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Measurement of Relative Humidity Using Electrochemical Sensors

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Abstract: Highly sensitive and accurate determination of relative humidity of technical gases is required in many branches of human activities (health care, food packing, etc.). In this paper, a new series of electrochemical sensors manufactured by BVT Technologies is introduced; they measure changes in conductivity of hygroscopic materials with changing content of water vapour in ambient gas. The main topics of the contribution focus on a description of the physical principles of these electrochemical sensors taking advantage of a hygroscopic layer, sensor arrangements, sensor signal processing and electronic equipment architecture. Achieved results and errors analysis are discussed in detail.

Keywords: Relative humidity, Hygroscopic material, Electrical conductivity, Synchronous detection, Microcontroller.

1. Introduction

Humidity is an important parameter which is necessary to control many technological processes. There are many methods for measuring humidity. Psychrometric methods are based on measuring a difference between two temperatures – the ambient temperature and the temperature decreased due to evaporation of water present in the gas under given conditions [1]. Other methods are based on absolute measurement of water content in the gas phase. Alternatively, it can be determined by absorption of water by hygroscopic materials such as P_2O_5. Another method is based on the measurement of a dew point – the dew point temperature being dependent on the humidity of a gas sample [1].

The methods mentioned above are examples of laboratory methods. The measurement itself is not complicated but it is quite difficult to incorporate such measurements as a part of a technological process control. This obstacle is solved by utilising humidity sensors. These sensors operate on a few different principles. Some of them are based on automation and miniaturization of the above mentioned laboratory methods; a small mirror connected with a Peltier element could be a good example of such. The mirror is cooled and the dew point can be calculated from changes of reflexivity. Another type of sensors is based on changes of mechanical properties of certain materials due to humidity changes. A typical example is a sensor utilising elongation of human hair with changing content of water vapour present in the gas [1].

The majority of humidity sensors is based on a detection of an equilibrium that is established between the sensor material (its specific property) and the water vapour upon contact with the measured gas. Measurements of conductivity of hygroscopic materials exposed to the gas phase can be considered as a typical example. Another principle is based on a dependence of the equilibrium of a hygroscopic material with measured gas on temperature. Extremely precise measurement of humidity is based on the colorimetric principle.

The schematic drawing of a commercial humidity sensor based on changes of conductivity is in Fig. 1. Usually, the sensor taking advantage of the hygroscopic material resistance measurement is placed on a silicon substrate, on which the electrode system composed of the substrate itself and the porous gold electrode is placed. It is capable of directing the measured gas to the active hygroscopic layer. This layer consists of an aluminum base on which the active hygroscopic layer of alumina is applied as shown in Fig. 1 [4].

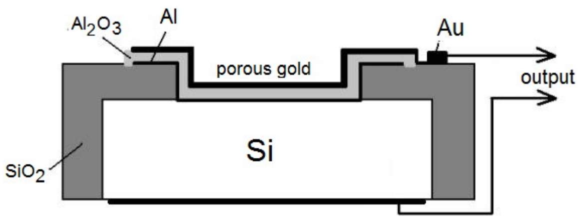


Fig. 1. The resistive relative humidity sensor placed on the silicon substrate.

The humidity sensors based on the conductivity changes of a hygroscopic material are discussed in this article from the potential for a precise conductivity measurement point of view. The commercially available conductivity sensor manufactured by BVT Technologies, a.s. is an electrochemical basis of this humidity sensor.

2. Theory

2.1. Basic Principles of Humidity Measurement

This section provides the basic terminology regarding the topic of humidity measurement, as well as definitions used [1, 2, 11].

Absolute gas humidity Φ is defined as the mass of water vapour m contained in gas divided by a volume V of wet gas:

$$\Phi = \frac{m}{V} \quad (1)$$

The main unit of the absolute humidity is 1 kg m^{-3}. In practice, sub-units are used more often, particularly 1 g m^{-3} (10^{-3} kg m^{-3}) and 1 mg m^{-3} (10^{-6} kg m^{-3}). Other units which are also used are 1 g l^{-1} (10^{-3} kg 10^{-3}m^{-3}) and 1 mg l^{-1} (10^{-6} kg 10^{-3}m^{-3}).

