Journal of ELECTRICAL ENGINEERING, VOL. 58, NO. 2, 2007, 98–103

NOVEL APPROACH IN RATIOMETRIC TECHNIQUE OF SENSING

Vladimír Tvarožek [*] — **Erik Vavrinský** [*] — **Zdeněk Řezníček** [**]

A novel method of ratio and relation measurement is introduced. On the basis of this principle, asymmetric ratio resistance and conductance microsensors have been developed which are set to an arbitrary relation temperature or electrochemical concentration. The combined resistance temperature sensor allows both to adjust its sensitivity to the defined value by trimming the asymmetry resistor resistances and to increase the accuracy 10 times in comparison with the classical ratiometric arrangement. The electrochemical conductance micro-sensor is able to monitor the concentration changes in μmol/L range with constant sensitivity adjustable by the frequency of the supply voltage.

Keywords: ratiometric technique, relation measuring systems, resistance sensors, temperature, electrochemical conductance

1 INTRODUCTION

One of the main goals of sensor development is to reach and surpass the functions of human sensors. From comparison between human and technical sensors an important knowledge is outcoming: the technical sensor is an integral type (*ie*, it directly senses temperature), while the human sensor is a differential type (sensitive to a change of temperature). A further major drawback of today's technical sensors is their lack of intelligence in comparison with human sensors. Although the neuro-fuzzy sensor development is going on rapidly, it has to be joined with a research of intelligent materials and structures to solve that problem. Therefore the future sensors should be able to combine micro/nanoscopic ("one-point", "digital") and macroscopic ("total-view", "analog") sensing. The method we present is based on the differential principle of sensing well-known in nature combined with a "smart" analog sensor structure realized by microelectronic technologies.

Intelligent operation intended to reinforce the inherent sensor characteristic (transfer function) is the monitoring compensation — a ratiometric technique belongs to the most powerful compensation methods which can suppress the influence of undesirable variables on the measurand [1, 2].

Resistance (or impedance) sensors are one of the largest groups of physical and chemical sensors for non-electric quantities measurements, *eg*, temperature, pressure or gas/liquid concentrations. Almost every industrial process involves the need to know and control the temperature. The main problems are in accurate and reproducible monitoring of not only the temperature itself but also of small temperature differences. The same requirements are frequent for measurements of gas/liquid concentrations in chemical, food industry, medicine and environment. We illustrate the principles of our novel approach by presenting ratio and relation asymmetric resistance/conductance sensors for monitoring of temperature or concentration changes.

2 THEORETICAL

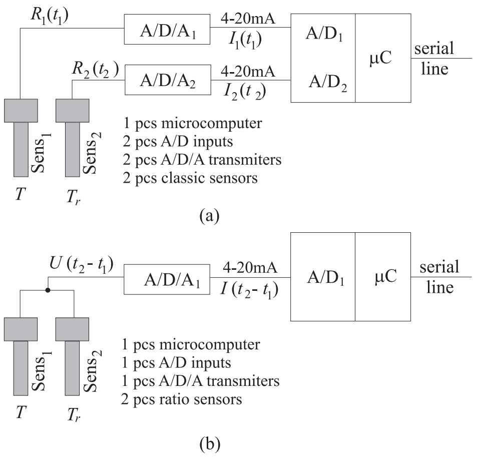
The today's resistance temperature sensors are based on the temperature-resistance relationships of the sensing resistors with a defined temperature coefficient of resistance (*TCR*). Measuring methods are mostly exploiting the evaluation of the voltage across a temperature sensitive resistor supplied by a constant current source. The total relative inaccuracy of temperature determination is given by the contribution of several effects and parameters, such as the total of relative inaccuracies of *TCR*, resistance at 0 °C and supply current. The *TCR* inaccuracy is affected by material purity, quality of technological processing during sensor production and stabilization of its parameters. This property is not variable in the final sensors and the *TCR* cannot be adjusted additionally. The inaccuracy of resistance at 0 °C is given by the level of technological processes including sensor trimming (reproducibility of resistance adjustment, the accuracy of temperature control during trimming). Temperature sensor's accuracy is normalized and classified into single categories ([DIN IEC 751] class A and B). The absolute error around the calibrating value of 0 °C has a value approximately in the range of 0.1–0.2 °C and is increased with larger differences of the monitored temperature from the firmly defined "reference temperature" of 0 °C. At temperatures above 600 °C (top limit of the most frequently used platinum sensor Pt 100) the error can reach several °C. Classical ratiometric measuring system consist of two complete channels including two sensors, two temperature Analog/Digital/Analog (A/D/A) transmitters, two A/D

