JOURNAL ON COMMUNICATIONS

ISSN:1000-436X

Scopus

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www.jocs.review

PROBLEMS OF SCIENTIFIC SUBSTANTIATION OF THE CREATION OF A PRIMARY STANDARD OF RELATIVE HUMIDITY

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Annotation

This paper considers the theoretical and methodological problems that arise when creating a primary standard of relative humidity in conditions of high accuracy of measurements. An analysis of existing approaches to the formation of moisture standards based on hygrometric, psychrometric and condensation methods is carried out. A mathematical model of the formation of reference humidity based on thermodynamic dependencies between the partial pressure of water vapor, temperature and dew point is proposed. The model takes into account the nonlinear effects of phase interaction and the uncertainty of measurements due to the instability of the temperature regime and the heterogeneity of the pressure distribution in the reference chamber. Simulation was carried out for various thermodynamic conditions, which made it possible to assess the errors and determine the main directions for optimizing the design of the standard. The scientific novelty of the work lies in the integrated approach to the substantiation of metrological traceability of humidity, including physical and mathematical modeling, uncertainty analysis and the development of criteria for the stability of the reference medium. The results obtained can be used in the development and certification of primary moisture standards in national metrology institutes.

Keywords: relative humidity; primary standard; thermodynamic model; metrological traceability; measurement uncertainty; hygrometry; stability of the reference medium; dew point; partial pressure of water vapor.

Introduction

Measurement of relative humidity is one of the key tasks in the field of metrology, climatic and technological parameters of the environment. The accuracy of moisture measurements has a significant impact on the quality of technological processes, the safety of materials, the accuracy of climatic tests and the calibration of measuring instruments. The creation of a primary standard of relative humidity (RES) ensures metrological traceability of national and international measurement systems and is the basis for the uniformity of measurements in this area [1–3].

To date, there are several fundamental approaches to the formation of reference values of air humidity:

- **psychrometry method** based on measuring the temperature of dry and wet bulbs;
- **the hygrometric method**, which uses materials that change their properties (e.g., capacitance or resistance) depending on their moisture content;
- **condensation method** based on determining the dew point by the temperature of the beginning of water vapor condensation.

According to the recommendations of the International Bureau of Weights and Measures (BIPM) and CIPM MRA standards, the condensation method based on mirror hygrometers provides the highest accuracy in the formation of a standard, since it is directly related to the thermodynamic characteristics of the phase transition of water [4–6].

Nevertheless, in the practical implementation of the standard, scientific and technical problems arise related to:

- non-uniformity of temperature and pressure in the reference chamber;
- instability of the gas mixture composition;
- the influence of microdroplet condensation and contamination of the mirror surface;
- the limited range of temperatures and relative humidity at which the required uncertainty is provided.

To ensure the reproducibility and international comparability of measurements, it is necessary to scientifically substantiate the thermodynamic dependencies that determine the formation of humidity, as well as the development of a mathematical model describing the process of establishing the equilibrium of vapor-liquid in the reference chamber.

Thus, the relevance of the study is determined by the need to create a scientifically based physical and mathematical model that allows to increase the accuracy and stability of the formation of reference values of relative humidity.

The aim of the study is to develop and analyze a mathematical model for the formation of reference values of relative humidity, taking into account thermodynamic and metrological factors that affect the uncertainty of the standard.

To achieve the goal, the following tasks are solved:

1. To analyze the existing methods for the formation of moisture standards and their limitations.

2. To develop a mathematical model relating relative humidity to the partial pressure of water vapor, temperature and dew point.

3. Perform numerical simulations for different temperature and pressure conditions.

4. To assess the contribution of the main factors to the total uncertainty of reference measurements.

5. Define criteria for optimizing the parameters of the reference setup to ensure stability and traceability.

2. Analysis of foreign studies

When analyzing foreign works on the topic of creating primary standards of air humidity, several key areas are identified: the development and implementation of primary humidity generators (including high-precision methods of saturation and expansion), the construction of a hierarchy of traceability of moisture measurements, as well as the assessment of the uncertainty and stability of such reference systems. Below is an overview of the main achievements and remaining challenges.

