Jacek MAJEWSKI

Lublin University of Technology, Faculty of Electrical Engineering and Informatics

doi:10.15199/48.2016.08.20

Polymer-based sensors for measurement of low humidity in air and industrial gases

Abstract. *Some problems concerning low humidity measurements using polymer-based humidity sensors are characterized. An exemplary calibration procedure applied to a humidity/temperature module is presented, as well as low-humidity range characteristics of humidity/temperature modules, and possible ways to extend the measurement range of these sensors towards low humidity levels of air and industrial gases are discussed.*

Streszczenie. *Scharakteryzowano zagadnienia związane z pomiarami niskich wilgotności sensorami z polimerowym materiałem wilgotnościoczułym. Przedstawiono przykładową procedurę kalibracyjną zastosowaną do modułów termohigrometrycznych, i rozpatrzono możliwe sposoby rozszerzenia zakresu przetwarzania sensorów z polimerową warstwą wilgotnościoczułą na poziom wilgotności niskich w powietrzu i gazach przemysłowych.(**Sensory z polimerową warstwą wilgotnościoczułą do pomiaru wilgotności niskich w powietrzu i gazach przemysłowych**).*

Keywords: polymer-based humidity sensors, low humidity measurement, industrial gases humidity measurement.
Słowa kluczowe: sensory z polimerową warstwą wilgotnościoczułą, pomiary wilgotności niskich, pomiary wilgotności gazów przemysłowych.

Introduction

The knowledge of humidity level in air and industrial gases is of paramount importance for the quality of end products in many modern technological processes, e.g. in semiconductor industry [1], pharmaceutical processing, or chemical gas purification [2]. Moreover, in some cases the water vapour content inside gas flowing through pipes should be monitored incessantly in order to detect possible leakage from the ambient into the pipe, and to trigger alarms in control installation. In such emergency situations, the response time of the monitoring sensors is crucial for avoiding deterioration of product or other consequences violating technological regime. Also, the pressures and temperatures applied in industry to gases can differ considerably from ambient conditions, and influence sensor's performance. In facilities of critical importance, the low humidity measurement and monitoring can be performed using sophisticated instruments based on optical principles like cavity ring-down spectroscopy, but they are very expensive (tens of thousands USD). In comparison with measurement of other process variables, the humidity measurements lag behind e.g. temperature measurements; in the range of low humidity that contrast is even more impressing. Moreover, in industrial operating condition the humidity sensors are prone to non-reversible contamination collection which results in changes of the transfer function, or even complete sensor failure.

The measurement of relative humidity from 20 % to 80 % is well supported with various electronic sensors of linear characteristic, based mainly on polymeric or ceramic humidity-sensitive materials. Polymer-based humidity sensors, both capacitive and resistive types, have the advantage of providing faster desorption mechanism of water molecules than ceramic sensors which need a heater to accelerate desorption process. However, below relative humidity of 20 %, the polymer-based sensors often exhibit an increasing drop in accuracy together with nonlinearity of characteristic curve in case of the capacitance-type sensing elements. Most recently, new materials, e.g. graphene oxide, ZnO, ZnS, TiO_2, and composites containing CNT are tested as promising novel low humidity-sensitive layers [3]. Porous polymer-based sensitive materials are doped with nanoparticles (e.g. SiO_2) to enhance stability and sensitivity of the polymer matrix. Also, conducting polymers composed of polymer matrix filled with CNT or carbon black allow for obtaining relatively low impedance at low humidity level in resistive-type sensors. Simultaneously, efforts are aimed at shortening the response time of humidity sensors to fractions of a second.

