СЕНСОРИ ТА ІНФОРМАЦІЙНІ СИСТЕМИ

SENSORS AND INFORMATION SYSTEMS

UDC621.317
DOI: https://doi.org/10.18524/1815–7459.2023.3.288160

HARDWARE AND SOFTWARE COMPLEX FOR CONDUCTOMETRIC MEASUREMENTS WITH HIGH METROLOGICAL RELIABILITY

V. G. Melnyk[1], S. V. Dzyadevych[2], P. I. Borshchov[1], V. K. Beliaev [1], O. D. Vasylenko[1], Nicole Jaffrezic-Renault[3]

[1] Institute of Electrodynamics National Academy of Sciences of Ukraine,
Peremohy ave., 56, Kyiv, 03057, Ukraine. E-mail: melnik@ied.org.ua
[2] Institute of Molecular Biology and Genetics National Academy of Sciences of Ukraine,
Zabolotnoho st., 150, Kyiv, 03680, Ukraine. E-mail: dzyad@yahoo.com
[3] Institut des Sciences Analytiques, Université Claude Bernard Lyon 1, 5 Rue de La Doua, F69100 Villeurbanne FRANCE

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Abstract. The article summarizes and supplements the results of the development of methods and tools for improving the reliability of differential measurement of local changes in electrical conductivity in electrolyte solutions using a pair of interdigitated transducers, which are used in conductometric biosensors. The aim of the work is a deeper suppression of the error due to the influence of background changes in a solution when the parameters of a pair of transducers are not completely identical. The essence of the issue, the causes and mechanism of the resulting error, and possible ways to reduce it are considered. The structure and algorithms of operation of a computer biosensor system with an intelligent module of a differential conductometric channel based on an alternating current bridge, with balancing in absolute value and phase of the disequilibrium signal, are described. Methods have been developed for tuning such a bridge to a special quasi-equilibrium state, in which a change in the background electrical conductivity does not change its output informative signal. The results of experimental studies are presented.

Keywords: Conductometry, AC Bridge, balancing, differential sensor

АПАРАТНО-ПРОГРАМНИЙ КОМПЛЕКС ДЛЯ КОНДУКТОМЕТРИЧНИХ ВИМІРЮВАНЬ З ВИСОКОЮ МЕТРОЛОГІЧНОЮ НАДІЙНІСТЮ

В.Г. Мельник, С.В. Дзядевич, П.И. Борщев, В.К. Беляев, А.Д. Василенко, Ніколь Жаффрезік-Рено

Анотація. У статті узагальнено та доповнено результати розробок методів та засобів підвищення достовірності диференціального вимірювання локальних змін електропровідності в розчинах електролітів за допомогою пари зустрічно-гребінчастих перетворювачів, які застосовуються в кондуктометричних біосенсорах. Метою роботи є глибше придушення похибки через вплив фонових змін у розчині при неповній ідентичності параметрів пари перетворювачів. Розглянуто суть питання, причини та механізм виникнення похибки, можливі шляхи її зменшення. Описано структуру та алгоритми роботи комп'ютерної біосенсорної системи з інтелектуальним модулем диференціального кондуктометричного каналу на основі моста змінного струму з балансуванням по модулю та фазі сигналу нерівноваги. Розроблено методи налаштування такого мосту в особливий стан квазірівноваги, при якому зміна фонової електропровідності не змінює його вихідний інформативний сигнал. Наведено результати експериментальних досліджень.

Ключові слова: Кондуктометрія, мост змінного струму, балансування, дифференциальный сенсор

Introduction

Conductometric measurements of the concentration of electrolyte solutions are used in many technological processes, to determine the composition of the working environment, raw materials and finished products, as well as in biomedical and environmental studies, in particular, in biosensor analyzers. Their advantages are the speed and low cost of obtaining results, the simplicity of the equipment and measurement methods, the possibility of using for automatic monitoring [1–5]. The disadvantages of traditional conductometric methods that use direct measurement of electrical conductivity are the low selectivity of determining an informative change in the electrical conductivity of a solution relative to non-informative influences, as well as the effect of technological deviations in the parameters of a conductometric transducer on the sensitivity of the measuring channel. Partially, this problem is solved by using bio- or chemo-selective membranes, when the change in conductivity in the solution inside biological membrane on the sensor surface occurs only when there is a certain change in the parameters of the medium during the biological reaction [6].

Earlier studies have shown the possibility of significantly reducing these disadvantages due to the use of differential measurements using a measuring channel (MCh) with a balanced alternating current bridge [7–12]. The direction of their use with impedance sensors, in particular with conductometric ones, turned out to be very promising [6, 9, 13, 14]. The arms of this bridge contain identical conductometric transducers forming a differential sensor [15]. One of these converters is selective (working, active). It perceives the background electrical conductivity of the solution and its local (informative) change, while the second transducer (reference, passive) perceives only the background electrical conductivity. When preparing for measurements, the bridge is balanced to the minimum final output signal. During measurements, a certain amount of the substance under investigation (analyte) is introduced into the buffer solution. In proportion to its concentration, the electrical conductivity of the solution in the selective membrane changes locally. The value of the corresponding informative change in the final output signal of the bridge is recorded by MCh means. When introducing the analyte, it is also possible changing the background electrical conductivity of the solution in the measuring cell, which is in-phase (common mode) interference. Note that the background conductivity changes both when the composition or concentration of the solution changes, and when the temperature changes (approximately 2% per degree).

When the RC-parameters of the equivalent circuit of the converters differ by up to several percent (which is ensured by their manufacturing technologies), a sufficiently high suppression (up to 100 times) of the signal of such common-phase interference is achieved. This ensures high selectivity and sensitivity of MCh. Thanks to this, the differential measurement method has shown effectiveness when using working transducers with selective membranes in biosensor devices [16]. The paper [17] summarizes the results of previous studies of the most essential questions of such measurements and the principles of construction of the necessary equipment. With changes in the background electrical conductivity, which does not exceed a small informative change in the local electrical conductivity (usually of the order of 1%), the relative error of determining the latter does not exceed a few percent. Consequently, the relative value of the additive error from the change in background electrical conductivity, which determines the resolving power of the differential measuring channel, can reach hundredths of a percent.

However, during the practical use of conductometric transducers, it is difficult to maintain a high identity of their parameters for a long time, even with the most advanced manufacturing technology. The reason for this is that the equivalent circuits of the transducers contain near-electrode impedances in addition to the informative parameter – the R_S resistance of the solution between their electrodes. They consist of parallel-connected double-layer capacitance C_{dl} and active charge transfer resistance R_{ct}, which are connected in series with R_S. The impedance parameters of such an object are determined using an equivalent two-element series RC circuit. The active resistance in this scheme differs from the resistance of the solution due to the presence of charge transfer resistance.