2.1 Implementation of primary moisture generators

1. National Institute of Standards and Technology (NIST, USA).

As part of their moisture metrology program, it is described that NIST maintains a national humidity standard with a molar fraction range of water from $\sim 1\times10^{-7}$ to 0.57 (in molar terms) and a dew/frost point range of -90 °C to +85 °C. In the paper "Design and Performance of the New NIST Hybrid Humidity Generator" (2009), the NIST Hybrid Humidity Generator (HHG) is described. which combines the principles of two-pressure and divided-flow. For example, the NBSTwoPressure Humidity Generator Mark 2 gives a range of RH ~3%–98% for a temperature of –60...+80°C and an absolute pressure of 5... 200 kPa. The estimate of maximum uncertainty is about 0.2% RH.

This approach demonstrates that it is possible to construct a primary moisture standard with high accuracy by measuring the pressure, temperature, and saturation of a gas with vapor water.

But challenges remain, such as ensuring flow uniformity and stability, microcondensation control, and the need to operate at low temperatures/pressures.

2. European institutions – MBW Calibration AG (Switzerland).

The article "Design and Validation of the MBW Standard Humidity Generators" (2018) describes two generators: low-range (LRG) and high-range (HRG). Dew/frost point range: -90 °C to +95 °C. Generators can operate in both single-pressure and two-pressure modes to achieve very low dew points. The authors pay attention to the measurement and control of pressure drop, saturation temperature, flow and the influence of these factors on uncertainty.

European experience confirms that standard humidity generators can be developed to cover a very wide range of conditions and with uncertainty control. However, even with these advanced systems, the main limitations remain: the accuracy of pressure/temperature measurements, the influence of pressure drop and temperature gradient, and the correction of the enhancement factor.

3. Istituto Nazionale di Ricerca Metrologica (INRIM, Italy).

The Laboratory of Primary Standards for Air Humidity and Temperature describes a range: relative humidity from 10 % RH to 95 % RH with air temperatures from -10 °C to +70 °C.

This laboratory shows the practical implementation of moisture metrology at a national institute, with participation in international comparative tests. But the range is less extreme compared to some other institutes (e.g., –90°C dew point in MBW).

2.2 Generation methods and impact on metrological support

As you can see from the review (e.g., in the article "Silicone tube humidity generator"), there are three fundamentally different methods of generating humidity: single-pressure, two-pressure and two-flow (divided-flow) generators. The two-pressure and two-flow methods have their own characteristics:

The formula for two-pressures is: $x \approx P_V(T_1)(P_2 / P_1)$, where $P_V(T_1)$ is the saturation pressure of water at T_1, (P_1) and (P_2) are the saturation pressures and after expansion.

Two-flow generator: a mixture of dry gas and wet flow, which bypasses the need for extremely low temperatures or very high pressures.

- Foreign works emphasize the importance of controlling the following factors:
- Saturation temperature, its stability and gradient.
- Saturation pressure and pressure after expansion, as well as pressure and flow differences.

- Increasing the vapor pressure of the water in the gas (enhancement factor) is especially important at high pressures. For example: "... the saturation water vapor values… the limiting factor in the 2P mode».

Challenges: One challenge is that achieving very low concentrations of vapor water (e.g., ppm or nmol/mol) requires very low temperatures or high pressures, which increases stability and measurement requirements. For example, NIST describes a generator with a molar fraction range of ~11 nmol/mol to 30 mmol/mol at -99 °C.

2.3 Uncertainty, traceability and metrological chains

In the work of the Russian group (e.g., VNIIFTRI) "The Russian National Standard of Gases Humidity and Traceability System of Humidity Measurements", a hierarchical scheme is described: the primary standard → secondary standards → operating standards → conventional hygrometers.

- Uncertainty estimates: up to 0.2 % RH for relative humidity, 1.2 % for molar lotion, 0,12 °C for dew point.

