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REALISATION OF THE PHASE EQUILIBRIUM METHOD IN THE STANDARD LOW FROST-POINT HUMIDITY GENERATOR

G. Mamontov [1], D. Mamontova [2] , and L. Konopelko [1]
[1] D. I. Mendeleyev Institute for Metrology (VNIIM), 19, Moskovsky pr., 198005
Saint-Petersburg, Russia
[2] Saint-Petersburg State University, 11, Universitetskaya nab., 199034
Saint-Petersburg, Russia

Abstract: Results of theoretical analyses of the phase equilibrium method of required low frost-point temperature generation are given, on the basis of which the described standard dynamic humidity generator is designed for testing and calibration of hygrometers. The generator allows to produce the required and exactly known frost-point temperature of vapour-gas mixture of down to -120 °C in wide range of mixture flow rates with the estimated uncertainty of ±0.1°C of frost-point temperature, which is almost equal in the whole range.

Keywords: Standard low frost-point generator, phase equilibrium method, calibration; thermal and temperature measurement.

1 INTRODUCTION

Metrological assurance of existing and prospective humidity measuring instruments and validation of new measurement methods is that certain condition which enables to provide the accuracy and reliability in humidity measurements. And one of the most important problems in solution of the problem of metrological assurance is development of the humidity standard, allowing to reproduce the quantity, characterising the moisture content of the humid gas in the given range at known uncertainty and to transfer it to the instruments. The operation principle of the standard, should not require calibration in terms of humidity, in its turn, but provide traceability in measurements.

Today, many national hygrometric laboratories use standard humid gas generators as primary standards of humidity, based on various methods of humidity generation in gases and gas mixtures [1]. In VNIIM, the standard humidity generator has been designed, intended to produce the vapour-gas mixture with the required frost-point temperatures in the range of moisture microconcentrations. The range of generated dew/frost point temperatures is from –100 °C (although practically -120 °C has been reached) to +20 °C with the uncertainty of ±0.1 °C at 95% confidence level [2]. The uncertainty of generated dew/frost point temperature is almost equal in whole range, which is undoubtedly a consequence of advantages of the method used in the generator.

This paper briefly describes the theoretical approach to the analysis of the method of low frost-point temperature generation. The obtained theoretical results enabled to determine main constructive parameters of the saturator. Design of the low frost-point generator, which is used as a primary standard of humidity, is also submitted.

2 PHASE EQUILIBRIUM METHOD

The method used in the standard low frost-point generator and called "phase equilibrium method", consists in direct reproduction of the humid gas saturation state over a plane condensed layer at a given temperature, which represents the dew (or frost) point temperature, according to definition. At this moment, the dynamic phase equilibrium between gaseous and condensed phases of water vapour is established. Generally, reproduction of the saturation state underlies most of the methods, of humidity generation used in many national laboratories. The basic difference consists in those conditions, under which the phase equilibrium is achieved and, of coarse, in practical realisation.

Thus, the necessary part of the standard generator development is the analysis of state of saturation achievement in the saturator. In general, this kind of analysis should usually consist of the theory of thermodynamic processes, which cause the saturation, and experimental works using existing moisture analysers. However, considering experience of the authors of [3,4], the assumption has been made in this work that it is impossible to obtain any accurate and reliable experimental results in the range of very low frost-point temperatures. Therefore, the role of theoretical analysis is dominant. The following section gives the results of the theoretical analysis, validating the phase equilibrium method being used in the standard.

2.1 Theory of the phase equilibrium method

While a vapour-gas mixture flows over an ice-covered cooling surface (saturator surface), which temperature is lower than the vapour crystallisation temperature, the closest approach to the equilibrium between the gaseous and the condensed phases of water vapour with respect to the surface temperature can be reached. At this moment, the vapour-gas mixture temperature represents the frost-point temperature that can be determined by direct measurement.