---

[*] Department of Microelectronics, Slovak University of Technology, Ilkovičova 3, SK-812 19 Bratislava, Slovakia. Email: vltvar@elf.stuba.sk

[**] Hybrid Integration Technology, Ltd., CZ-687 15 Nedachlebice 233, Czech Republic. Email: hit@cmail.cz

ISSN 1335-3632 © 2007 FEI STU



(a)

(b)

Fig. 1. Ratiometric measurement setup: (a) classic industrial configuration, (b) novel ratio/relation configuration.

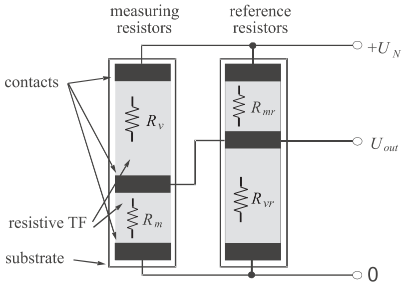


Fig. 2. The layout of the ratio/relation asymmetric resistance sensor.

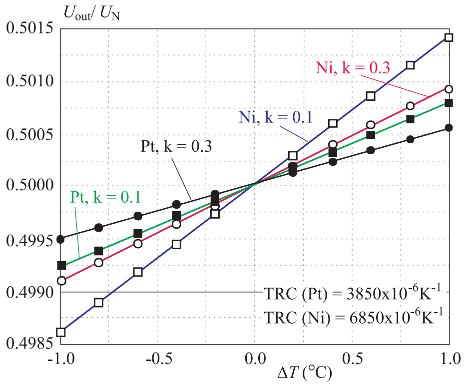


Fig. 3. The influence of TCR (Pt, Ni) and of the asymmetric coefficient k upon the sensor's sensitivity.

inputs to a microcomputer, where single signals are compared and the temperature differences are finally determined (Fig. 1a). If classical resistance temperature sensors (Pt 100, Ni 1000) are used for ratiometric measurements or temperature difference determination between two independent points, the error is given by the sum of errors in each of the two measuring channels. Therefore the use of the classical ratiometric method is improper for measuring small temperature differences at temperatures further away from the calibration temperature of 0 °C.

A novel ratio/relation asymmetric resistance method is conveying the same idea how to overcome the technological residual defects and imperfections in the production of highly accurate temperature sensors [3]. The new ratiometric circuit design is based on one combined asymmetric ratio resistance sensor, where the output voltage signal directly indicates the temperature difference. Therefore only one measuring channel is needed consisting of: two ratio sensors, one A/D/A transmitter converting the voltage sensor signal to standard industrial electrical signals and one A/D input to microcomputer, where the value of temperature difference is computed exactly (Fig. 1b). A lot of effects (power supply non-stability, self-heating effect, electro-magnetic compatibility, *etc*) are compensated by application of the ratio principle method. All sensors or wire contact defects are automatically indicated by the defined non-standard output signal critical level. Temperature difference measurements are based on a combination of two couples of resistors with unequal resistance values R_m, R_v and identical TCR (Fig. 2). Such paired resistors are located in two different temperature zones: "measuring" and "reference (arbitrary relation)" temperatures (T and T_r, respectively) and connected in non-parallel. The resistance value of each individual resistor of the pair R_m and R_v located at temperature T can be expressed by the resistance value R_{mr}, R_{vr} of the paired resistors situated in a location with temperature T_r according to equation:

$$R_x = R_{xr}\big(1+TCR(T-T_r)\big)\,. \tag{1}$$

The normalized output voltage signal U_{out}/U_N (U_N is the supply voltage) can be expressed as a ratio of the resistor combinations in the circuit

$$\frac{U_{out}}{U_N} = \frac{\frac{R_r R_{mr}}{R_r+R_{mr}}}{\frac{R_v R_{mr}}{R_v+R_{mr}} + \frac{R_{vr} R_m}{R_{vr}+R_m}} \tag{2}$$

and by using relation (1)

$$\frac{U_{out}}{U_N} = \frac{R_{vr} + R_{mr}\big(1+TCR(T-T_r)\big)}{\big(R_{mr}+R_m\big)\big(2+TCR(T-T_r)\big)}\,. \tag{3}$$