Specific humidity φ_x *is* defined as a ratio of a mass of water vapor m contained in a specific volume of gas and a mass m_v of dry bulk of the same volume of gas:

$$\varphi_x = \frac{m}{m_v} \quad (2)$$

The specific humidity φ_x is a dimensionless quantity and it is used not only for gases but for liquid and solid substances as well [1, 2].

Relative humidity is the degree of saturation of a gas (air) with water vapor and it is defined as aratio of an absolute humidity of the gas and an absolute humidity of the gas saturated with water vapor at the same pressure and temperature:

$$\varphi = \frac{\Phi}{\Phi_{MAX}} \quad (3)$$

Relative humidity is a dimensionless quantity which is expressed as percentage. Relative humidity can be also expressed as a ratio of the partial pressure of water vapour p' in the tested gas and at a specific temperature and the partial pressure of saturated water vapour p'_{sat} at the same temperature.

The relative humidity expressed as the ratio of partial pressures is merely approximate because water vapor does not behave as an ideal gas. The deviation is not large, it does not exceed 2 % [1, 2].

Gas humidity is also expressed by a dew point, a temperature at which the gas is fully saturated with water vapour. If the gas is cooled down to below the temperature of the dew point, the water vapour condenses.

The content of water vapour in the gas is highly dependent on temperature and gas pressure. If the humidity is measured at a constant pressure, only the temperature needs to be taken into consideration.

2.2. Principle of Electrochemical Humidity Sensors Function

The principle of the electrochemical humidity sensor function is illustrated in Fig. 2.

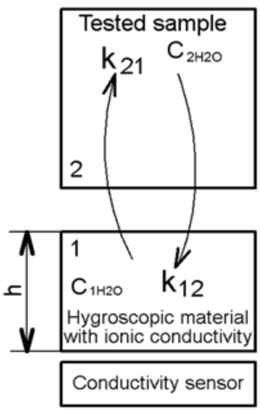


Fig. 2. The schematic sensor structure which describes the sensor function.

The molecules of water are transferred from the sample to the sensor active layer by the rate $k_{12}C_{2H_2O}$ and they are removed from the active layer by the rate $k_{21}C_{1H_2O}$. The sensor dynamics is described by

$$\frac{dC_1(\tau)}{dt} = -k_{21}C_{1H_2O} + k_{12}C_{2H_2O}, \quad (4)$$

where k_{xx} are the rate constants, C_x is the water vapor concentration in a particular environment and τ is the certain time moment.

The solution of this equation characterizes the time constant of the chemical part of the sensor. It is obvious that the time constant will be decreased by the decrease of the active layer thickness (h). At a very low thicknesses, the equilibrium state is reached nearly immediately (a few microns corresponds to $t \cong 1\ s$), $\frac{dC_1(\tau)}{dt} \to 0$ and

$$C_{2H_2O} = \frac{k_{21}}{k_{12}}C_{1H_2O} \quad (5)$$

The concentration of water in the sample is proportional to the concentration of water in the active compound of the sensor via the equilibrium constant K_e.

It is necessary to in mind that K_e depends on temperature, pressure and state of the boundary between the measured sample and the sensor active layer. The last dependency is the most variable. It depends on the surface charge, sample flow and surface roughness.

The concentration of water in the sensor active layer can be measured by its conductivity.

The theory of conductivity measurement is described elsewhere [9, 10, 12, etc.]. In comparison to the electrical resistance measurement (Ohm's law), the measurement of electrolytes conductivity is a much more complex problem. In general, the dependence between charge carriers (and their mobility) and conductivity is nonlinear. The measured conductivity also depends on the measurement method and it is influenced by the electrophoretic effect, relaxation effect, Wien and Debye-Falkenhagen effects [12]. The optimum method of conductivity measurement needs to take such effect in account, namely with the respect of the sensor electrodes design, frequency of applied voltage and voltage itself. If, for example, the gap between electrodes is in μm and the applied voltage in volts, then the measurement can be influenced by Wien effect. If the measurement frequency is higher than 1 MHz then the measurement will be influenced by Debye-Falkenhagen effect [12].