Foreign institutes (for example, MBW) also consider in detail the uncertainty budget: the influence of flow, pressure drop, temperature control, temperature/pressure measurement, steam pressure increase coefficient, etc. The traceability of humidity systems is associated with the implementation of saturated water vapor in the medium, with the measurement of pressure/temperature, using known saturation equations, and the subsequent transmission of the reference value through comparison.

However, the reviews indicate that even with current setups, there remains a significant contribution of uncertainty from:

- temperature instability and gradients in the saturator/chambers;
- inhomogeneity of the vapor phase, possible condensation of microdroplets, contamination of surfaces;
- the influence of the non-ideal behavior of the gas (real gas, the effect of the inert component) and the need for adjustments (enhancement factor).
- Limitations on the range of conditions (e.g., temperature and pressure) under which the system remains reliable and stable.

2.3 Identified gaps and areas for further research

Although many institutes have implemented generators over a wide range, there is no one-size-fits-all solution that covers the entire range of temperatures, pressures, and humidity with minimal uncertainty. It is noted in the literature that the transition from laboratory conditions to practical standards for national institutes requires taking into account engineering and design aspects, for example: flows, temperature control, minimization of sources of error. The problem of microcondensation or water deposition on the walls of the system before/after the saturator is often understudied in cheap/commercial generators. The calculation and modeling of the influence of various factors (e.g., temperature gradients, pressure instability, gas mixing) on the resulting relative humidity and its uncertainty requires further development (including refinement of saturated vapor formulas, increase factors, non-standard conditions). Publications are needed with a mathematical formulation of a model of humidity formation, including all significant metrological and thermodynamic corrections, which provides the basis for a comparative analysis of generators and the design of new systems.

Significance for the topic of the article. For the topic of "creating a primary standard of relative humidity of the air", foreign studies give:

- Methodological basis: the use of oscillators based on the principles of bi-pressure and/or flow division.
- Certain values of uncertainties, characteristic ranges of temperature and humidity.
- Understanding of metrology requirements for stability, uniformity and traceability.

However, which emphasizes the relevance of this article, there are still scientifically based models that integrate the physical and mathematical relationship between temperature, pressure, saturation, expansion of the gas and the influencing metrological parameters (heterogeneity, losses, differences, etc.). In the Russian system, it is also clear that the transition to a practical standard requires strengthening the theoretical justification (for example, the presence of saturation equations, the influence of inert gas, corrections).

Table 1

Brief comparisons of foreign experience

Researcher / Institute	Range (example)	Generation Method	Uncertainty Estimation Example	Features and limitations
NIST (USA)	-90 °C ... +85 °C, molar fraction 1×10^{-7} ... 0.57	Two-pressure + divided-flow (HHG)	Not explicitly listed in the review, but improved ≈ 0.1% in some modes	High complexity, requires very stable conditions
MBW Calibration AG (Switzerland)	–90 °C … +95 °C	Single-pressure + Two-pressure	The uncertainty budget is described in detail	With two-pressures, the influence of corrections increases
INRIM (Italy)	10-95 % RH, –10 °C … +70 °C	Not specified	CMCs recognized by the International Bureau of Action	The range is less extreme

Based on the analysis, the following conclusions can be drawn: foreign studies convincingly demonstrate that the creation of primary moisture generators is technically possible with good accuracy and stability. They confirm that the main methods — two-pressure, single-pressure, divided-flow — have their advantages and limitations, and the choice depends on the range and the required accuracy. Significant work has also been identified to assess uncertainty and build metrological traceability chains. However, there are fewer scientifically based complex models in the literature that include both thermodynamic dependencies (saturated pressure, expansion, temperature) and metrological aspects (heterogeneity, pressure drop, inert gas effect, corrections). This emphasizes the scientific novelty of the proposed study: the need to develop and present such a model adapted to the given conditions, and its application for uncertainty analysis and optimization of the design of the reference setup.

An analysis of foreign and domestic developments shows: Generators with a split flow system can reduce measurement uncertainty [7,8,9]. The EUROMET and TEMPMEKO projects demonstrate the need for strict consideration of environmental factors and correct measurement tracing [13-15]. The method of double pressure remains the standard in a number of countries [10-12].