If an asymmetry coefficient is introduced as $k = R_v/R_m$

$$\frac{U_{out}}{U_N} = \frac{k+1+TCR(T-T_r)}{(1+k)\big(2+TCR(T-T_r)\big)}\,. \tag{4}$$

It is apparent that the value of the normalized output voltage ratio in the circuit configuration mentioned above is given solely by the asymmetry coefficient of the paired resistors, the temperature coefficient of resistance TCR and the temperature difference between the measured locations (Fig. 3). Also it is evident that the normalized output voltage ratio signal will be equal to 0.5, when the resistors are at the same temperature, $T = T_r$.

When both of the temperatures are identical, we designate the "reference sensitivity" C_r (at an arbitrary relation temperature T_r)

$$C_r = \frac{\mathrm{d}\frac{U_{out}}{U_N}}{\mathrm{d}T} = -\frac{1-k}{1+k}\,\frac{TCR}{4}\,. \tag{5}$$

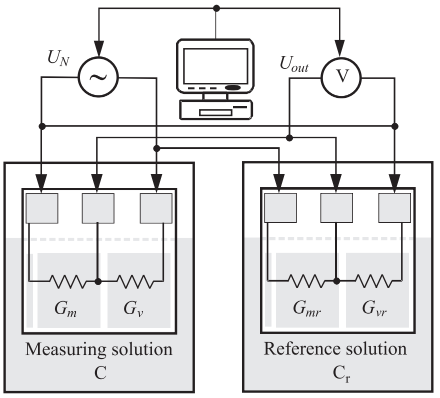


Fig. 4. The layout of the ratio/relation electrochemical conductance sensor.

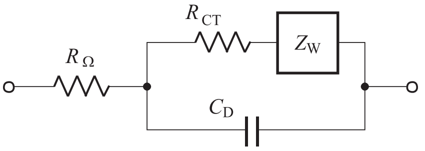


Fig. 5. Electrical model of the electrochemical cell.

The reference sensitivity C_r of that combined sensor is a function of only TCR and asymmetry coefficient $k = R_m/R_v$ (straight lines in Fig. 3) and it is adjustable by trimming the resistor values.

Small temperature differences ($\Delta T \leq 10\,°\mathrm{C}$) between both measuring locations can be expressed by relationships (4) and (5):

$$\Delta T = T - T_r = \frac{(k-1)\left(1 - 2\frac{U_{out}}{U_N}\right)}{4C_r\left(1 - (k+1)\frac{U_{out}}{U_N}\right)}\,. \tag{6}$$

From this theoretical analysis a very important conclusion is resulting: any variation of TCR values of a material used for the temperature sensitive paired resistors can be easily compensated by adjusting their asymmetry coefficient to keep the reference sensitivity of all the sensors identical as well as to calibrate them for the constant temperature difference at an arbitrary temperature.

Ratio/relation electrochemical conductance sensor

The conductance G of an electrochemical cell in a solution with electrolytic conductivity κ can be expressed by relationship

$$G = A_c \kappa \tag{7}$$

where constant A_c is dependent on the cell electrode arrangement and frequency f of the supply voltage, κ is a function of solution concentration C. For small concentration differences $\Delta C = C - C_r < 1 \times 10^{-3}$ mol/L (molarity M), C_r is an arbitrary reference (relation) concentration, we can assume a linear relationship between conductance G and concentration C

$$G = G_r\left[1 + c_G(C - C_r)\right] \tag{8}$$

by introducing a concentration coefficient of conductance c_G

$$C_G = \frac{1}{G_r}\frac{G - G_r}{C - C_r} = \frac{1}{\kappa_r}\frac{\kappa - \kappa_r}{C - C_r}\,. \tag{9}$$

The concentration difference measurements were made on a combination of two couples of two cells with unequal conductance values G_m, G_v and identical c_G (Fig. 4). They were connected in non-parallel configuration (Fig. 2) and immersed in "measuring" and "reference (arbitrary relation)" solutions (concentrations of C and C_r respectively).

By introducing the asymmetry coefficient $k = G_m/G_v = G_{mr}/G_{vr}$, and using relation (8) we designated the "reference sensitivity" S_r for small concentration differences (according to equations (2–5))

$$S_r = \frac{\mathrm{d}\frac{U_{out}}{U_n}}{\mathrm{d}C} = -\frac{1-k}{1+k}\frac{C_G}{4}\,. \tag{10}$$

The reference sensitivity S_r of that combined sensor is a function of only c_G and asymmetry coefficient $k = G_m/G_v$.