The transducers of the differential sensor retain their identity if the parameters of the near-electrode impedances are the same. However, when the transducers are used, processes occur on the surfaces of the electrodes that change them. The values of these changes can reach tens of percent and differ greatly in transducers forming a differential pair, which leads to differences in active resistances in their equivalent two-element circuits [17, 18]. There are also differences in the phase angles of the impedance of the transducers. The multiplicity of suppression by the differential scheme of the background influences of the measurement environment at the same time decreases from hundreds of times to several units [19]. Therefore, conductometric analyzers with an ordinary, balanced bridge circuit guarantee good metrological characteristics only under the condition of constant control over the sufficient identity of the parameters of the transducers and when ensuring minimal changes in the background electrical conductivity in the measuring cell [20]. It is not always possible to comply with these requirements in the conditions of real practice. As a result, the metrological reliability of measurement results decreases and the application of the selective differential conductometric method for determining the concentration of electro-conductive substances is limited [21].

To solve the described problem, it is necessary to achieve the invariance of the determination of the difference in the resistance of the solution in the working and reference transducers in relation to the difference in their near-electrode impedances. Theoretically, it is possible to determine the parameters of three-element equivalent circuits of transducers by the data of separate measurements of their two-element circuits parameters at several frequencies [22], and then calculate this difference. Such a way is very complicated, inefficient due to non-simultaneity of the required measurements (this reduces the accuracy of the result), and most importantly, the advantages of the differential method are lost – the mutual subtraction in bridge circuit the background components of the transducers' signals, of some errors and interference.

As our studies have shown, a more promising way is to pre-balance the bridge in a special state of quasi-equilibrium, in which the minimum value is achieved not of its output signal, but of the response to changes in the background electrical conductivity. The bridge circuit can be brought to such a state by setting the parameters of its mode (voltage modulus and phase on the conductometric transducers), obtained by calculation from the previously measured parameters of their two-element equivalent circuits. The purpose of the presented work is to create and study the metrological characteristics of the hardware and software complex of the conductometric analyzer, which allows implementing such a measurement method and achieving a significant reduction in errors from difficult-to-control changes in the background conductivity of the working solution.

Principles of equipment construction and measurement methods

Structure and principle of operation of differential conductometric analyzers with a quasi-balanced bridge circuit.

The structure and operating principle of the device for implementing such an approach to building a differential conductometric analyzer were firstly proposed in [23]. To set the necessary parameters of the bridge circuit mode, it used analog functional converters: an integrator, a DAC, an adder, a phase shifter, which made it possible to adjust the test voltage vectors on the converters by two quadrature components.

Further studies have shown that in such a structure, using the existing analog element base, it is difficult to provide the necessary accuracy in setting the parameters of the above quasi-equilibrium mode at frequencies that are optimal for conductometric measurements. Therefore, a bridge circuit was developed for a differential conductometric analyzer with digital balancing in absolute value and phase of its output signal (in polar coordinates). Its circuit contains digital generators of two coherent quasi-sinusoidal test signals with precise, frequency-independent amplitude adjustment and accurate digital setting of their phase relationships within ±90°. A detailed description of the principles of construction of such a generator, its characteristics and application for measuring the impedance is given in [24, 25].

To understand the set of algorithmic solutions proposed below, we first briefly consider the structure of the bridge circuit of a conductometric analyzer with digital balancing in polar coordinates and the electrical signals in it. This is described in more detail in [26].

The diagram in Fig. 1 illustrates the principle of operation of this device. The arms of the bridge circuit consist of synthesizers (generators) DG1 and DG2 of quasi-sinusoidal test voltages U_a and U_p, to which conductometric transducers are connected by keys SW1 and SW2: working (active, a) with impedance Z_a and reference (passive, p) with impedance Z_p. They can be modeled by a two-element circuit R_S, C_S, by which their parameters are measured, or by a three-element circuit with the parameters of the near-electrode layer C_{dl}, R_{ct}, which more accurately reflects the nature of their impedance.

The complete equivalent circuit of a conductometric transducer also contains an interelectrode capacitance in parallel with R_S and a Warburg impedance. However, they have very little effect on the value of R_S and C_S at the used frequencies of 30–100 kHz. Therefore, we can assume $C_{dl} \approx C_S$. The additional local conductivity of the solution ΔG, which occurs when the analyte is introduced into the measuring cell, is the informative measured value. The synthesizers consist of a ring counter CNTR according to the Johnson code, a decoder that extracts pulses from the counter signals to form quasi-sinusoid steps, and a digital-to-analog converter DAC that forms these steps from a constant reference voltage U_{ref}. This voltage can be adjusted with a DAC_B digital-to-analogue converter to change the amplitude of the quasi-sine wave. Synthesizers are clocked by fc pulses from the MC microcontroller. To provide an adjustable phase shift between U_a and U_p, the circuit has a PHASE SHIFT block, which forms sequences Ic1 and Ic2 from fc. The delay between them is determined by the code Δφ. Pulses Is1 and Is2 synchronize the counters with each other. The output current signal of the bridge is converted to voltage in the I/U block. Synchronous detector SD extracts the in-phase or quadrature U_a component from it using one of the quadrature reference voltages U_{QF} or U_{IF}, which are obtained from the

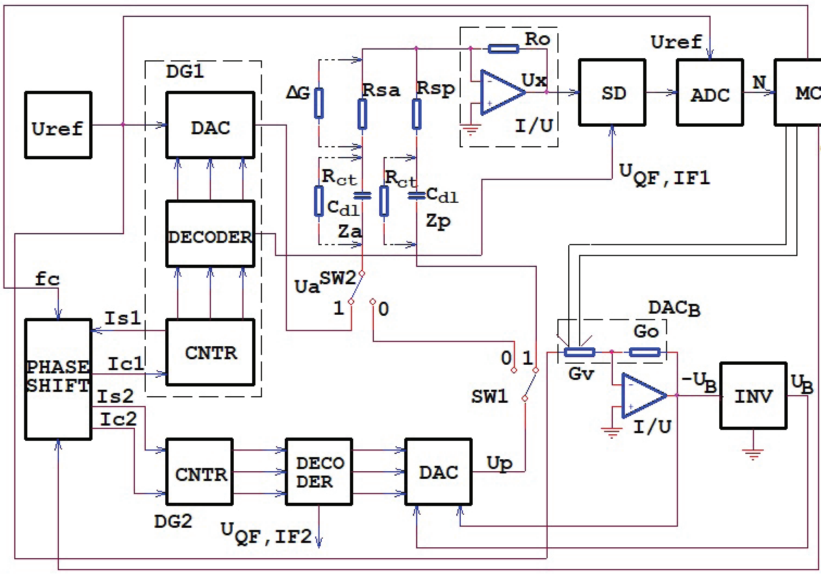


Figure 1. Structural diagram of the bridge circuit of a conductometric analyzer with digital balancing in polar coordinates.

CNTR. These signals are converted into codes by a highly sensitive multi-bit integrating ADC and transferred to the microcontroller for primary processing. The data obtained as a result of it are transmitted through a standard interface to a personal computer of the hardware-software complex for further processing, accumulation and presentation as analysis results in the required form.