In general, it is impossible to create a reasonable practical sensor theory which enables us to create an analytical transfer function between the measured signal and humidity. Sensors must be calibrated experimentally.

Table 1 summarizes the inorganic materials which can be used as the active compound in the active layer of a sensor [13].

Table 1. Hygroscopic materials used for humidity sensors.

Material	$\frac{\rho_{H_2O}}{gm^{-3}}$
P_2O_5	$2.\ 10^{-5}$
Al_2O_3	0.003
MgO	0.008
Silica gel	0.03
CaO	0.2
$ZnCl_2$	0.85

Table 2 summarizes the inorganic materials which can be used to create the defined humidity to calibrate the sensor [13].

Table 2. Materials which are used for humility sensor calibration.

Solid state materials	t[°C]	φ[%]
$ZnCl_2$	20	10
$LiCl \cdot H_2O$	20	15
$CaCl_2 \cdot 6\ H_2O$	24.5	31
$CaCl_2 \cdot 6\ H_2O$	18.5	35
$CaCl_2 \cdot 6\ H_2O$	5	39.8
$K_2CO_3 \cdot 2\ H_2O$	18,5	44
$NaHSO_4 \cdot H_2O \cdot Na_2Cr_2O_7 \cdot 2H_2O$	20	52
$Mg(CH_3COO)_2 \cdot 4\ H_2O$	20	65
NH_4Cl	20	79.3
KBr	20	84
$KHSO_4$	20	86
$Na_2CO_3 \cdot 10\ H_2O$	24.5	87
$ZnSO_4 \cdot 7\ H_2O$	20	90
$Na_2SO_3 \cdot 7\ H_2O$, $Na_2HPO_4 \cdot 12\ H_2O$	20	95
K_2SO_4	20	99

The typical dependence of the resistance of a hygroscopic material (alumina) on the humidity is in Fig. 3.

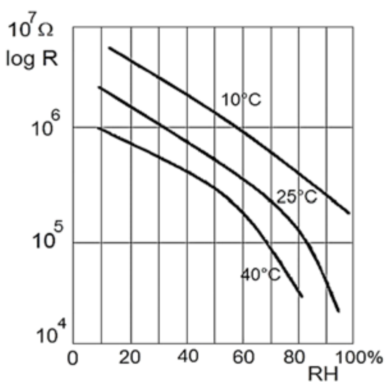


Fig. 3. Typical resistance vs. relative humidity curve of alumina [3] at different temperatures.

3. Sensor Performance

As described above in Fig. 1, the usual resistive relative humidity sensor is placed on a silicon substrate, to which the electrode system is attached. It is composed of an active substrate and a porous gold electrode. The substrate layer consists of an aluminum base on which the active hygroscopic layer of alumina is applied [4].

In our case, a different sensor arrangement has been used. The sensor, provided by the local manufacturer of electrochemical sensors, BVT Technologies, uses a corundum ceramic base on which the electrode system is applied. The electrodes are made of platinum – gold alloy and are shaped as two combs, inserted into each other (Fig. 4.) [5]. The electrodes are connected with a sensor connector by silver paths, covered by an insulating protective layer.

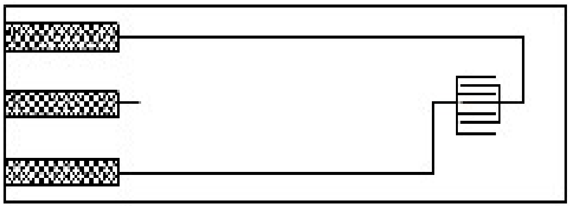


Fig. 4. The BVT Technologies CC1 conductometric sensor.

As an active part of a sensor, a layer of P_2O_5, a layer of Al_2O_3 in polymeric binder or the alumina ceramic itself can be used. In this case, the electrodes are not covered by a hygroscopic material layer to create the sensor active part, but the humidity is absorbed by the ceramic between electrodes and this influences the ceramic surface conductivity.

The sensor dimensions are 25.4 × 7.62 mm and the active electrode system takes up a space of 2 × 2 mm.