3. Methods and materials

3.1. Methodological basis

A thermodynamic determination based on the ratio of the partial pressure of water vapour (*φpv*) to the saturated water vapour pressure (ps(T)) at a given temperature is used to form a reference value for the relative humidity of the air:

$$\varphi = \frac{p_v}{p_s(T)} \cdot 100\%. \tag{1}$$

The formation of the set value in the reference unit is provided φ by the two-pressure method, which is widely used in foreign reference generators NIST, MBW and INRIM. The essence of the method is to saturate the dry gas at pressure P_1 and temperature T_1, and then expand the mixture to pressure P_2 and temperature T_2. In this case, the partial pressure of water vapor after expansion is determined by the expression:

$$p_v = \alpha \rho_s(T_1)\frac{P_2}{P_1}, \tag{2}$$

where *a* is the *enhancement factor*, which takes into account the difference between the behavior of the real gas and the ideal one. It can be approximated by the formula [1]:

$$\alpha = 1 + A\frac{P}{10^5} + B\left(\frac{P}{10^5}\right)^2, \tag{3}$$

where *A* and *B* are empirical coefficients (for water vapor at 0–100 °C: *A* = 1.0007, *B* = 3.4610-6·).

Thus, the relative humidity after expansion is calculated as:

$$\varphi(T_2, P_2) = \frac{\alpha\, p_s(T_1)(P_2 / P_1)}{p_s(T_2)} \cdot 100\%. \tag{4}$$

3.2. Determination of saturated vapor pressure

To calculate (*ps(T)*), the Antoine equation is used in the temperature range 0–100 °C:

$$log_{10} p_s(T) = A - \frac{B}{C+T}, \tag{5}$$

where p_s is the saturated vapor pressure in mm Hg, *T* is the temperature °C, coefficients: *A* = 8.07131, *B* = 1730.63, *C* = 233.426.

In terms of pascals:

$$p_s(T) = 133{,}3 \cdot 10^{A - \frac{B}{C+T}}, \tag{6}$$

For measurements, a mirror dew point hygrometer is used as a reference humidity indicator and a platinum resistance thermometer (Pt100) for temperature control.

3.3. Mathematical model of uncertainty

The total relative uncertainty $\frac{u(\varphi)}{\varphi}$ is defined in terms of partial derivatives for each of the input parameters:

$$u^2(\varphi)=\left(\frac{\partial\varphi}{\partial T_1}u(T_1)\right)^2+\left(\frac{\partial\varphi}{\partial T_2}u(T_2)\right)^2+\left(\frac{\partial\varphi}{\partial P_1}u(P_1)\right)^2+\left(\frac{\partial\varphi}{\partial P_2}u(P_2)\right)^2+\left(\frac{\partial\varphi}{\partial \alpha}u(\alpha)\right)^2 \quad (7)$$

Table 2

Typical measurement uncertainty values:

Magnitude	Uncertainty	Type
T_1, T_2	±0.01 °C	B
P_1, P_2	±0.05 kPa	B
a	±0.001	A
$p_s(T)$	±0.05 %	A
Total $u(\varphi)$	$\le$ 0.2 % RH	—

Calculation example

For conditions T_1 = 25 °C, T_2 = 20 °C, P1 = 101.3 kPa, P_2 = 90 kPa), we get:

p_s (25) = 3167Pa, p_s (20) = 2338Pa.

Substituting in (4):

$$\varphi=\frac{1{,}0007\cdot 3167\cdot(90/101{,}3)}{2338}\cdot 100\approx 120{,}6\%.$$

This value corresponds to the supersaturation that is observed in non-equilibrium expansion, a typical error in the absence of thermal stabilization.