For experimental studies of the balancing process and metrological characteristics of the conductometric analyzer, the electrical equivalent of a differential conductometric sensor with adjustable parameters of series-connected R and C components was used. The values of these parameters lie in the range typical for planar intercomb conductometric transducers widely used in biosensors with gold electrodes with a width and gaps between them of 20 μm with a total grating size of 1.5 × 1.5 mm. [15]. The equivalent's circuit is shown in fig. 2. The RC-parameters of the transducers can vary by ±20% relative to the average values of 1 kΩ and 5.6 nF, which corresponds to the allowable values for such sensors. In this equivalent, it is possible to connect an additional component Rn in parallel with the capacitance, simulating the charge transfer resistance Rct.

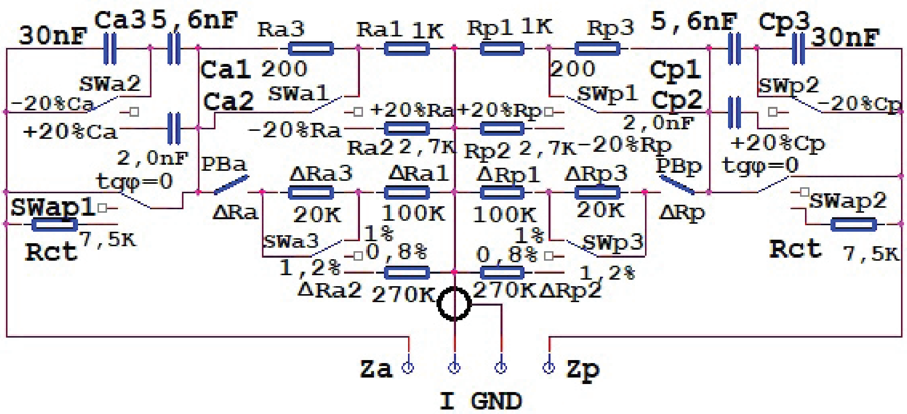


Figure 2. Equivalent circuit for experimental studies of the balancing process and metrological characteristics.

Analytical models of measurement processes with a quasi-equilibrium bridge circuit.

The vector diagram in fig. 3 explains the changes in currents and voltages in the bridge circuit during its preliminary balancing and during measurements. It is built on the complex plane with coordinate axes Re and Im. The generator voltages U_a and U_p, which are antiphase in the initial state, are located on the Re axis. The voltages on the active (R) and reactive (C) components of the impedances of the active and passive conductometric transducers in the initial state of the bridge are designated U_R and U_C, respectively. They form vector triangles with U_a and U_p. For ease of comparison, the vectors of the active transducer are shown with a "-" sign. The voltages U_{Ra} and U_{Rp} coincide in phase with the currents of the transducers I_a and I_p and differ in phase by the difference in their phase angles Δφ. At the output of the bridge, the summation of the current vectors $-I_a$ and I_p takes place, and a signal of disequilibrium of the bridge $\Delta \acute{I}_{ap}$ is formed. At subsequent stages of balancing the bridge, these vectors take positions indicated by the numbers 1, 2, 3. At stage 1, the U_p vector turns to the U_{p1} position, and at stage 2, its amplitude decreases to the U_{p2} position. The current vectors of the active ($-I_a$) and passive (I_{p2}) converters coincide in this case, i.e. the bridge is balanced.

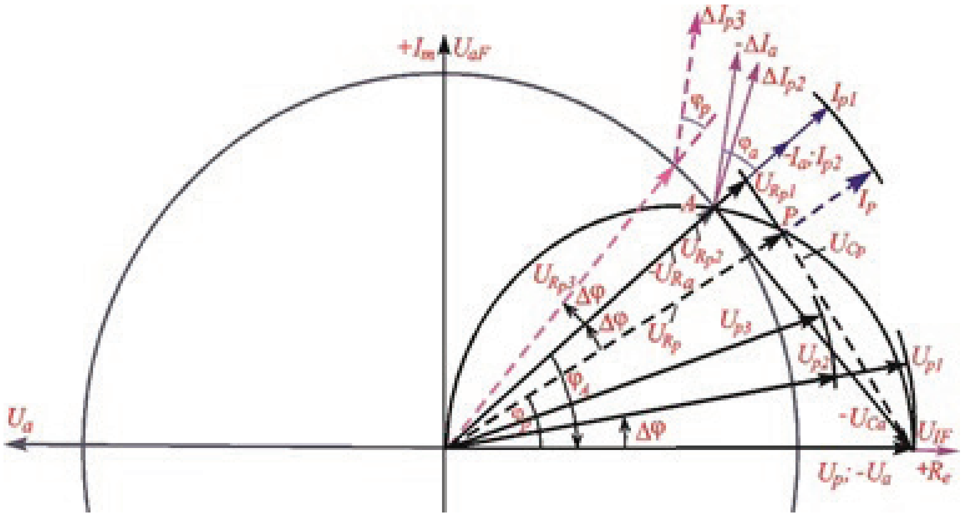


Figure 3. Vector diagram of currents and voltages in the bridge circuit during its preliminary balancing and under measurements.

In the case of equality of R_{SA} and R_{SP} at different C_{SA} and C_{SP}, the result of this balancing stage is the alignment of the ends of the voltage vectors U_{Ra} and U_{Rp} along the arc between points P and A. In this state of the bridge, the current increment vectors are $-\Delta I_a$ and ΔI_{p2} with the same background effect on the sensors have the same amplitude, but different phase angles relative to the current vectors (they are equal to the phase angles φ_A and φ_P, respectively). To eliminate this difference, at the next tuning stage (stage 3), the bridge is transferred to a quasi-equilibrium state by an additional rotation by an angle Δφ of the voltage vector on the passive sensor from the position U_{p2} to U_{p3}. In this state of the bridge, these background actions lead to current increments (now $-\Delta I_a$ and ΔI_{p3}) that become collinear (with opposite phases) and equal in absolute value, and therefore cancel each other out in the bridge output signal.

The initial data for this bridge presetting method is obtained by measuring the quadrature parameters (along the Re, Im axes) of the current vectors of the working and reference transducers, and then calculating the values of their phase angles and active conductivity G_{SA}, G_{SP}.

The complex currents through the sensors in the initial state of the bridge are determined by the following expressions [27]:

$$\dot{I}_{a1} = \frac{U_a}{\dfrac{1}{j\omega C_{SA}} + \dfrac{1}{G_{SA}}} = U_a G_{SA} \frac{\exp[arctg(tg\varphi_A)]}{\sqrt{1+tg^2\varphi_A}}; \; \dot{I}_{p1} = \frac{\left|\dot{U}_p\right| \exp(\varphi_P)}{\dfrac{1}{j\omega C_{SP}} + \dfrac{1}{G_{SP}}} \left|\dot{U}_p\right| G_{SP} \frac{\exp(\varphi_P)\cdot \exp[arctg(tg\varphi_P)]}{\sqrt{1+tg^2\varphi_P}};$$

where: $tg\varphi_A = G_{SA}/\omega C_{SA}$; $tg\varphi_P = G_{SP}/\omega C_{SP}$ are phase angle tangents φ_A and φ_P of sensor's impedances.