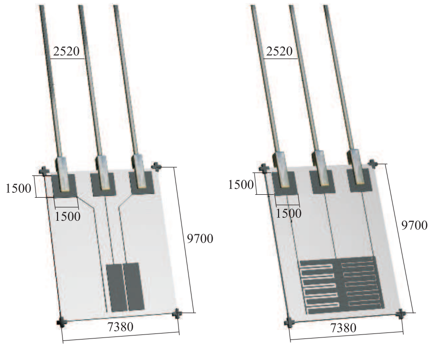


Fig. 6. Planar thin-film electrochemical cells with strip and interdigital asymmetric configurations.

The equivalent electrical model of the electrochemical cell (Fig. 5) consists of the solution ohmic resistance R_Ω and impedances of electrode-solution interfaces: R_{CT} — charge-transfer resistance, C_D — double-layer capacitance and Z_W — Warburg impedance [4]. The Warburg impedance is formed by a serial connection of a resistor and a capacitor, $R_W = \sigma/\omega^{1/2}$ and $C_W = 1/(\sigma\omega^{1/2})$, σ is the Warburg coefficient. Because the Warburg impedance is dependent on frequency ω, also cell conductances G_v and G_m will differ at various frequencies of the supply voltage. Then, according to relation (10), the reference sensitivity S_r is controllable by setting the frequency of the voltage supply. This is a very important output of the novel electrochemical conductance sensor design with a significant contribution to practical sensing.

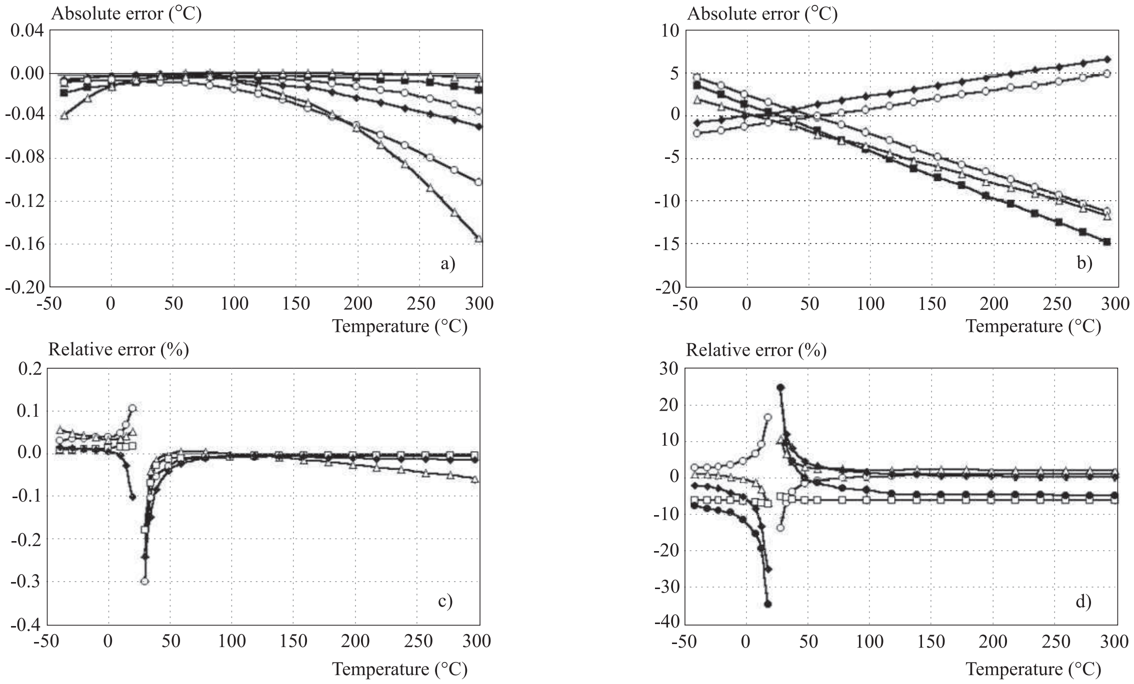


Fig. 7. Absolute and relative inaccuracy of sensors for $T_r = 25\,^{\circ}\mathrm{C}$: (a, c) asymmetric resistance sensors after calibration (6 samples), (b, d) classic sensors trimmed and pared (5 samples).

