sulfate (7)
5	–	7.4 ± 0.8	13 ⁽³⁾	–	33.6 ± 0.3	43.1 ± 0.5	63.5 ± 0.8	73.3 ± 0.4	75.7 ± 0.3	87.7 ± 0.5	98.5 ± 1.0
10	–	7.1 ± 0.7	13 ⁽⁴⁾	23.4 ± 0.6	33.5 ± 0.3	43.1 ± 0.4	62.2 ± 0.6	72.1 ± 0.4	75.7 ± 0.3	86.8 ± 0.4	98.2 ± 0.8
15	4.3 ⁽¹⁾ ± 1.4 ⁽²⁾	6.9 ± 0.7	12 ⁽⁵⁾	23.4 ± 0.4	33.3 ± 0.3	43.2 ± 0.4	60.7 ± 0.6	71.0 ± 0.3	75.6 ± 0.2	85.9 ± 0.4	97.9 ± 0.7
20	3.8 ± 1.1	6.6 ± 0.6	12 ⁽⁶⁾	23.1 ± 0.3	33.1 ± 0.2	43.2 ± 0.4	59.1 ± 0.5	69.9 ± 0.3	75.5 ± 0.2	85.1 ± 0.3	97.6 ± 0.6
25	3.4 ± 1.0	6.4 ± 0.6	11.3 ± 0.3	22.5 ± 0.4	32.8 ± 0.2	43.2 ± 0.4	57.6 ± 0.4	68.9 ± 0.3	75.3 ± 0.2	84.2 ± 0.3	97.3 ± 0.5
30	3.0 ± 0.8	6.2 ± 0.5	11.3 ± 0.3	21.6 ± 0.6	32.4 ± 0.2	43.2 ± 0.5	56.0 ± 0.4	67.9 ± 0.3	75.1 ± 0.2	83.6 ± 0.3	97.0 ± 0.4
35	2.7 ± 0.7	6.0 ± 0.5	11.3 ± 0.3	–	32.1 ± 0.2	–	54.6 ± 0.4	67.0 ± 0.3	74.9 ± 0.2	83.0 ± 0.3	96.7 ± 0.4
40	2.4 ± 0.6	5.8 ± 0.4	11.2 ± 0.3	–	31.6 ± 0.2	–	53.2 ± 0.5	66.1 ± 0.3	74.7 ± 0.2	82.3 ± 0.3	96.4 ± 0.4
45	2.2 ± 0.5	5.7 ± 0.4	11.2 ± 0.3	–	31.1 ± 0.2	–	52.0 ± 0.5	65.3 ± 0.3	74.5 ± 0.2	81.7 ± 0.3	96.1 ± 0.4
50	2.1 ± 0.4	5.5 ± 0.4	11.1 ± 0.3	–	30.5 ± 0.2	–	50.9 ± 0.6	64.5 ± 0.3	74.5 ± 0.9	81.2 ± 0.4	95.8 ± 0.5
55	2.0 ± 0.4	5.4 ± 0.3	11.0 ± 0.3	–	29.9 ± 0.2	–	50.2 ± 0.7	63.8 ± 0.4	74.5 ± 0.9	80.7 ± 0.4	–
60	2.0 ± 0.4	5.3 ± 0.3	11.0 ± 0.3	–	29.3 ± 0.2	–	49.7 ± 0.8	63.1 ± 0.4	74.4 ± 0.9	80.3 ± 0.5	–
65	2.1 ± 0.5	5.3 ± 0.3	10.9 ± 0.3	–	28.5 ± 0.3	–	49.5 ± 1.0	62.5 ± 0.4	74.2 ± 0.9	79.9 ± 0.5	–
70	2.2 ± 0.6	5.2 ± 0.3	10.8 ± 0.4	–	27.8 ± 0.3	–	49.7 ± 1.1	61.9 ± 0.4	74.1 ± 0.9	79.5 ± 0.6	–
75	2.4 ± 0.7	5.2 ± 0.2	10.6 ± 0.4	–	26.9 ± 0.3	–	50.3 ± 1.3	61.4 ± 0.5	74.0 ± 0.9	79.2 ± 0.7	–
80	2.6 ± 0.8	5.2 ± 0.2	10.5 ± 0.5	–	26.1 ± 0.4	–	51.4 ± 1.5	61.0 ± 0.5	73.9 ± 0.9	78.9 ± 0.8	–

- 1) HFP : humidity fixed point
2) ΔHFP_D : the uncertainties with which the HFP values are reported in literature rounded to 0.1 % (these values can be considered as equivalent to expanded uncertainties calculated with $k = 2$)
3) Values dispersion from 11.2 % to 14.0 %
4) « from 11.3 % to 14.3 %
5) « from 11.3 % to 13.8 %
6) « from 11.1 % to 12.6 %
7) HFP values according to L. Greenspan [6]
8) HFP values according to a) L. Greenspan from 5 °C to 45 °C [6]
b) P.H. Huang and J.R. Whetstone from 50 °C to 80 °C [14]