Balancing the measuring circuit is to achieve equality of the modules and phase shifts of the currents I_{a1} and I_{p1}. Based on this condition, the relative value of the modulus of the regulated voltage of the dependent generator to the voltage of the independent generator ND1 (this is the DAC_B control code) and the phase shift between these voltages $\Delta\varphi_{P1}$ are found, corresponding to the equilibrium state of the measuring circuit:

$$\Delta\varphi_{p1} = \varphi_A - \varphi_P \; ; \; ND_1 = \frac{G_{SA}}{G_{SP}} \cdot \frac{\sqrt{1+tg^2\varphi_P}}{\sqrt{1+tg^2\varphi_A}}. \quad (1)$$

The quasi-equilibrium of the bridge is obtained by addition rotation of the vector I_p by the angle $\Delta\varphi$.

In [27], a justification is given for achieving the necessary quasi-equilibrium also in the case of inequality between R_{SA} and R_{SP}. To do this, after reaching the equality of the current's modules of the converters, the current's module of the reference converter is corrected, depending on the ratio of active resistances of the differential pair of converters. This correction brings the bridge into a state of quasi-equilibrium (in terms of current) and equilibrium in terms of voltages across their active resistances. The latter ensures the equality of current increments in converters with a difference in R_{SA} and R_{SP} when the background electrical conductivity changes. The analysis of the mathematical model of the measuring process also showed that at the third stage it is necessary to perform an additional correction of the voltage modulus U_p by a coefficient depending on the ratio of the phase angles of the passive and active converters:

$$K = \frac{\sqrt{1+tg^2\varphi_P}}{\sqrt{1+tg^2\varphi_A}}.$$

Thus, the correction values of the voltage vector on the reference sensor in phase and modulus to achieve the necessary quasi-equilibrium have the following values:

on phase $\Delta\varphi_{p2} = 2(\varphi_A - \varphi_P)$;

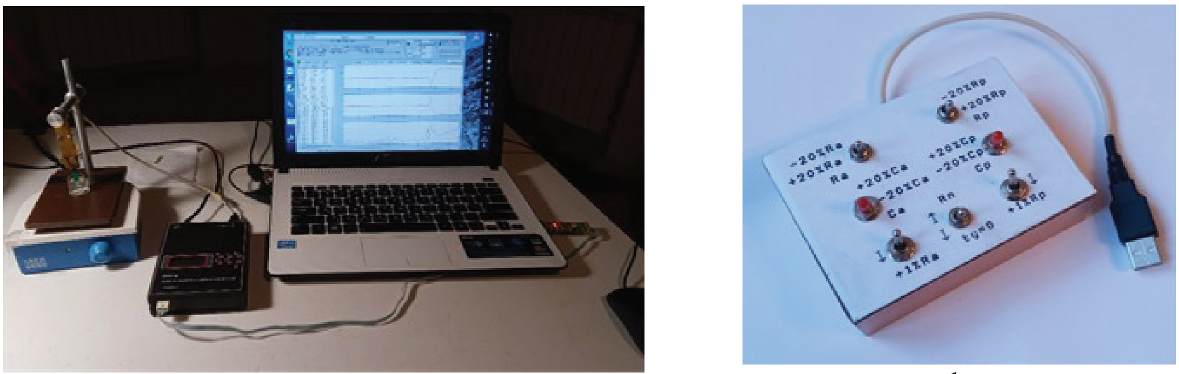
on modulo

$$ND_2 = \frac{\Delta G_{SA}}{\Delta G_{SP}} \cdot \frac{1+tg^2\varphi_P}{1+tg^2\varphi_A} = \frac{G_{SA}}{G_{SP}} \cdot \frac{1+tg^2\varphi_P}{1+tg^2\varphi_A}. \quad (2)$$

Experimental studies of suppression of background influences.

Due to the described corrections of the state of the bridge circuit, the increments of the current amplitudes in the converters with the same changes in the background electrical conductivity on them coincide with a higher accuracy. This ensures their more complete mutual compensation at the output of the bridge circuit. Therefore, the weakening of the influence of changes in the background electrical conductivity is much higher. In [27], the results of computer simulation and research on an experimental sample of a differential conductometer are presented for several typical values of the parameters of planar interdigitated conductometric transducers with gold electrodes, which are used in conductometric biosensors. The increase in the suppression of changes in the background electrical conductivity using the described device and measurement method ranged from 10 to 60 times if to compare with the devices of the previous generation [17, 19, 20]. On fig. 4a and 4b show photographs of the hardware-software complex (HSC) of the conductometric analyzer and the electrical equivalent of the differential conductometric cell.

Table 1 shows the results of testing of the suppression factor of additive error due to the influence of changes in the background conductivity of the buffer solution in the cell using a real analyzer. Three differential sensors were used: 1 – with an average difference between the values of the parameters R and parameters C of the transducers (the differences is 5% and 10%) under low values of the phase angles; 2 – with a small differences in the values of the parameters (less than 5%) and with an increased (more than 0.5) values of the phase angle tangent; 3 – with an increased differences in the values of the parameters R and C (7% and 46%) at low phase angles. Studies were carried out by adding 0.1 ml of distilled water to a phosphate buffer solution (volume 2 ml, concentration 5 mM/l, pH 7.0). The suppression coefficient was calculated as the ratio of the response of the working transducer to such an addition to the change in the output signal of the bridge circuit during the in-phase effect of this addition on both transducers. An analysis of the test results shows a large increasing in the suppression of the influence of background changes compared to the devices of the previous generation [17, 19, 20] under moderate differences in the R and C parameters values of the transducers both at normal and at increased values of their phase angles. With a significant difference in phase angles (which is not recommended for the operation of sensors), the suppression coefficient drops significantly. However, it should be pointed out that in devices of the previous generation the suppression is only a few units in this case.



a b

Figure 4. Photo of the hardware-software complex for the conductometric analyzer and the electrical equivalent of the differential conductometric cell.

Due to a significant reduction in the additive error from poorly controlled factors, the real measurement range of differential conductometric analyzers expands towards small values of informative quantities. However, the most important thing is to increase the metrological reliability of the results obtained.

Usually, such parameters as the measurement range, sensitivity, resolution, linearity and stability of the conversion function are used as metrological characteristics of measuring instruments. These parameters allow you to estimate the expected basic measurement error – relative or absolute.

The methods for their determination and normalization are well known, as are the methods for estimating and accounting for random (noise) interference. However, for complex measurements, which include those considered in this article, the errors associated

Table 1.