A more detailed drawing of the sensor is given in Fig. 5. It provides information about sensor dimensions and electrode and protective cover arrangements.

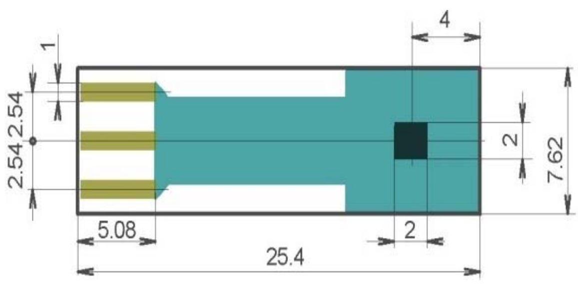


Fig. 5. Real electrochemical sensor, including its dimensions.

The main advantages of the resistive humidity sensors are a short response time of 30 – 50 s as declared by the sensor producer [7] and a high resolution which can be further improved by using signal amplification.

4. Signal Processing Unit

The electronic design and construction of the signal evaluating unit were the main goals of our work. The design rules have been determined by assigned parameters.

4.1. Required System Parameters

The essential parameter is the range of the measured resistances to be from 1 kΩ to 10 MΩ.

Secondly, once the hygroscopic material absorbs water, the polarization of electrodes occurs. To prevent this, the sensor must be supplied by an ac signal, the frequency of which is above Warburg frequencies [6], i.e., above 5 kHz. The equivalent schematic diagram of the sensor, that has absorbed water, is created as a parallel combination of a resistor and a capacitor. In the ideal case, its frequency characteristic in the Gaussian plane has a semicircle shape (Fig. 6). In the real case, sensor electrodes polarization due to the diffusion of ions occurs at lower frequencies and causes the frequency characteristic of the equivalent circuit deformation. For our purposes, the supplying signal frequency of 10 kHz was selected.

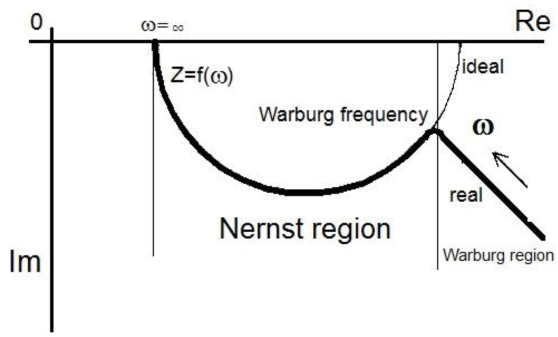


Fig. 6. The complex impedance frequency characteristic of an electrolyte in the Gaussian plane. See the characteristic distortion in the Warburg region.

To achieve both high precision and high resolution of the measured resistance, the use of highly precise analog to digital converters (AD converter) was necessary. The requirement of the resistance measurement over four decades with the precision at least 1 % requires the use of the 24 bit AD converter (the required resolution is $10^{-4} \times 10^{-2}$, it is 10^{-6}, the 24 bit AD converter resolution is 5.9×10^{-8}). Thus, the AD must have its effective number of bits equal to 20. As the effective number of bits of the used AD converter (integrated to the used microcontroller) is less than required, an additional digital filtering has to be done.

As for the mechanical arrangement, minimized electronic unit dimensions have been required, comparable to a common plug-in flash disc unit.

For the resistance measurement, the Ohm's method has been selected [6], based on the measurements of the voltage drop on the sensor, and current flowing through it.

Another problem of the applied method of measurement is the strain capacity of the sensor. To avoid this problem, the synchronous detection must be applied to separate the real resistance from the imaginary reactance.

The relative humidity magnitude depends on the temperature. This means, the system must be equipped with a precise thermometer capable of measuring to the nearest 0.1 °C.

The transport of measured results to a host computer is provided by a USB 2.0 standard interface (Universal Serial Bus).

These requirements led to the electronic circuit arrangement, the schematic block diagram of which is in Fig. 7.

The equipment is designed so that it will create a small plug-in unit, which can be directly inserted into a computer USB connector.

The sensor is inserted to the unit by means of a connector placed on the opposite side of the electronic printed circuit card.