3 EXPERIMENTAL

3.1 Technology

Ratio/relation temperature resistance sensor

For the purposes of verification of the theory discussed above, several equivalent test sample sensors were fabricated with different topologies and technologies to be used: (i) thick Pt films prepared by both screen printing and photo-sensitive Pt-paste (FODEL) technologies; (ii) thin Pt films prepared by RF sputtering. Resistance temperature sensors were formed on ceramic substrates as planar strip resistors (in the case of thick films) or very narrow meander resistors (based on thin films).

Trimming was performed using corrective cutting with a laser beam in the same manner as in the case of classical sensors, the only difference being that it was carried out on a standard workbench at room temperature.

Ratio/relation electrochemical conductance sensor

The thin film electrochemical cells were designed and fabricated of two asymmetric configurations: strip and interdigital shapes (Fig. 6). The microelectrodes of Pt (to remove the polarization effect) were fabricated by standard thin film technology: Pt films (150 nm in thickness) and underlying Ti film (50 nm) were deposited by RF sputtering on alumina substrates. Microelectrodes were photolithographically patterned by lift-off technique. The strip configuration of the microelectrodes consists of three separate electrodes with different areas and gaps between electrodes, which creates unequal conductance values of planar electrochemical cells (widths of strips were $40\,\mu$m and $1000\,\mu$m, gaps were $300\,\mu$m and $100\,\mu$m wide,). For interdigital configuration: widths of fingers were 60 mm and 200 mm, gaps were 120 mm and 50 mm wide.

3.2 Results and discussion

Ratio/relation temperature resistance sensor

The measurements and simulations were been performed in such a way that individual resistance values were measured at temperatures 0 °C and 100 °C and appropriate *TCR* were calculated from them. Then the measurements of asymmetry coefficient k were carried out and identity of these coefficients at different temperatures was checked. Finally, the values of reference sensitivity for all temperatures were calculated and their identity was verified at the samples each to each and for all the temperatures that were used for measurements of the asymmetry coefficients k. The identity of reference sensitivity for individual sensors with a given value of $-0.0005\,^{\circ}\mathrm{C}^{-1}$ was demonstrated by these measurements up to three significant digits, that means $C_r = -500\,\mathrm{ppm}/\,^{\circ}\mathrm{C}$, in spite of the values of individual *TCRs* differing from each other by 20 % maximally.

Then two models for evaluation of experimental data were created. The first one — a mathematical model respecting real values of parameters of individual sensors was used. The values of really expected proportional output ratio voltage of real couples of sensors in dependence on temperature in the range from −40 °C up to +300 °C were generated using relationships (1) and (2). The second one — a reverse mathematical model of an ideal couple of sensors was applied and the values of temperature differences were reversibly calculated from equation (6).

Differences of the calculated and originally required temperature values are presented as an error of the real couple of sensors due to a dispersion of its real parameters. Analogous models were created also for the simulation of sensor's behaviour at the classical configuration.

To improve the accuracy of measurement, calibrating constants can be found for each of the individual pairs of sensors. These calibrating constants specified by an independent measurement were inserted into the exact relationship for temperature difference calculation. The calibrating constants can be updated anytime during the life of the sensor, in other words, the calibration of a given pair of resistors can be easily restored anytime. The calibration allows an increase of accuracy up to ten times.

The temperature difference measurement of functional characteristics was performed by placing one sensor of the appropriate pair in a precisely controlled oil bath with temperature set to the value of 25 °C and the second sensor was placed in another oil bath adjusted to the desired temperature. All the pairs were placed in temperature baths simultaneously.

It is evident from a comparison of absolute and relative inaccuracies of classic sensors (trimmed and paired) and asymmetric ratio sensors (Fig. 7) that an increase of accuracy (approx. 10 times) is the result of the asymmetric configuration. It allowed a physical adjustment of the output characteristic (sensitivity) by trimming the reference sensitivity C_r to a defined value (-500 ppm/ °C). In addition a specific value of individual calibration constants could be used for each individual pairs of sensors.