Sensor number	R_{SA}, Ohm	$tg\varphi_A$	C_{SA}, μF	R_{SP}, Ohm	$tg\varphi_A$	C_{SP}, μF	Work transduc. influence response	Common mode influence response	Common mode influence suppression
1 (5–2)	623	0,321	12,7	596	0,379	11,3	8490	30	283
2 (7–2)	523	0,763	6,93	541	0,683	6,9	6960	50	139
3 (6–2)	612	0,60	6,88	654	0,386	10,0	6485	380	17

with a complex of deterministic, but unstable factors of measurement conditions are very significant. Their cumulative impact on the results obtained can be very significant, and it is very difficult to determine and correct it. Therefore, we have to talk about the metrological reliability of measurements by various means in various conditions. In our article, we mean by this the ability to obtain a reliable result with significant differences in the values of the RC-parameters of conductometric transducers and the presence of changes in the electrical conductivity of the buffer solution during the measurement process.

The considered technical solutions for preliminary balancing of the conductometric analyzer's bridge circuit were based on the representation of the equivalent circuit of the differential sensor in the form of two pairs of RC-components connected in series. However, as mentioned above, such a model of the object of measurement is not always sufficiently adequate to real practice. First of all, this concerns cases of significant nonidentity of the RC-parameters of transducers when working with electrically conductive analytes. The latter leads to significant changes in the background electrical conductivity when they are introduced into the measurement environment. In such cases, for a sufficiently accurate setting of the quasi-equilibrium state of the bridge, it is necessary to take into account the charge transfer resistances R_{ct} in conductometric transducers buffer solution during measurements.

Balancing the bridge circuit taking into account the effect of charge transfer resistance.

In [28], a method for solving this problem is presented, based on a simple method for estimating the values of R_{ct}, which is described in detail in [29]. It consists in measuring the RC-parameters of converters at two frequencies in the region where their equivalent circuit is close to serial (from 30 to 100 kHz) and recalculating the obtained differences in R_{SA} and R_{SP} values at these frequencies into active resistances connected in parallel C_{SA} and C_{SP}.

Table 2 shows the data for determining R_{ct} for one of the studied differential conductometric sensors (No. 3 in Table 1), which has significant differences in the RC-parameters of the transducers, in the range of buffer solution concentrations used. Simulation data of changes

Table 2.

Transducer	Solution concentration	62,5 kHz			100 kHz			R_{ct}, Ohm
		R_S, Ohm	Cs, nF	tgφ	R_S, Ohm	Cs, nF	tgφ	
Working (Za)	3 mM pH7PB	1810	4,257	0,33	1741	3,47	0,263	7703
	8 mM	770	5,63	0,587	718	5,06	0,438	4863
	10 mM	529	5,97	0,805	483,8	5,44	0,606	4785
Reference (Zp)	3 mM pH7PB	2017	5,81	0,217	1967	4,47	0,18	6406
	8 mM	814	8,2	0,38	780	7,2	0,28	3631
	10 mM	544	8,96	0,52	513	8,12	0,382	3131

in R_S values depending on R_{ct} values under typical values of RC-parameters of applied sensors show that these changes can be from 3% to 7% of the R_S value. However, they can increase by several times with increasing transducer tgφ values, which often occurs in practice and is one of the main factors for reducing the metrological reliability of biosensor measurements. Note that the above data were obtained in the absence of electrochemical reactions that change R_{ct}.

The article [28] gives an analytical justification for refining the value of the correction of the ratio of the voltage amplitudes of the bridge circuit generators, which is necessary for its equilibrium, depending on the R_{ct} values of the converters.

Taking into account such a correction, the ratio of the voltage of the dependent generator to the voltage of the independent bridge at equilibrium has the form:

$$N_{D1}=\frac{|U_P|}{|U_A|}=\frac{G_A}{G_P}\cdot\frac{\sqrt{1+(\omega\cdot R_{Act}\cdot C_{SA})^2}}{\sqrt{1+(\omega\cdot R_{Pct}\cdot C_{SP})^2}}\cdot\frac{\sqrt{(1+G_{SP}\cdot R_{Pct})^2+(\omega\cdot R_{Pct}\cdot C_{SP})^2}}{\sqrt{(1+G_{SA}\cdot R_{Act})^2+(\omega\cdot R_{Act}\cdot C_{SA})^2}}, \quad (3)$$

where G_A, G_P are the electrical conductivity of the solutions between the electrodes of the transducers.

It is shown that in order to achieve the necessary state of quasi-equilibrium, the ratio of generator voltages should have the value:

$$N_{D2}=N_{D1}^2\frac{G_P}{G_A}. \quad (4)$$

To find the correction factor according to (4), the approximate values of R_{Act} of the active (working) and R_{Pct} of the reference (passive) transducers are determined. The results of measurements of the next values are used for that: of the active components Re(Z_{A1}), Re(Z_{R1}) and of the reactive components Im(Z_{A1}), Im(Z_{R1}) of their impedances at the operating frequency ω and the values of components Re(Z_{A2}), Re(Z_{R2}), Im(Z_{A2}), Im(Z_{R2}) at the frequency ω1. The values of ω1 is greater than the frequency ω (at least 1.5 times).

$$C_{SA}\approx\frac{1}{\mathrm{Im}(\dot{Z}_{A2})\cdot\omega_1};\ R_{Act}\approx\frac{1}{[\mathrm{Re}(\dot{Z}_{A1})-\mathrm{Re}(\dot{Z}_{A2})]\cdot C_{SA}^2\cdot\omega_1^2};$$

$$C_{SP}\approx\frac{1}{\mathrm{Im}(\dot{Z}_{R2})\cdot\omega_1};\ R_{Pct}\approx\frac{1}{[\mathrm{Re}(\dot{Z}_{R1})-\mathrm{Re}(\dot{Z}_{R2})]\cdot C_{SP}^2\cdot\omega_1^2}.$$

Next, we find and substitute in (4) the values of the conductivity of the solution between the electrodes:

$$G_A\approx\frac{1}{\mathrm{Re}(\dot{Z}_{A2})-\dfrac{R_{Act}}{1+(\omega_1\cdot R_{Act}\cdot C_{SA})^2}};$$

$$G_R\approx\frac{1}{\mathrm{Re}(\dot{Z}_{R2})-\dfrac{R_{Pct}}{1+(\omega_1\cdot R_{Pct}\cdot C_{SR})^2}}.$$

Detailed substantiation of this bridge circuit balancing method is given in [28]. In this work, a comparative computer simulation of the error suppression from a change in the background electrical conductivity of the buffer solution was also carried out for conductometric analyzers using the quasi-equilibrium balancing method described in [27] and the last of the considered methods.