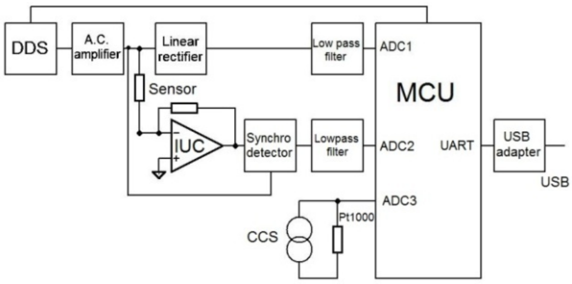


Fig. 7. Hygrometer block diagram. DDS – direct digital synthesizer, IUC – current/voltage converter, CCS / constant current source, MCU – microcontroller.

4.2. Electronic Design: the Analog Part

The analog part of the system involves three basic building blocks, the Direct Digital Synthesizer (DDS) with an amplifier of the ac signal supplying the sensor, and two signal traces measuring the voltage drop on the sensor and the current flowing through it.

The DDS part principle is visible from the schematic diagram in Fig. 8.

It produces a harmonic signal, the frequency of which is 10.06 kHz as shown in Fig. 9. It should be mentioned, the generated signal is symmetrically spread round the analog ground (AGND), which is kept on the constant potential, equal to the half of the power supply voltage.

The voltage trace consists of a usual linear full-wave rectifier and a low pass filter that rejects residual ac signal components. This method is used, because the voltage signal is strong and has a good signal-to-noise ratio.

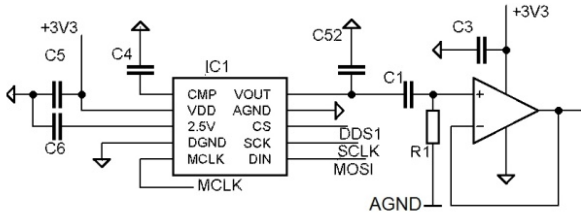


Fig. 8. The principle schematic diagram of the DDS with an ac amplifier. DDS1, SCLK, MOSI and MCLK are interface signals of the microcontroller.

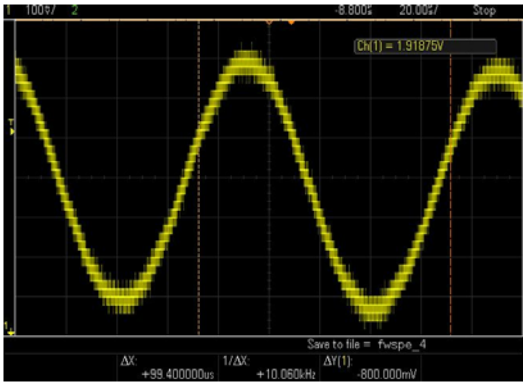


Fig. 9. Output harmonic signal supplying the tested sensor.

The current trace arrangement begins with the current-to-voltage converter (IUC), the output signal of which is detected in the full-wave synchronous detector. The purpose of this detection type is to gain the real part of the measured current and to improve signal-to-noise ratio of week current signals (Fig. 10).

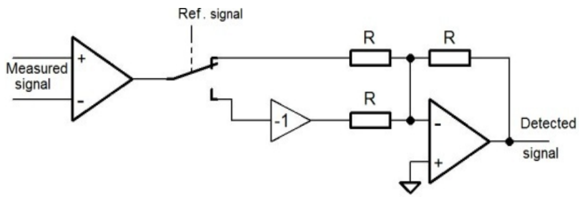


Fig. 10. The basic principle of the used full wave synchronous detector.

The detector takes advantage of the Analog Devices ADG 819, a single-pole, double-throw (SPDT) switch, which is fast, has a small on-resistance (less than 0.8 Ω) and has a low residual electric charge. The switch is controlled by the reference rectangular signal, the frequency and phase of which are the same as of the signal, supplying the sensor. In spite of careful switch selection, the residual charge causes ripples on the detected signal (Fig. 11). These ripples cause an additive error of the measurement, as is discussed later.

After the detection, the output detected signal contains a useful dc component and a residual ac component, which is filtered out in the low pass filter.