The thermodynamic processes of heat and mass transfer causing the phase equilibrium achievement, are described by three basic differential equations: equation for the gas flow energy, equation for the heat transfer process, equation for the mass transfer process [5,6]. Simultaneous solution of these equations allowed to obtain the differential equation for water vapour concentration in a mixture flow as a function of its temperature. In order to derive the integral formula for water vapour concentration in a mixture flow along a saturator, the assumption has been made that the heat and mass transfer processes are similar when the analysed frost-point temperatures are below –20 °C. Correctness of this assumption has been substantiated by theoretical analysis of simultaneous heat and mass transfer processes. The analysis showed that if the initial frost-point temperature is –20 °C or lower, the effect of heat transfer intensification due to the mass transfer (transversal flux of water vapour from the flow to the cooling surface) is negligible. The assumption made is also supported by the experimental results, given in [5,7].

Finally, after integration and transformation, the formula for partial water vapour pressure in the mixture flow as a function of its temperature is derived:

$$e = e_s + \left(e_0 - e_s\right) \cdot \left(\frac{T - T_s}{T_0 - T_s}\right)^{1/e} \tag{1}$$

where T_0 is the initial temperature of the mixture, K

T_S is the saturator surface temperature, K

e_0 is the initial partial vapour pressure, Pa

e_S is the saturation vapour pressure, Pa

ε is the Lewis coefficient, characterising the ratio of heat transfer to mass transfer intensities.

The equation (1) is valid at the initial frost-point temperatures below –20 °Ñ. Solution of the set of dimensionless equations for independent similar processes of heat and mass transfer allows to derive the formula for the Lewis coefficient, also proposed in [8] and [9], referring to Threlkeld [10]:

$$e = \left(\frac{a}{D}\right)^{1-m} \tag{2}$$

where à is the thermal diffusion coefficient of the mixture, $m^2\ s^{-1}$

D is the diffusion coefficient of the mixture, $m^2\ s^{-1}$

m is the coefficient, depending on a mixture flow in a saturator. The choice of this coefficient is discussed in [5-7]. For the preliminary calculations, assuming the turbulent mixture flow it was taken as $m = 0.36$.

As shown in equation (2), the Lewis coefficient e is a function of the mixture properties and the flow and weakly depends on the mixture temperature. As described in [7], a completely saturated surface layer of the mixture with respect to the surface temperature occurs, i.e. $e_S = const.;\ T_S = const$.

Further, carrying-out the heat analysis of the saturator [7,11], the temperature variation of the vapour-gas mixture along the saturator can calculated. Then, partial vapour pressure variation along the saturator is obtained using equation (1), which allows to estimate the minimum saturator length over which the required closest approach to the saturation of the mixture can be achieved.

At any particular time, a non-saturated mixture vapour content may correspond to vapour subsaturation or supersaturation with respect to a surface temperature, depending on a number of factors: temperature head between mixture and surface, temperature field in the saturator, etc. The supersaturation coefficient S_n characterises a ratio of the mixture partial vapour pressure e to the saturation vapour pressure $e_S(T)$ with respect to the mixture temperature:

$$S_n = \frac{e}{e_s(T)} \tag{3}$$

If the water vapour is supersaturated with respect to the mixture temperature, the volume crystallisation of the vapour is possible [8,11-13]. In this case, the generated double-phase mixture consists of saturated vapour and suspended crystals. This effect is most inadmissible because the vapour concentration in the mixture will be significantly higher than the saturation vapour pressure with respect to the surface temperature. Thus, generation of the required frost-point temperature of the formed double-phase mixture is almost impossible. In order to prevent the volume crystallisation of water vapour and fog formation, the following condition has been observed while the theoretical analysis:

$$S_n < S_{cr} \tag{4}$$

where S_{cr} is the critical supersaturation coefficient;

Theoretical analysis of the critical supersaturation coefficient as a function temperature for homogeneous (spontaneous) condensation of water vapour on the basis of the theory of fluctuations was carried-out by R. Becker and W. Dering and also by Frenkel. Results of the analyses are also given in [8,12,13].