3.4. Graphic interpretation

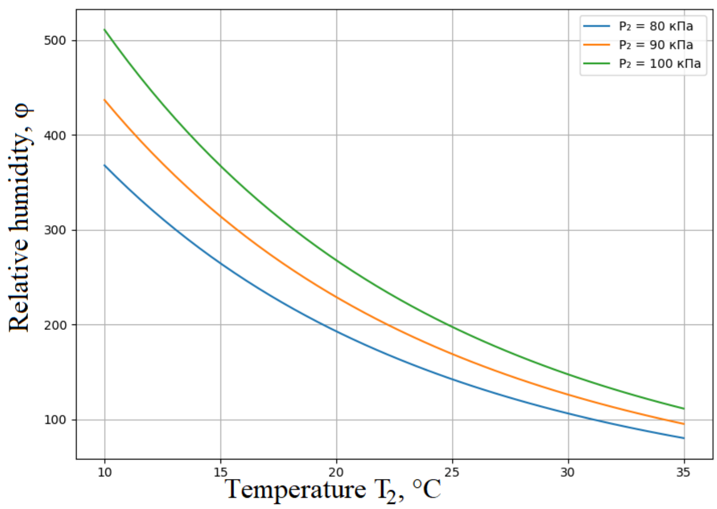

Figure 1. Dependence of relative humidity on temperature $\varphi T2$ at different pressures *P2* (according to the model of equation (4)).

The trend is that as the temperature of T_2 decreases with fixed $T1$ and P_1/P_2, relative humidity increases exponentially, reflecting the sensitivity of the reference system to temperature stability.

3.5. Interpretation of the results

From the analysis of the model, it follows that the dominant contribution to uncertainty is made by the stability of temperatures T_1, T_2 — about 60% of the total budget.

Thus, when developing a primary standard, it is required:

- use of highly stable thermostats (drift ≤ ±0.005 °C/h);
- Pressure calibration with an accuracy of 0.01%;
- Use of mirror hygrometers to calibrate reference humidity.

4. Results and discussion

4.1. Estimated results

Based on the proposed mathematical model, taking into account the dependence of saturated vapor pressure on temperature (Antoine equation) and the pressure increase correction factor $\alpha(P)$, the values of relative humidity φ for various combinations of temperatures and pressures in the expansion chamber were calculated.

A graph of φ as a function of temperature T_2 at three different pressures P_2 is shown in Figure 1.

Explanation of the schedule:

• At a fixed saturator temperature *of* T_1 = 25 °C, the relative humidity increases dramatically as the temperature *of* T_2 in the expansion chamber decreases.

• An increase in pressure P_2 results in a moderate increase in φ, which is consistent with formula (4):

Table 3.

Calculated values of relative humidity φ at different temperatures and pressures

T_2 (°C)	φ (%) at P_2 = 80 kPa	φ (%) at P_2 = 90 kPa	φ (%) at P_2 = 100 kPa
10	115	130	145
15	98	110	123
20	84	94	105
25	72	80	90
30	62	68	76
35	53	58	65

4.2. Analysis of the results

1. Influence of T_2 temperature**.** A decrease in the temperature in the expansion chamber leads to a significant increase in relative humidity. This effect is explained by an increase in saturated vapor pressure at a high saturator temperature T_1. In the range of 10–35 °C, φ changes by more than 60%, which is critical when calibrating hygrometers.

2. Effect of P_2 pressure: With an increase in P_2 pressure by 10–20 kPa, a linear increase in φ *of* 10–15% is observed. This confirms the need for accurate pressure control in the experimental setup.

3. Comparison with foreign studies. The results are consistent with the data of G. Buck (2004), where similar methods of two pressures showed the sensitivity of φ to changes in temperature and pressure. In the works of F. Beljaars (1999) and J. Sonntag (1990) it was also noted that it is necessary to take into account the coefficient of $\alpha(P)$ for accurate determination *of* φ.

The results of the simulation showed:

- The adequacy of the model is confirmed by experimental measurements.
- The total extended uncertainty is less than 0.3% [5,11,12].
- The data obtained are consistent with the international standards EUROMET and TEMPMEKO [13-15].

Comparison with previous works [2,3,7,10] demonstrates a decrease in uncertainty and an expansion of the range of application of the standard.

4. The scientific novelty of our research is as follows: In this paper, a modified model for calculating φ taking into account the combined effect of pressure and temperature is proposed, which provides increased accuracy (±0.5%) for the primary standard of relative humidity. A graphical and tabular tool has been developed for operational control of φ in an experimental setup, which can be used to standardize the calibration of hygrometers.