In industry, a lot of gases (e.g. nitrogen, oxygen, argon, carbon dioxide, hydrogen, ammonia, acetylene) are used under various thermodynamic conditions, and are subject to broad changes in temperature or pressure which can cause condensation of water vapour contained in a given process gas. The measurement of the humidity level in industrial gases is aimed at reducing negative consequences of excessive amount of water vapour. The acceleration of corrosion, leaching of lubricants, formation of acids and other aggressive chemicals, catalyst deactivation or drop in oven temperature are the most common interactions of water in industrial plants. The acceptable or permissible level of water vapour depends on the user's requirements, e.g. in food industry the compressed air should contain less than 0.14 g/m^3 of water if contact with food is possible; otherwise, 5.5 g/m^3 is allowed. Another problem is the moisture content in flue gases; all components of combustion process must have temperature higher than the dew point of the gas, and only fast turbulent flow can partly mitigate that requirement.

Polymer-based humidity sensors

Generally, the polymer-based humidity sensors are divided into resistive type (polyelectrolyte-based, semiconductive and conductive [4]) and capacitive type. However, over 75 % of humidity sensors market is captured by capacitive humidity sensors with dielectric (non-conducting) polymers, and those as dominating in process measurements are the focus of this section.

The principle of operation is based on the tendency of water vapour contained in gas towards reaching a dynamic equilibrium with the concentration of water molecules adsorbed onto porous polymer structure. The water molecules in the polymer are bonded to the hygroscopic groups of the polymer molecules by weak van der Waals's interactions [5]. That uptake of water molecules by the hydroactive sponge-like polymer structure results in a change of the relative dielectric permittivity ε_r of the polymer layer. For a sandwich design of the humidity sensor with the polymer layer between two metal electrodes forming a plate capacitor, the change in capacitance ΔC is proportional to the change in the relative dielectric permittivity $\Delta\varepsilon_r$ of the polymer:

(1) $$\Delta C = \Delta\varepsilon_r \varepsilon_0 \frac{A}{d},$$

where: A – the surface of the plates, d – the distance between the plates, $\Delta\varepsilon_r = \varepsilon_r(\varphi) - \varepsilon_{rp}$, φ – relative humidity of gas existing in dynamic equilibrium with polymer, ε_{rp} - the relative dielectric permittivity of dry polymer. Usually, ε_{rp} is about 3, and at φ = 100 %RH the resultant permittivity $\varepsilon_r(\varphi)$ is about 4 (the amount of water with ε_{rw} about 80 is very small inside the polymer layer).

The response of the polymer-based capacitive-type sensor to the change in the amount of water vapour in its ambient gas is mainly linearly proportional to the change in relative humidity of the gas, because the driving force of the process of water vapour solubility in polymer is the free energy for adsorption, G:

(2) $$G = RT \cdot \ln\frac{p}{p_s},$$

where: R – the universal gas constant, T – absolute temperature, p – the partial pressure of water vapour in gas, p_s – the saturation pressure of water vapour in gas. As the relative humidity is defined as $\varphi = p/p_s$, it is directly related to the amount of water molecules adsorbed in the polymer.

The overwhelming approach to manufacture the polymer-based humidity sensors is thin film technology (film thickness less than 1 μm), easily compatible with CMOS technology for integrating the signal conditioning circuitry closely to the humidity sensitive element.

The sensors can easy be miniaturized, and high design flexibility is allowed. Two designs are most common: the sandwich structure, and the interdigitated layout [6]. In the sandwich structure, the upper electrode must be very thin, in order to allow the transport of water molecules to the polymer. it is usually made of evaporated or sputtered gold; the thickness of the electrode is 10-20 nm.

The polymers used are in most cases polyimides (PI), typically Kapton, or polyesters, e.g. cellulose acetate butyrate (CAB). The chemical structure of the polymer is very important as it determines the practical performance of the sensor: its sensitivity, stability, reliability, or hysteresis. The requirements imposed on the polymer-based capacitive humidity sensors are: high reproducibility of the sensor characteristic, high linearity, fast response, high sensitivity to water vapour, high selectivity (or low cross-sensitivity to other vapours, or gases). Also, the sensors should exhibit low temperature effect and low hysteresis, be resistant to pollutants and fully recoverable from condensation. Most of these conditions are met at low cost, while the alternative, i.e. the aluminium oxide-based capacitive sensors, are more expensive.