Table 3 shows the simulation results for sensors with different parameters of the equivalent RC circuit, which were previously selected for experiments. The results of calculations of coefficients K of the amplitude correction and the obtained values of the coefficients of suppression of the influence of changes in the background electrical conductivity of the K_{supp} solution using the two methods described above are presented: using two-element and three-element equivalent circuits of the transducers. The suppression coefficients were calculated as the ratio of the change in the current modulus in the bridge branch with the working transducer to the change in the informative current at the bridge output with a change in the background electrical conductivity in the differential sensor transducers. The simulation results show that for close values of the phase angles of the transducers (1–4 lines), taking into account the values of R_{ct} (if they differ little) has practically no effect on the coefficient of suppression of background influences. However, with a larger difference in phase angles (rows 5 and 6), considering them makes it possible to increase it approximately in proportion to the ratio of tgφ of the converters. This is consistent with the electrical properties of their equivalent circuit. We also note that the data in line 5 correspond to the data of sensor No. 3 in Table 1. 1. Thus, a significant decrease in the suppression of background influences when using this sensor (Table 1) is also due to the lack of accounting for Rct.

As noted above, the results presented here assume that there are no electrochemical processes during measurements that significantly change R_{ct}, but in practice, this is quite possible. Therefore, we additionally carried out a simulation of the suppression of background influences with differences in R_{ct} of the converters of the differential pair. The data obtained in this case are shown in Table 4. For comparison, this table also shows data for sensor No. 3 in Table 1 with real values of R_{ct}.

As can be seen, in this case, considering R_{ct} can give a very large gain in suppressing the

Table 3.

G_A, mS	R_{Act}, Ohm	C_A, nF	$tg\varphi_A$	G_P, mS	R_{Pct}, Ohm	C_P, nF	$tg\varphi_P$	Method 1		Method 2	
								K	K_{supp}	K	K_{supp}
1,55	5529	6,69	0,5645	1,55	5716	6,68	0,5670	1,001	255	1,0	262,5
1,68	4601	6,61	0,6101	1,686	4921	6,4	0,6325	1,01	125,6	1,01	125,6
1,633	4791	6,67	0,5902	1,541	5415	6,22	0,5988	1,004	84,5	1,002	85,4
1,815	4359	8,7	0,5107	1,634	4572	7,9	0,5054	0,998	117,1	0,999	118,8
1,299	4863	5,63	0,5524	1,229	3631	8,2	0,3669	0,933	38,1	0,913	71,5
1,393	5386	4,63	0,7036	1,474	4661	5,4	0,6435	0,973	60,0	0,966	67,3

Table 4.

G_A, mS	R_{Act}, Ohm	C_A, nF	tgφA	G_P, mS	R_{Pct}, Ohm	C_P, nF	tgφP	Method 1		Method 2	
								K	K_{supp}	K	K_{supp}
1,613	3000	3,82	0,8346	1,333	4000	4,0	0,7315	0,9512	11,6	0,8784	165,4
1,613	4000	3,82	0,8908	1,6	10000	4,8	0,8101	0,9609	8,0	0,8565	189,7
1	9000	5,0	0,4935	1,01	4000	5,1	0,4679	0,99	31,8	1,022	151,2
1	3000	4,9	0,464	0,833	10000	5,0	0,414	0,9819	15,1	0,9232	99,1
1	4000	6,2	0,3901	1,01	9000	7,3	0,3471	0,9861	35,4	0,9598	354,6
1,754	3817	6,36	0,6476	1,597	2665	9,16	0,4201	0,9104	32,8	0,8877	77,4

effect of changes in the background electrical conductivity.

Implementation of the hardware-software conductometric complex.

A photograph of the HSC is shown in fig. 4. It is based on an MCh module, which is connected to a personal computer (PC) using a standard USB interface, and to a sensor unit with a conductometric cell using a signal cable with a special holder. This block is mounted on a magnetic mixer for mixing the buffer solution in the cuvette during measurements. To test and calibrate the measuring channel, as well as to study its metrological characteristics, the complex is supplied with an electrical equivalent of a conductometric cell (for practical operation, it is performed according to a simplified scheme).

The hardware structure of the IR module is shown in fig. 1. Its implementation was based on the unified impedance measuring base module MXP-6, developed at the Institute of Electrodynamics of the National Academy of Sciences of Ukraine for precision measurements in a wide frequency range, which is described in detail in [25]. It should be noted here that in order to achieve the depth of suppression of the influence of background changes, which can be provided by the methods presented above, it is necessary to balance the bridge circuit with errors of 0.01% at frequencies up to 100 kHz.

The software component of the measuring complex consists of two parts: the lower-level software package for the microcontroller of the IR module and the upper-level software package that is installed in the PC. Their structures and interaction are organized in such a way that simple functions of a conductometric analyzer without of registering arrays of results, their complex processing and graphical representation, could be performed by the microcontroller of the measuring channel without connecting a PC, including under mobile using.

Low-level software package.

The microcontroller controls the process of adjusting the bridge circuit into a state of quasi-equilibrium, as well as measuring changes in the electrical conductivity of the solution in the working transducer. Important components of its software are shown in fig. 5. In fig. 5a presents a block diagram of the microcontroller's operation algorithm. The operation of the device consists of six stages.

Stages 1, 2: measurement of the reference and working converters parameters (blocks 1–8). The microcontroller sets the switches: SW1 to the "1" position, and SW2 to the "0" position (block 1). The voltage of the regulated generator DG2, which is equal to the voltage of the independent generator DG1, is connected to the reference transducer, there is no voltage on the working transducer. In-phase U_{IF} and quadrature U_{QF} reference voltages are alternately connected to the reference input of the synchronous detector SD. The in-phase and quadrature components of the current through the reference transducer are measured (unit 2) for further determination of its impedance parameters. The variation of the generator voltage is also performed by changing the N_{DAC} code by one-step and the corresponding increment of the in-phase component of the InfToDac current is determined to match the scales of the DAC_B and ADC, which is necessary when balancing the bridge circuit. The switches are set: SW1 to the "0" position, SW2 to the "1" position (block 5). The DG2 voltage is connected to the working transducer; there is no voltage on the reference one. In a similar way, the components of the current through the working transducer (unit 6) are measured to further determine its impedance parameters. Moduli and tangents of phase angles of currents through transducers are calculated and memorized. The difference in the tangents of the phase angles of the transducers is calculated and displayed on the indicator (block 8). That is used to diagnose the quality of the sensor.

Stage 3: assembly of the bridge measuring circuit (blocks 9, 10). Switches SW1 and SW2 are set to the "1" position. DG1 is connected to the working transducer and DG2 to the reference one. In the initial state, the voltage amplitudes of the generators are equal, and the phases are opposite (the Δφ code corresponds to 180º). As a result, a bridge measuring circuit is formed with the comparison of currents through the transducers of the sensor. Next the operations of block 10 is performing. The microcontroller sets the parameters of the regulated generator, calculated for balancing the bridge: the initial N_{DAC} code is multiplied by the ratio of the modules of the currents through the transducers; the value corresponding to the difference in the phase angles of the currents of the transducers is added to the initial code Δφ.