But, in practice, value of the critical supersaturation coefficient of the mixture depends on many factors: presence, dimensions and concentrations of crystallisation centres, such as molecular complexes formed due to the temperature and density fluctuations, gas ions, condensable impurities, dust particles, etc. Therefore, the theoretical analyses can give only an approximate estimation of the critical supersaturation coefficient. For instance, in presence of small particles (radius about 10^{-6} m) or ice crystals, carried away from the condensation surface, the supersaturation coefficient can reach S_{cr} *»1.* Therefore, in order to take into account possible presence of volume crystallisation centres in a real saturator, it was also assumed that the maximum supersaturation $S_{n\ max}$ should not exceed 3.

2.2 Practical realisation of the method

Diagram of the standard low frost-point generator is given in Figure 1. The main part of the generator is the heat and mass transfer apparatus, which consists of a pre-saturator and a main saturator set in a thermal insulated temperature-controlled chamber.

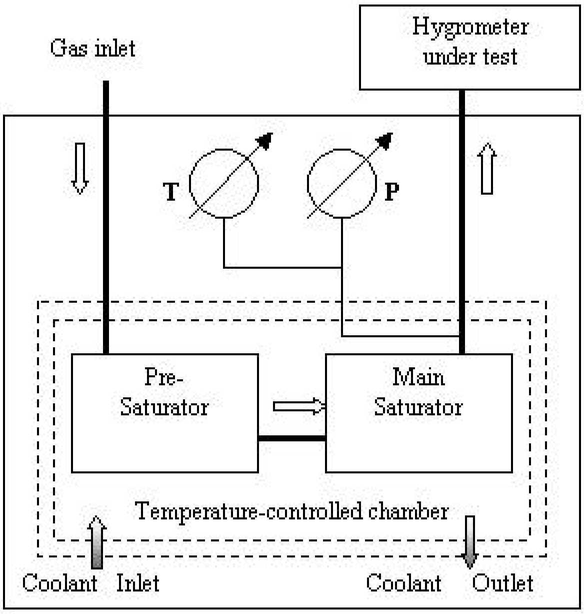


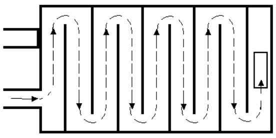
Figure 1. Diagram of the standard low frost-point humidity generator.
1 - thermometer; 2 – pressure gauge.

Evaporated liquid nitrogen is used as a coolant, circulating in the chamber. Temperature inside the chamber is stabilised and equals to the required frost-point temperature. A humid gas, applied to the generator inlet, is fed to the pre-saturator and then to the main saturator. Then the saturated mixture is supplied to a hygrometer being tested. The frost-point temperature of the mixture is determined by measurement of its temperature *Ò* and pressure *Đ* at the outlet of the main saturator.Design of the humidity generator is optimised to produce a wide range of frost-point temperatures down to –120 °C. Therefore, great concern has been taken to ensure reliable operation of all parts of the generator under very low temperatures.

3 DESIGN OF THE SATURATOR

The design of a saturator, in which the heat and mass transfer processes occur, influences significantly on the achievement of the state of saturation of a mixture and, in particular, on the supersaturation of the mixture. A number of experimental works [8,11,14] shows that the freezing-out process in a coil tube heat exchanger with a smooth inner surface may lead to a significant supersaturation of a mixture at the outlet that is most unsuitable to generate the required humidity. Besides, formation of a vapour condensate as porous snow on a smooth inner surface is also unsuitable because snow can be easily carried away by the flow [14].

Diagram of the mixture flow in the pre-saturator:



and in the main saturator:

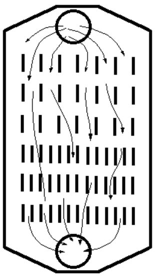


Figure 2. Plate-finned heat exchanger. Upper part is the pre-saturator, positioned horizontally to the coolant flow. The lower part is the main saturator, divided by four plate-finned sections. Fitting holes for SPRT and pressure gauge are shown in the lower left part of the heat exchanger.

The supersaturation effect is reduced by using a plate-finned heat exchanger as a saturator as fins provide multiple crystallisation centres and filter the mixture. Besides, turbulisation of the flow allows to equalise the cross-section temperature and concentration fields of the heat exchanger and therefore improve the accuracy of the required frost-point temperature generation. The heat analysis of the heat exchanger has been carried-out using the theoretical models, suggested in [5] (for the pre-saturator) and [11] (for the main saturator). It allowed to obtain the values of minimal surface areas of preliminary and main saturators, over which the mixture approaches the thermal equilibrium after its single pass in the flow rate range from 10 to 100 L/min.