An important application of polymers in low humidity measurement is the capacitive dew point hygrometer [7]. To avoid problems with contamination of chilled mirror, it is replaced by a capacitive sensor. The condensation of dew droplets on the surface of polymer causes a sharp rise of the capacitance because of high dielectric constant of water (or ice) at low temperatures (ca. 88 at 0°C)[8].

Experiment

The experimental setup (Fig.1) was composed of the reference dew point hygrometer DEWMET-02 TDH (Michell Instruments Ltd./UK), the humidity generator VAPORTRON H 100L (Buck Research Instruments L.L.C./US), and the Rotameter Type V 100 (Vögtlin Aesch/Switzerland). The device under test was the Humidity/Temperature Module EE03 (E+E Elektronik Ges.M.B.H/Austria). During the calibration process, humid air form the humidity generator was pumped through PTFE piping to the dewpoint hygrometer and back to the measurement chamber of the generator. The temperature of the air inside the chamber was controlled with a Pt-100 RTD, and the air velocity was set at 90 litres per hour using a high precision valve mounted on the rotameter. The temperature value was kept at 21°C as stated in the NPL-traceable certificate of calibration for the reference hygrometer.

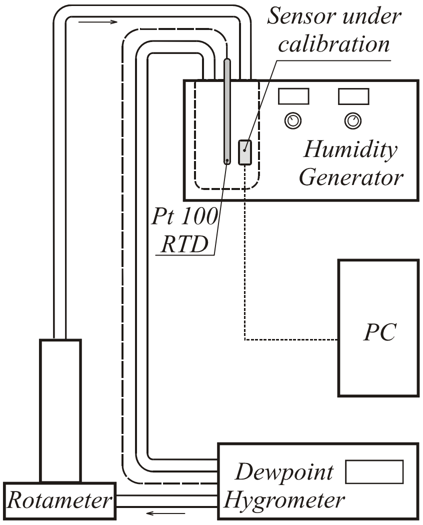

Fig.1. The schematic of the measuring arrangement for calibration of humidity sensors using the Vaportron humidity generator

The set of n=18 calibration points distributed rather equidistantly within the humidity range from 10.9 %RH to 76.9 %RH was collected. That range at the air temperature of 21°C was equivalent to the dew point hygrometer range of dew point temperature values t_d from -10.7°C to 17.0°C (these values were obtained after correction performed in agreement with the certificate of calibration, using linear interpolation between the reported points). For the EE03 calibration purposes, there was the necessity to convert the t_d values displayed on the dew point hygrometer to the relative humidity values using a Free Professional Humidity Calculator, based on the formulae known as Sonntag (ITS-90).

The calibration fit was linear, because the coefficient of correlation between the humidity values generated inside the humidity generator and measured with the dew point hygrometer, and the indications of the EE03 module, was r=0.99992. The calibration points, the fit straight line, and the confidence belt around this line are shown in Figure 2. The expanded uncertainties of the calibration values in the certificate of the dew point hygrometer were reported as based on a standard uncertainty and a coverage factor k=2, providing a coverage probability of approximately 95 %. On the other side, the accuracy of the EE03 was reported in the datasheet as ±3 % RH within the 10...100 %RH interval; this value can be treated as the type value, and for an individual piece of EE03 that value can be lowered. In that case it turned out that the accuracy within the calibration range is less than ±1.8 % RH.

The calculations of the expanded uncertainty U_{95} of the linear approximation were conducted after the EURACHEM/CITAC Guide [9]. The smallest uncertainty value of 0.58 % RH was for the EE03 indication equal 36.5 %RH. At the ends of the calibration interval, the U_{95}

uncertainties were 0.61 % RH and 0.63 % RH. That means low impact of the distance of the calibration point from the centre of the point set on the approximation uncertainty [10].