Stage 4: checking the balance of the bridge according to the quadrature component of the unbalance current and, if necessary, final balancing according to this component (unit 11). This is done by adjusting the phase delay of the voltage of the regulated generator relative to the voltage of the generator DG1 by the PHASE SHIFT block (Fig. 1). The block diagram of the "CompenPhase" subprogram in the general algorithm of the microcontroller is presented in Fig.5b.

Stage 5: the balance of the bridge according to the in-phase component of the unbalance current is checking and, if necessary, final balancing according to this component is performed (block 12, Fig. 5a). That perform by changing the N_{DAC} code, which sets the voltage amplitude value of the regulated generator. The block diagram of the "CompenInf" routine is shoun in fig. 5c.

Stage 6: the state of quasi-equilibrium of the bridge measuring circuit is establishing and the informative changes in electrical conductivity of the solution of the working measuring transducer is measuring (block 13, Fig. 5a).

After reaching equilibrium of the bridge, it is transferred to a specific state of quasi-equilibrium according to the method described in [27] for mutual compensation of the in-phase effect of changes in the background electrical

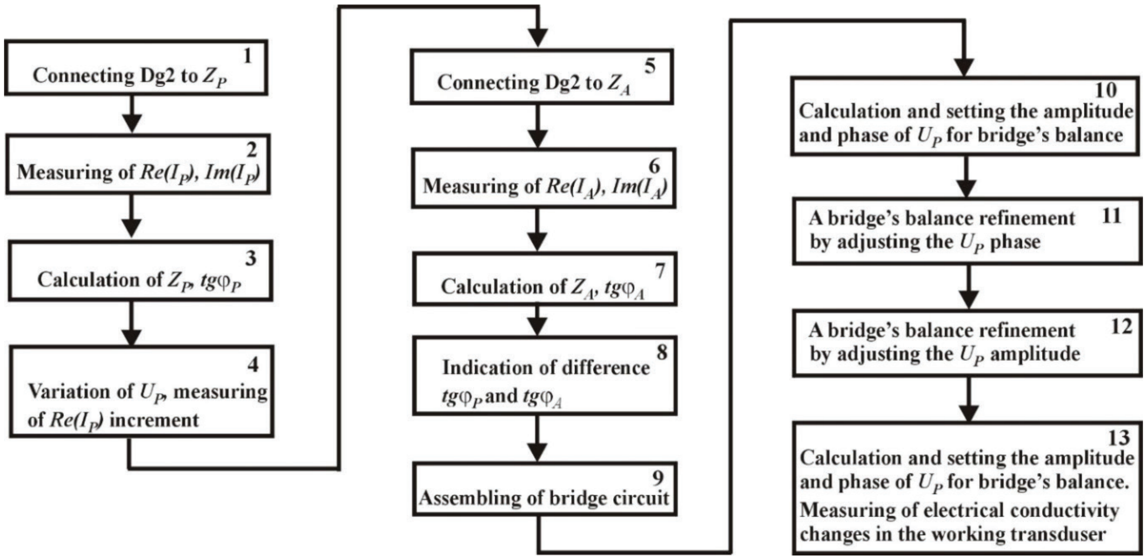


Figure 5a

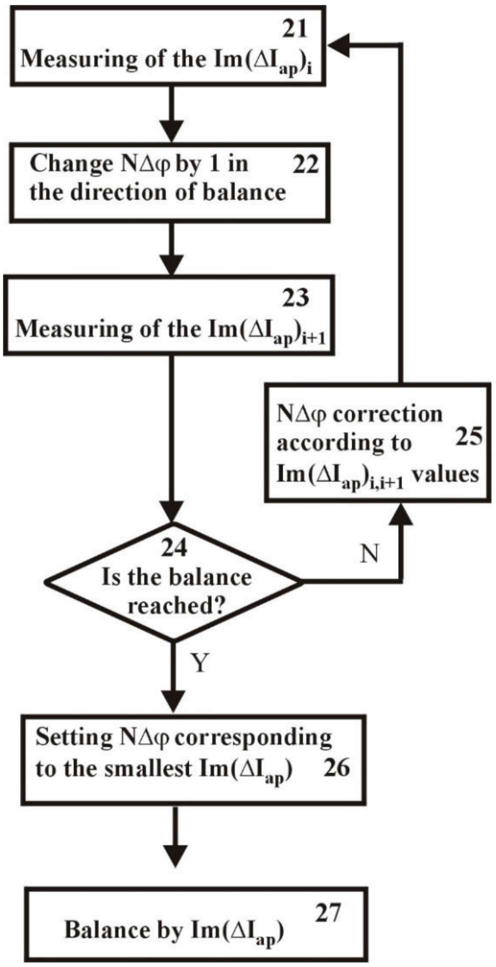


Figure 5b

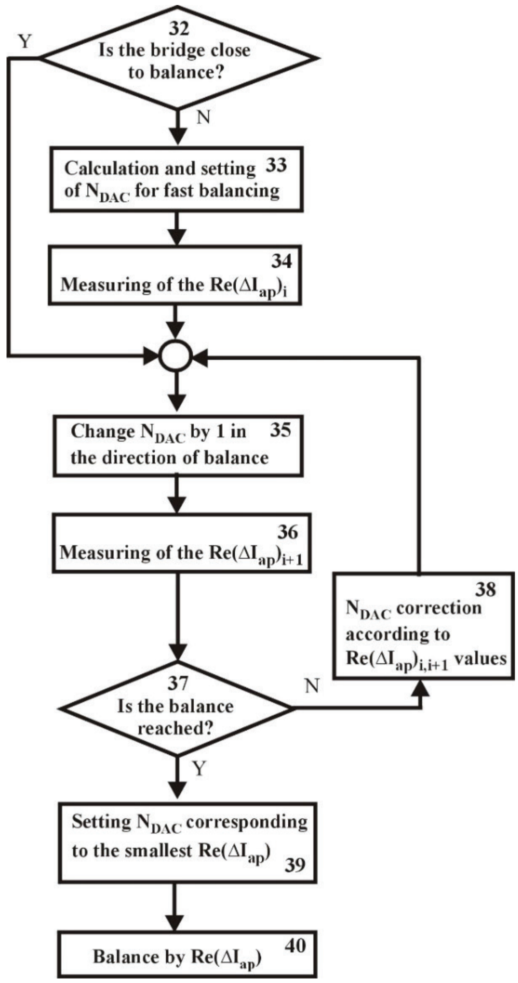


Figure 5c

Figure 5. Block diagram of the microcontroller operation algorithm.

conductivity of the buffer solution on the working and reference transducers. For this, two operations are performed: adding to the code Δφ the value, corresponding to the difference in the phase angles of the currents through the working and reference transducers and multiplication of the N_{DAC} code by a correction factor that depends on the tangents of the phase angles of the sensor transducers.

After the state of quasi-equilibrium is reached, the components of the imbalance current are periodically measured, which carry information about changes in the informative parameter of the differential sensor – the electrical conductivity of the solution on the surface of the working transducer.