The cut-off frequency of the second order low pass filters in both traces is 10 Hz. This frequency ensures sufficient 126 dB rejection of the residual 20 kHz component of the full-wave detected signals. Besides, the filters serve as anti-aliasing filters for AD converters (AD converter sampling frequency is 250 Hz – see the next paragraph).

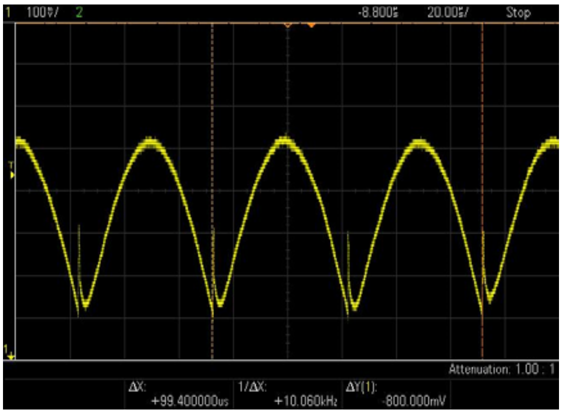


Fig. 11. The full-wave detected signal at output of the synchronous detector. Narrow ripples are caused by the switching reference signal penetration through the parasitic switch gate-substrate capacitor.

The resistance thermometer using a platinum Pt1000 sensor is the last analog element of the circuit. The sensor is supplied from a constant current source (CCS).

From the technological point of view, high precision operational amplifiers have been used for the analog signal processing at the operating frequency, and the chopper stabilized amplifiers for the detected signal filtering and for the constant current source for supplying the Pt1000 thermometer.

4.3. Digital Signal Processing and Control

The digital part of the equipment is controlled by the TI microcontroller unit (MCU) MSP430AFE253, which has small power consumption and contains three independent 24 bit analog to digital converters needed for the system realization. The AD converters of the microcontroller can be synchronized, and thus they offer their results simultaneously. As the built-in converters are very fast Σ-Δ converters having a low effective number of bits, it was necessary to correct it using oversampling and additional digital filtering. The conversion results are obtained by an averaging filter taking advantage of the sum of 256 AD converter samples, shifted 8 bits right. The AD converter sampling period is 4 ms, thus the measurement itself takes about 1 s.

The microcontroller also controls and sets the direct digital synthesizer producing the ac 10 kHz signal used to supply the sensor. For this communication, the microcontroller takes advantage of the synchronous serial interface (SSI) link. Further on, the microcontroller evaluates the measured resistance and calculates the relative humidity taking advantage of the polynomial approximation of the diagram in Fig. 1. The calculated data are sent to a host computer via the standard USB link.

4.4. Metrological Aspects

Determination of the system accuracy requires system calibration and error analysis as discussed below.

4.4.1. System Calibration

The sensor conductivity measurement is the substantial problem of the relative humidity determination. To measure it accurately, a highly accurate calibration method must be used. This calibration comes out of the comparison of conductance standards with the conductance of the sensor. So, the first step is the standard selection. For our purposes, the Tesla TR16x resistors (Czech products) with good temperature and time stabilities have been selected and their conductance has been measured using the highly accurate ohmmeter Agilent 34410A – the 6.5 digit multimeter. The data obtained by these measurements have been considered the conventional true values of the standard conductance (G_N). The calibration process is carried out automatically by the microprocessor firmware and consists of two steps. The maximum conductance of a measuring range is applied on sensor terminals and values of the voltage and current are measured by embedded 24 bit AD converters in the first step. Then, the zero current and voltage points of both AD converter channels are determined, in the second step. The transfer constant of the instrument is obtained using the formula:

$$G_N = k_G \frac{ADCN_I - ADC0_I}{ADCN_U - ADC0_U}, \quad (6)$$

where G_N is the conventional true value of the standard conductance, $ADCN_I$ and $ADC0_I$ are the current AD converter data,when the standard or zero conductance is applied respectively, $ADCN_U$ is the voltage AD converter data measured, when the standard conductance is applied and $ADC0_U$ is the ADC data, when the zero voltage is applied on the voltage signal trace input, and k_G is the transfer constant between AD converters data and the conductance expressed in S (Siemens). The transfer constant is calculated from the Equation (6) and stored in the parameter memory.