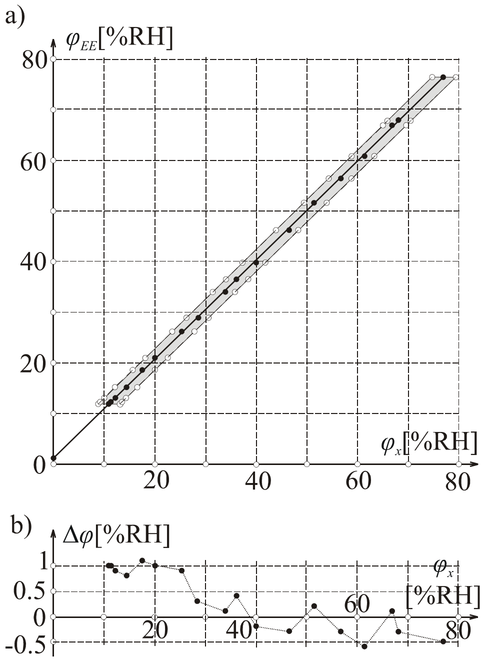

Fig.2. a) the plot of calibration linear fit, and the confidence belt; full circles mark the calibration points, and open circles mark the limits of the U_{95} area shadowed in grey, b)The plot of differences $\Delta\varphi$ between the EE03 humidity sensor and the Dewmet indications

The EE03 module contains the HC103 polymer-based capacitive humidity sensor, and an embedded microprocessor retaining calibration data and allowing for compensation of some error components (hysteresis, nonlinearity, temperature) of the sensor. That results in considerable decrease in accuracy reported by the manufacturer (from ca. 5 % to 3% RH). For the calibrated EE03 module's accuracy ±1.8 % RH, the standard uncertainty value is equal $u_{EE}(\varphi)\approx 1$ %RH. After combining this value with the values of standard uncertainties of the linear approximation, the expanded uncertainty U_{95} (k=2) of the measurement of relative humidity with the given EE03 piece practically does not change from 2.16 %RH at the indication of the EE03 equal 11.3 %RH to 2.17 %RH at 76.4 %RH.

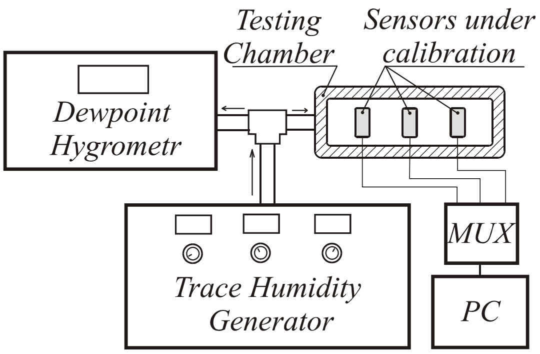

Fig.3. The schematic of the measuring arrangement for calibration of humidity sensors using the trace humidity generator and special testing chamber

Because of difficulties with using the EE03 module in calibration facility for relative humidity below the Vaportron range (10 %RH), the setup shown in figure 3 was used. The dew point hygrometer was the GE Optica 1311 XR (GE Sensing/US), and was furnished with NPL-traceable certificate of calibration. Three humidity and temperature sensors SHT 71 (Sensirion/Switzerland) were placed in a special thick-walled (for temperature equilizing) testing chamber made of stainless steel with small orifices for sensors. All tubing was made of stainless steel, too. The air flow with precisely adjusted low humidity level was supplied from the trace humidity generator and devided in a T-shape fitting with a gas flow flux of 200 l/h. The frost/dew point temperature values in this experiment were set over the interval from -60°C (0.04 %RH) to -5°C (13.40 %RH). The pressure and the ambient temperature values were controlled during the experiment. The results are depicted in the figures 4 and 5.