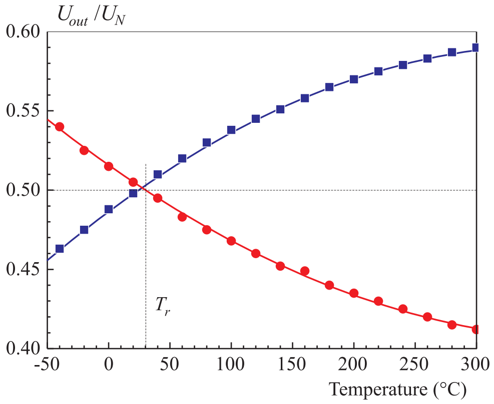


Fig. 8. Temperature dependence of normalized output ratio voltage for combined asymmetric ratio resistance sensors. Curves of 12 samples are overlapping.

The accuracy of ratiometric measurements performed by classical sensors is limited by the fact that they are calibrated at one fixed temperature 0 °C. Unlike classical sensors, asymmetry ratio sensors are adjustable (calibrated) at an arbitrary reference temperature and the accuracy of the output signal depends only on temperature differences. Therefore the absolute error is ±0.02 °C in the range -50 to $+100$ °C and the relative error is ±0.1 % (Fig. 7).

A test of 12 combined asymmetric resistance sensors confirmed that their transfer functions (output voltage signal normalized to supply voltage versus temperature) were identical and independent of the particular value of the total resistance of each combined sensor as well as of the level of the supply voltage (Fig. 8).

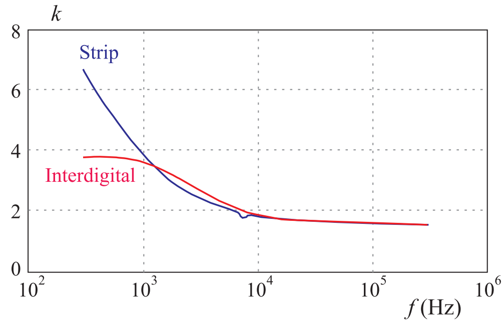


Fig. 9. Dependences of asymmetric coefficients k (strip and interdigital) on the frequency of the voltage supply.

Ratio/relation electrochemical conductance sensor

The parameters of strip electrochemical cells of unequal conductance were calculated (Tab. 1) according to electrical model (Fig. 5). Calculations were made using of the Cole-Cole graph [4] and measurements of the complex impedance by an LCZ bridge. From the parameters you can see clearly that the electrochemical cells differ mainly in Warburg coefficients and therefore asymmetric coefficient k will depend on the frequency of the voltage supply, which was confirmed experimentally (Fig. 9). The interdigital electrochemical cells have shown a similar behaviour — except for a difference in the asymmetric coefficients of strip and interdigital cells below a frequency of 1.5 kHz. Therefore we only present experiments obtained on strip electrochemical cells (results obtained by interdigital cells were similar).

Table 1. Electrical parameters of strip electrochemical cells of unequal conductance.

	G_S	G_L
R_Ω (Ω)	689	611
R_{CT} (Ω)	18 578	10 750
C_D (pF)	3.07	5.85
σ $\left((\Omega/\mathrm{F})^{1/2}\right)$	862 000	241 000

The influence of the voltage supply frequency on the normalized output ratio voltage at different concentrations of KCl was studied (Fig. 10). The reference concentration was 1000 μmol/L (molarity μM) and the measured concentrations were changed in the range 900 μM–1100 μM (measurement setup is in Fig. 4). Comparison of experimental data and simulations based on the calculated parameters has shown similar frequency dependences of the normalized output voltage on KCl concentrations.

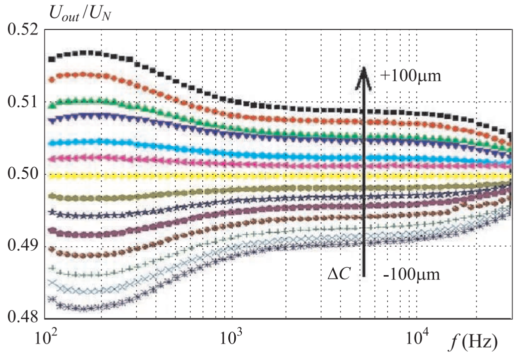


Fig. 10. The frequency dependences of the normalized output voltage on KCl concentrations.