When any unknown conductance G_X is being measured, the microcontroller calculates the conductance using the following formula:

$$G_X = k_G \frac{ADCX_I - ADC0_I}{ADCX_U - ADC0_U}, \quad (7)$$

where $ADCX_I$ and $ADCX_U$ are the current and voltage AD converters data, when measured conductance is applied on the sensor terminals.

4.4.2. Errors Analysis

The accuracy of the measurement is determined by the sensor calibration and the signal processing.

The calibration errors are mainly caused by the uncertainty of the multimeter used for the determination of the standard, as well as the errors of AD converters used.

As for the signal processing, the most important sources of errors are the low number of effective bits of used AD converters, the time stability of both zero signals $ADC0_I$, and $ADC0_U$, and the ripples caused by the synchronous detector switch (Fig. 11). These properties degrade the system accuracy in the case of weak current signals (the voltage signal is strong in all cases), when a small conductance (high resistance) is measured, as shown in Fig. 12. [14].

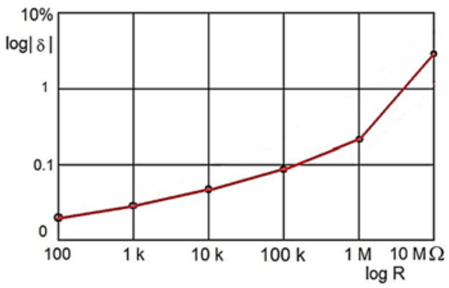
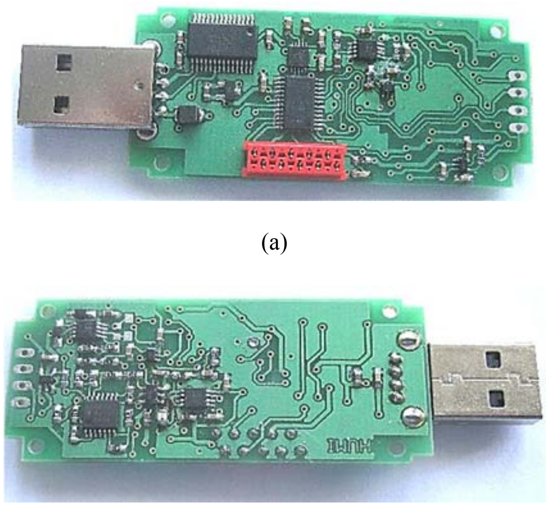


Fig. 12. The absolute value of relative error as a function of the measured resistance.

These results led to a decision to divide the required range of conductance into two ranges, using the possibility of the current signal amplification by means of an amplifier, which is a part of the AD converter. This adaptation contribution did not lead to a substantial accuracy improvement, because it did not solve the problem of a low signal-to-noise ratio at the output of the analog part of the current signal trace. The possible solution is to change the current to voltage converter sensitivity.

5. Conclusions

The electronic system has been designed and its firmware created. The firmware also includes the system calibration procedure as described above together with the calibration constants stored in the microcontroller internal electrically erasable programmable read only memory (EEPROM). The system performance, and the assembled printed circuit board (PCB) are shown in Fig. 13(a) and Fig. 13(b). The PCB dimensions are 59 × 25 mm. The achieved results do not meet all the required criteria and the design needs some further improvement, namely as for the signal-to-noise ratio of the current trace. At present, to get the introduced results, it is necessary to do the re-calibration of the instrument whenever it is switched on. Although this procedure is simple and does not require much time, it is a complication of the measuring procedure. The change of the current to voltage converter sensitivity was tested at two electronic units with different sensitivities and gave promising results. For further improvement, it is necessary to adapt the hardware, which offers a possibility to divide the current range into two subranges. However, this re-design is already finished and prepared for future realization.



(a)

(b)

Fig. 13. (a) Upper view on the PCB of the electronic unit, the digital signal processing part; (b) Bottom view on the PCB, the analog signal processing part.

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