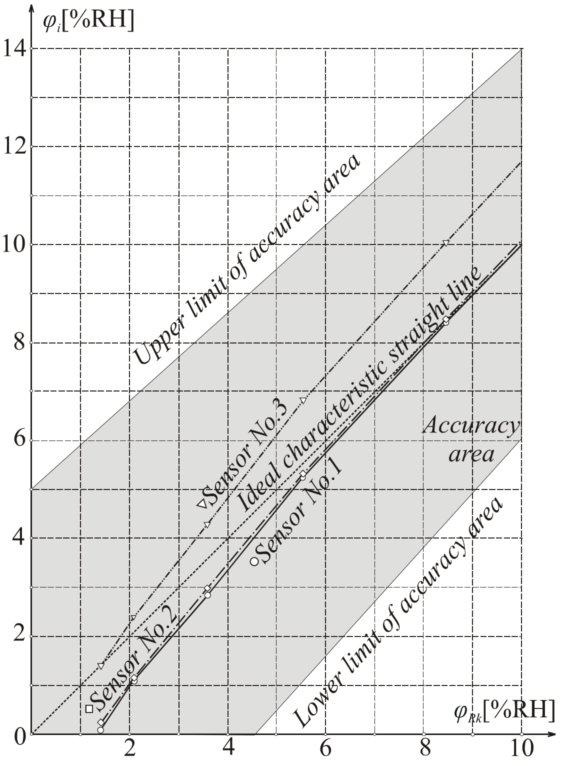

Fig.4. The plot of comparison of characteristics of three capacitive humidity sensors type SHT 71 (Sensirion) φ_i (i=1,2,3) against the reference low humidity dew point type hygrometer(φ_{Rk}). The manufacturer's reported accuracy area is shadowed in grey

The SHT 71 sensors are manufactured in the CMOS-technology and the signals passed to the multiplexer are processed first with the signal-conditioning circuits integrated with the sensor; for humidity below 0.5 %RH the sensors provided a dummy value of 0.1 %RH. It turned out that actual processing of measurement data from the sensor started only above 0.5 %RH, and the values of dew point temperature were calculated only for humidity levels above 2.5 %RH. It seems that although the manufacturer reported in the datasheet the operating range from 0 %RH to 100 %RH, the possibility of measuring humidity levels below 0.5 %RH was practically excluded.

As can be seen on figure 4, below ca. 10 %RH for sensors No.1 and No.2 an increase of measurement error towards lover humidity values can be observed. The characteristics of sensors No.1 and No.2 practically overlap, while sensor's No.3 characteristic exhibits a shift about 1.2 %RH to 1.6 %RH. The nonlinearity of the characteristics is the same for all sensors, and can be due to a change in the mechanism of water vapour sorption into the layer of polymeric material at low humidity levels.

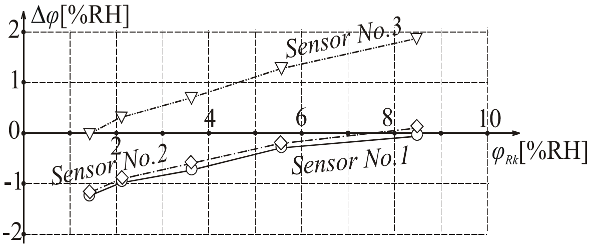

Fig.5. The plot of differences Δφ between the indications of each of the three capacitive humidity sensors type SHT 71 (Sensirion) against the reference low humidity dew point type hygrometer

The errors of sensors' characteristics are shown in figure 5 in more detail. The observed nonlinear segment shows slightly quadratic polynomial dependency which could be easily embedded into the sensor's electronics.

Conclusions

For introducing inexpensive and small polymer-based capacitive sensors in measurement of low humidity in process air and non-reactive gases, the problems of nonlinear characteristics and costly calibration within the humidity range below 10 %RH should be solved. Individual multipoint calibration can improve the sensors accuracy by a quarter of the typical value given in datasheet. New materials and new (nano)technologies may extend the linear segment of sensors characteristics. Redesigning towards larger surface and smaller thickness would increase the change in sensor's capacitance at low humidity but can cause extension of response time. The low humidity level can also be made measurable when increased by compression of a sample of humid gas in a bypass pipe containing measurement cell with sensor, or by cooling the gas in capacitive dewpoint hygrometer.