The recuperative counter-current plate-finned heat exchanger is shown in Figure 2. Its dimensions are 180 x 180 x 380 mm. The upper part of the heat exchanger is the preliminary saturator, positioned horizontally with respect to the coolant flow. Both the preliminary and main saturators are made of aluminium-magnesium alloy.

The massive 5 mm walls of the saturator, short fins and relatively high thermal conductivity of the material allow to achieve a uniform temperature field over the inner surface of the heat exchanger.

Humid gas, applied to the generator inlet, is fed to the pre-saturator through the right pipe in the upper side of the heat exchanger. The pre-saturator is intended to freeze-out a major amount of moisture at little temperature head between the vapour-gas mixture and the cooling surface, allowing to prevent volume crystallisation of water vapour even at relatively high initial humidity. Then, divided to four flows, the mixture flows downwards through four plate-finned sections of the main saturator, where the required closest approach to the state of saturation is achieved. The standard platinum resistance thermometer and pressure gauge are fitted at the outlet of the heat exchanger.

4 DESIGN OF THE STANDARD LOW FROST-POINT GENERATOR

The diagram of the standard generator is given in Figure 3. The generator has two main circuits: a humid gas circuit and an evaporated nitrogen circuit. The basic unit of the generator is the nitrogen cooling chamber 1, that consists of a closed thermal insulated volume in which the pre-saturator 2 and the main saturator 3 are mounted. The Dewar vessel 7, heater 6, measuring valve 9 and fan 5 form the nitrogen circuit.

The principle of operation of the generator is as follows. The heater 6 evaporates liquid nitrogen from the Dewar vessel 7, establishing the delivery pressure of the nitrogen vapour. Then, through the metering valve 9 and nitrogen injector, the evaporated nitrogen is supplied to the nitrogen cooling chamber 1. The nitrogen vapour is sprayed and mixed by the fan 5. The metering valve 9 maintains constant temperature in the chamber by adjusting the flow rate of the nitrogen vapour. Then the humid gas from the gas cylinder enters the gas circuit of the generator through the flowmeter. When the generator is in a steady mode, frost point temperature of the gas is measured by the standard platinum resistance thermometer 4, placed at the outlet of the main saturator. The metering valve 9 is operated by the controller 8.

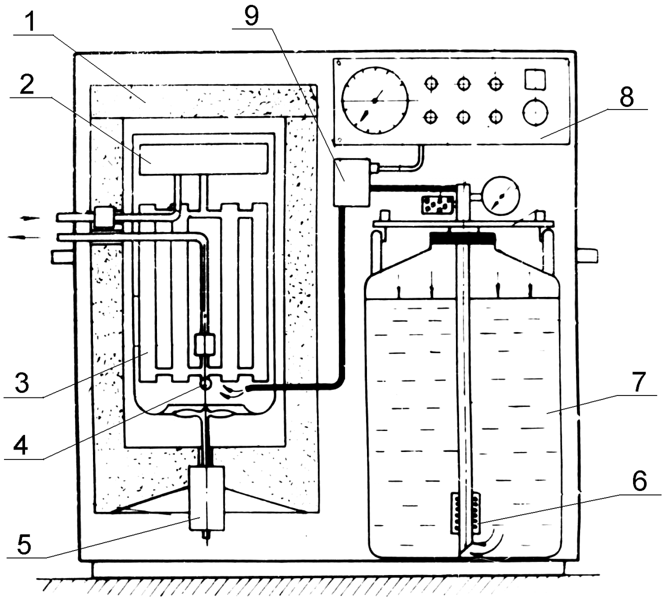


Figure 3. Design of the standard low frost point humidity generator.
1 – Nitrogen cooling chamber; 2 – Pre-saturator; 3 – Main saturator; 4 – Standard platinum resistance thermometer (SPRT); 5 – Fan drive; 6 – Heater; 7 – Dewar vessel; 8 – Controller; 9 – Metering valve.