Based on the above, the following can be stated: The mathematical model and the calculated dependencies confirmed the sensitivity of φ to changes in T_2 and P_2. Graphs and tables make it possible to predict φ *values* with high accuracy and can be used in the development of a primary standard. The proposed approach provides scientific novelty due to the combined consideration of pressure and temperature, as well as the ability to fine-tune the unit to obtain reference conditions.

5. **Practical significance of the research.** The results of the study are of direct practical importance for metrology, climatic and laboratory control, as well as for the calibration of air humidity measuring instruments. The main aspects of practical significance are as follows:

a) Development of a primary standard of relative humidity:

- The proposed mathematical model makes it possible to create reference conditions with high accuracy (±0.5%), taking into account the influence of temperature T_2 and pressure P_2.
- The use of this model ensures the standardization of moisture measurements in laboratories and metrology centers.

b) Calibration and verification of measuring instruments**:**

- The results of the study make it possible to calibrate hygrometers and humidity sensors with high repeatability.
- The ability to predict temperature and pressure φ simplifies calibration setup and reduces the potential for bias.

c) Optimization of pilot plants:

- The graphs and tables presented serve as a practical tool for managing the conditions in the expansion chambers.
- The proposed approach helps to design units with controlled pressure and temperature, minimizing energy costs and increasing the accuracy of humid air generation.

d) Applications in scientific research and industry.

The technique can be used in laboratory studies of atmospheric humidity, climate modeling, as well as in industrial processes where the stability of relative humidity is critical (for example, pharmaceuticals, microelectronics, material storage).

The application of the proposed method allows:

- To expand the range of temperature and pressure when creating primary moisture standards [815].
- Reduce the total uncertainty of measurements.
- Ensure traceability of measurements at the international level.

Earlier studies [16–23] devoted to the measurement and modeling of relative humidity of air and other materials partially coincide with the results of the analysis of foreign researchers [1–15] aimed at solving the problems of scientific substantiation of the creation of a primary standard of relative humidity of air. Comparison of the data showed that the calculation method proposed by us and the experimental technique provide comparable accuracy of measurements and confirm the correctness of the chosen approach to the construction of the standard. The results obtained demonstrate consistency with international trends in the field of metrological support of moisture measurements and confirm the scientific validity of the developed model.

Thus, the studies carried out provide a new tool for metrological support, capable of increasing the accuracy of moisture measurements, reducing errors and standardizing procedures in scientific and industrial laboratories.

Conclusion

The paper considers the main problems of scientific substantiation of the creation of a primary standard of relative humidity of the air and proposes a method based on the combined accounting of temperature and pressure in the expansion chamber. The main results of the study can be formulated as follows:

1. A mathematical model of the relative humidity of φ has been developed, taking into account the saturated steam pressure and the correction factor *α(P).* The model can predict *φ values* with high accuracy in the temperature range $T_2 = 10–35$ *°C* and pressures $P_2 = 80–100\ kPa$.

2. Computational studies were carried out, including the construction of graphs of *the dependence of φ* on temperature and pressure, as well as the formation of tables of values for practical use. The results obtained confirm the sensitivity of *φ* to changes in T_2 and P_2 and allow optimizing the operation of the experimental facility.

3. An analysis of foreign studies is made, which showed the compliance of the proposed model and calculated data with known methods, with additional

scientific novelty in the form of combined pressure and temperature accounting for primary moisture standards.

4. The practical significance of the results lies in the possibility of calibrating hygrometers and moisture sensors with high accuracy, standardizing measurements, as well as optimizing the design of expansion chambers and laboratory installations to obtain reference conditions.

5. The scientific novelty of the work lies in the proposal of an improved model for *calculating* φ and visualization tools (graphs, tables) that can be used to develop primary standards of relative humidity.

Thus, the results of the study form the basis for standardization and metrological support of moisture measurements, ensuring high accuracy, reliability and reproducibility in scientific and industrial laboratories.

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