The calibration measurements in the case of SHT 71 sensors were performed in an ascendant order only, because at low humidity the hysteresis of the sensor can be neglected. The accuracy of the SHT 71 sensors No.1 and No.2 (manufactured in the CMOS technology) at ca. 10 %RH was better than the EE03 and the sensing surface of the SHT 71 sensors was slightly smaller. Another advantage of CMOS-made polymer-based sensors is that the deposition of the polymer sensing layer in the CMOS process can be the last technological operation [11].

With a multipoint calibration within the low humidity range and thorough sensors' selection, many items of typical polymer-based relative humidity sensors could be applied for measurements down to 2 %RH with an accuracy of 1 %RH. If the nonlinear approximation of the sensor's characteristics within the low humidity range would be performed, even better accuracy down to 1%RH could be achieved. That means that at least some demands for low humidity measurement down to 0.5 % could be satisfied with market available spolymer-based relative humidity sensors. With sensors and signal conditioning circuits dedicated and designed specifically for low humidity measurements, both the bottom limit of the measurement range and the accuracy could be lowered.

The author is indebted to the team of the Working Group 6.4 at the Bundesanstalt für Materialforschung und -prüfung, Berlin, Germany, for practical support and scientific discussion.

Author: *dr inż. Jacek Majewski, Lublin University of Technology, Faculty of Electrical Engineering and Informatics, Nadbystrzycka Street 38, 20-618 Lublin. E-mail: j.majewski@pollub.pl.*

REFERENCES

[1] Abe H., Yamada K. M. T., Performance evaluation of a trace-moisture analyzer based on cavity ring-down spectroscopy, *Sensors and Actuators A: Physical,* 165 (2012), 230-238

[2] Wang Y., Hajhashemi M. S., Bahreyni B., A., Capacitive Relative Humidity Sensor Using Polymer Nanoparticles, *2012 IEEE Sensors Proceedings*, Sensors 2012 IEEE Conference, Taipei, Taiwan, 28-31 Oct 2012

[3] Pi-Guey S., Xian-Ren K., Low-humidity sensing properties of carboxylic acid funcionalized carbon nanomaterials measured by a quartz crystal microbalance, *Sensors and Actuators A: Physical,* 205 (2014), 126-132

[4] Chen Z., Lu C., Humidity Sensors: A Review of Materials and Mechanisms, *Sensor Letters,* 3 (2005), 274-295

[5] Kämpfner N. (Ed.)., "Monitoring Atmospheric Water Vapour", Springer 2013

[6] Farahani H., Wagiran R., Hamidon M. N., Humidity Sensors Principle, Mechanism and Fabrication Technologies: A Comprehensive Review, *Sensors,* 14 (2014), 7881-7939

[7] Kondrashow V., Schönberg J-N., Rühe J., A novel capacitive dew-point setting approach based on water-actuated swelling of a sensing polymer monolayer, *17th International Conference on Miniaturized Systems for Chemistry and Life Sciencies*, 27-31 Oct. 2013, Freiburg, Germany

[8] Libbrecht K., Capacitive sensor condensation-type hygrometer, US Patent Application Publication No.: US 2002/0005068A1, Jan.17, 2002

[9] Ellison S. L. R., Williams A., (Eds.), "Eurachem/CITAC Guide CG4: Quantyfying Uncertainty in Analytical Measurement", Third Edition (2012)

[10] Kessel R., Kacker R. N., Sommer K.-D., Uncertainty budget for range calibration, *Measurement,* 45 (2012), 1661-1669

[11] Rittersma Z. M., Recent achievements in miniaturised humidity sensors – a review of transduction techniques, *Sensors and Actuators A: Physical,* 96 (2002), 196-210