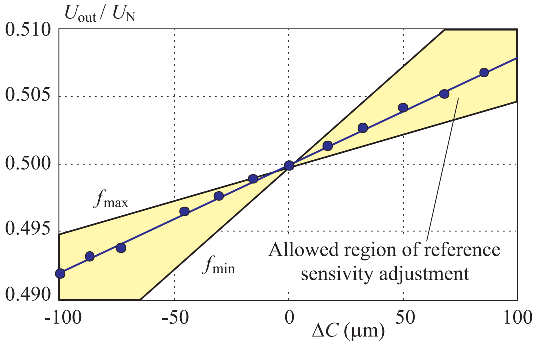


Fig. 11. Adjustment of the sensitivity of the electrochemical asymmetric conductance sensor by the voltage supply frequency.

The measured values were very close to a linear dependence in concentration range $1000 \pm 100\,\mu$M (Fig. 11). In the measurements, a reference sensitivity value $0.8\,\text{mM}^{-1}$ was chosen and this condition was fulfilled at the frequency of the supply voltage of 2.5 kHz. Experimental results have proved the ability of the sensor with a given asymmetric strip (or interdigital) configuration to change the reference sensitivity in the range from 0.5 to $1.4\,\text{mM}^{-1}$ (allowed region of reference sensitivity adjustment), which corresponds to the voltage supply frequencies from 300 kHz to 600 Hz.

4 CONCLUSION

The developed ratio and relation asymmetric resistance/conductance method can help to overcome the problems with accuracy and reproducibility of both technology and measurement. Sensors for measuring the temperature differences with high accuracy and adjustable sensitivity can be applied in house and industrial heating control systems, calorimeters, mass-flow meters, air filters foul indicators, *etc.* This approach paves the way to the development of miniature thermal biochemical sensors exploiting microelectrode arrays for multicomponent analyses as well as to the use of electrochemical conductance microsensors in flow injection analysis. The presented principle seems to be very prospective for applications in strain and pressure differential gauges and wherever the classical ratiometric methods are robust and nonsufficiently accurate, *ie*, in microsensors and microsystems as well. This concept has also been extended to the development of an integrated constant temperature sensor and heater for monitoring systems of process energy balance [5].

Acknowledgement

Presented work was supported by SK Grant VEGA 1/0168/03 of the Slovak Grant Agency and in part by the DAAD PPP Programme project 10/2003.

References

[1] FRADEN, J.: Handbook of Modern Sensors — Physics, Design and Application, Springer-Verlag, New York, 1996.

[2] BRIGNELL, J.—WHITE, N.: Intelligent Sensor Systems, IOP Publishing Ltd., 1994.

[3] REZNÍČEK, Z.—TVAROŽEK, V.—RALL, D.: A New RTD Concept and Design for Easy Laser Trimming and Greater Accuracy, The ISA 47th International Instrumentation Symposium, Denver Southeast, USA, May 9–10, 2001, #1016.

[4] LAMBRECHTS, W.—SANSEN, W.: Biosensors: Microelectrochemical Devices, IOP Publishing LTD.

[5] REZNÍČEK, Z.—TVAROŽEK, V.— SZENDIUCH, I.— ŘEZNÍČEK, M.: Temperature Balanced Process Media Energy Activity Monitoring, Proc. EDS ‘05 IMAPS CS International Conference, Brno, Czech Republic, September 15–16, 2005, pp. 94100.

Received 15 November 2005

Vladimír Tvarožek, (Prof, RNDr, PhD) received degrees of Dipl. Phys. (1967) and RNDr (1977) in experimental physics from Charles University, Prague. In 1980 he got PhD degree in Electronics from the Slovak Technical University in Bratislava. As a Professor (2002) at Microelectronics Dept., STU, he is responsible for the research and education in the domain of “Sensorics and Microsystem Technology”. His research activities are in the field of physics and technology of thin films, thin-film microsensors, electrochemical biosensors.

Erik Vavrinský (Ing, PhD) received his Ing degree from the Faculty of Electrical Engineering and Information Technology, Slovak University of Technology in 2002. His current research interests include thin-film microsensors and electrochemical biosensors.

Zdeněk Řezníček (Ing) received degrees of Ing (1978) from the Electro-technical Faculty of Brno Technical University. He is the managing director of the private research, development and sampling company HIT Ltd., sited in Nedachlebice, Moravian District, Czech Republic. He is responsible for the research in the domain of precision temperature, relation temperature difference measuring and process energy balance monitoring ratio technologies. His research activities are in the field of thin and thick-film ratio micro-sensors for balance energy monitoring micro systems in electrochemical biosensors and alternative bio-systems, bio-technologies and nano-applications.