When the generator is in a steady mode, dew/frost point temperature of the gas is measured by the standard platinum resistance thermometer 4, placed at the outlet of the main saturator. The metering valve 9 is operated by the controller 8. The standard low frost point humidity generator can be operated manually, remotely from the personal computer or in a fully automatic mode. When it is in fully automatic mode, only setting of required dew/frost point temperature is necessary. The generator acquires the desired temperature and maintains it automatically. Response time of the generator after starting the operation is 40 to 60 minutes. Time of transition between two generated temperatures is not more than 20 minutes. One 32 litre Dewar vessel ensures 8 to 16 hours of continuous operation. The generated gas with the required dew/frost point temperature is supplied to the hygrometers being tested. The photograph of the standard low frost point humidity generator is given in Figure 4. The carried-out analysis of uncertainty allowed to estimate the overall generated uncertainty to be not more than ± 0.1 °C and almost equal in the whole measurement range. The main analysed uncertainty components were: uncertainty due to temperature instability in the main saturator, uncertainty due the incomplete saturation of the mixture in the main saturator, uncertainty in temperature and pressure measurements in the main saturator. The analysis has validated the generator as the primary standard for dew-point temperature.

Figure 4. The photograph of the standard low frost point humidity generator at the D. I. Mendeleyev Institute for Metrology (VNIIM)

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REFERENCES

[1] *A guide to the measurement of humidity,* Institute of Measurement and Control, London, 1996, 68p
[2] Mamontova L., Mamontov G. Standard hygrometric equipment in Russia, in: *Proc. 3rd International Symposium on Humidity and Moisture* (6-8 April, 1998) NPL, Teddington, 1998, vol.**1**, pp 167-172
[3] Bell S. A., Validation of the NPL primary gravimetric hygrometer, in: *Proc. 3rd International Symposium on Humidity and Moisture* (6-8 April, 1998) NPL, Teddington, 1998, vol.**1**, pp20-27
[4] Heinonen M. *National basis for traceability in humidity measurements*, Doctor of Technology Thesis, Helsinki University of Technology , Helsinki, 1999, pp 4-6
[5] Mikheyev M., *Fundamentals of heat transfer,* Energia, Moscow, 1977 (In Russian)
[6] Bird R. B., Stewart W. E., Lightfoot E. N., *Transport Phenomena* , J. Wiley and Sons Inc., Dept. of Chem. Eng., New York, 1960, pp 642-648
[7] Isachenko V., *Heat transfer with condensation,* Energia, Moscow, 1977 (In Russian)
[8] Amelin A., *Theoretical principles of fog formation in vapour condensation,* Khimiya, Moscow, 1966 (In Russian)
[9] Visscher G. J. W. , Schurer K. The psychrometer coefficient: calculation versus calibration, in*: Proc. 3rd International Symposium on Humidity and Moisture* (6-8 April, 1998), NPL, Teddington, 1998, vol.**1**,pp 231-245
[10] Threlkeld J. L., *Thermal environmental engineering,* Prentice-Hall Inc., Englewood Cliffs, N J, 1st Ed., 1962 ,ch. 10
[11] Denton W. H. , Ward D. E. *Brit. Chem. Eng.,* **5,** (1960) No.1 pp 18-26
[12] Barnard A. J., The theory of condensation of supersaturated vapours in the absence of ions *Proc. Roy. Soc.*, London, (1953) **A220**, No.1140
[13] Hirth J. P., Pound G. M., *Condensation and evaporation nucleation and growth kinetics,* Pergamon Press, Oxford,1963
[14] Vasyunina G., Akselrod L., Freezing-out of moisture and carbon dioxide in coil heat exchangers, *VNIIKIMASH Proceedings* (1961) v.**4** (In Russian)

AUTHOR(S): George Mamontov, D.I. Mendeleyev Institute for Metrology (VNIIM), 19, Moskovsky pr., 98005 Saint-Petersburg, Russia, tel./fax direct: +7 812 176 9483