Operations of blocks 11 and 12 are performed by the classical method of balansing the alternating current bridge using quadrature detectors of the unbalance signal. The peculiarity is that the phase and amplitude of the voltage of the reference generator DG2 are regulated, and not by the amplitudes of its quadrature components. Phase adjustment is carried out by steps in the direction of reducing the quadrature component of the bridge imbalance signal, and amplitude adjustment is carried out by DAC code steps in the direction of reducing its in-phase component. Equilibrium is fixed when the signs of those components changes in adjacent steps. A state with a smaller amplitude of the controlled component is considered to be in equilibrium. Balancing of the bridge according to the in-phase component by adjusting the amplitude of DG2 is carried out with much greater precision and discreteness than its phase; because active conductivity is an informative parameter in conductometry. To reduce the time to perform a large number of DAC_B steps, block 12 may perform an extrapolation of the equilibrium value of the N_{DAC} code using the resulting InfToDac value (blocks 32–34).

Top-level software package.

The top-level program (control program "MXP_Conductometer") is implemented in the form of an executable file with modules of dynamic libraries, for work in the Windows OS environment on a PC. The main tasks of the upper-level program are to provide an interface for user interaction with the measuring module, to ensure interaction with the lower-level program, to ensure playback, analysis and saving of data obtained during measurement.

Communication of the upper-level program with the microcontroller program is implemented according to the Modbus protocol through a serial communication line using the RS-232 data exchange interface (connection through a virtual port). The main blocks of the top-level control program and their interaction are shown in the diagram of fig. 6. The program blocks (with the exception of the block for providing communication with the hardware

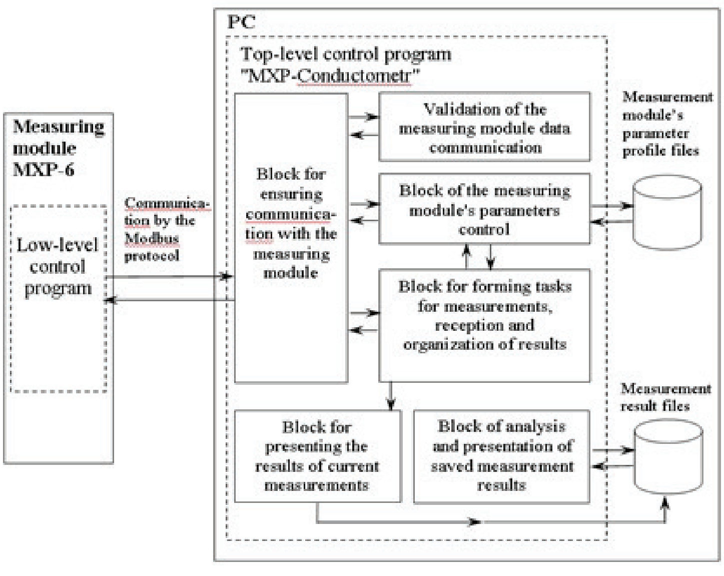


Figure 6. Block diagram of the top-level control program for the conductometric analyzer.

part) have their own graphical interfaces for management and interaction with the user, which are combined into a common multi-window graphical interface of the HSC control program. The main window of the control program is shown in Fig. 7.

The main management functions provided by the program:

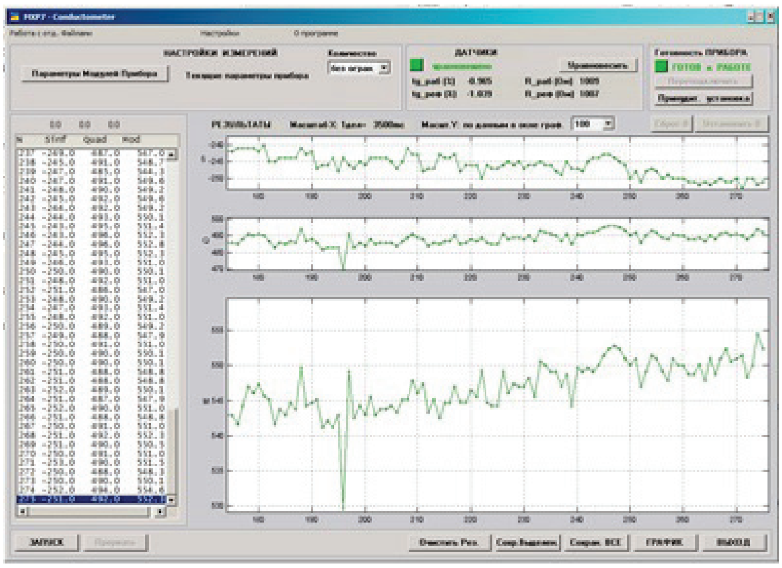


Figure 7. The main window of the control program «MXP_Conductometer».

– control of the mode parameters of the units of the measuring module of the complex;

– management of measurements;

– accumulation, presentation, analysis, storage and reproduction of the measurement data.

Management of the complex'es hardware units.

The program allows you to set the mode parameters of main blocks of the measurement channel blocks, as well as display the set parameters and save parameter profiles in separate files for further use. A set of parameters at which the measurement will be performed is the instrument's parameter profile), Parameters to be set:

– clock frequency of the ADC;

– clock frequency of the test signal generator;

– type of reference signal of the synchronous detector (in-phase or quadrature);

– voltage phase delay of generator DG2 (code Δφ phase shift of voltages U_a and U_p);

– DAC control codes of the measuring module.

Profiles of parameters can be saved in separate files, reloaded and installed in the measuring module, also parameters from the profile are written to files for storing the results obtained when they are used.

Organization of measurements.

After the complex is turned on and ready for measurements, it is necessary to balance the bridge circuit of the measuring module, for which the user submits the appropriate command from the main window of the program. A balancing perform by the device controller. After balancing, the complex is completely ready for measurements and the measuring module outputs the values of the current results of the conversion of the output signal of the bridge circuit. Their parameters (two quadrature components and the module) are displayed digitally and graphically on the main window of the program. These data change when an informative effect is applied to the differential sensor. The transfer of results perform in sets (data packets). A single packet can contain up to 62 values according to the limitations of the Modbus transmission protocol. The number of transmitted results in a packet determine by the program depending on: the ADC conversion frequency, the type of measurement, the transmission time and the number of results in the clipboard, as well as the time of processing and updating information on the screen. The logical scheme of implementation in the measurement mode program is presented in Fig. 8.

The presented measurement results together with the parameters of the device modules and parameters of the operating mode can be saved in files (ANSI coding). The saved measurement results can be viewed in the form of tables and graphs after the measurements are finished with the built-in viewer-analyzer (analysis and presentation of measurement results block). After balancing the bridge circuit of the measuring module, the main window displays the obtained values of the DAC_B and $\Delta\varphi$ codes, which correspond to the established state of quasi-equilibrium (readiness for measurements). Also, the conductometric transducers' parameters are calculated: resistances and tangents of the loss angle, which is necessary for evaluating the quality of the characteristics sensor and metrological reliability of measurement results.

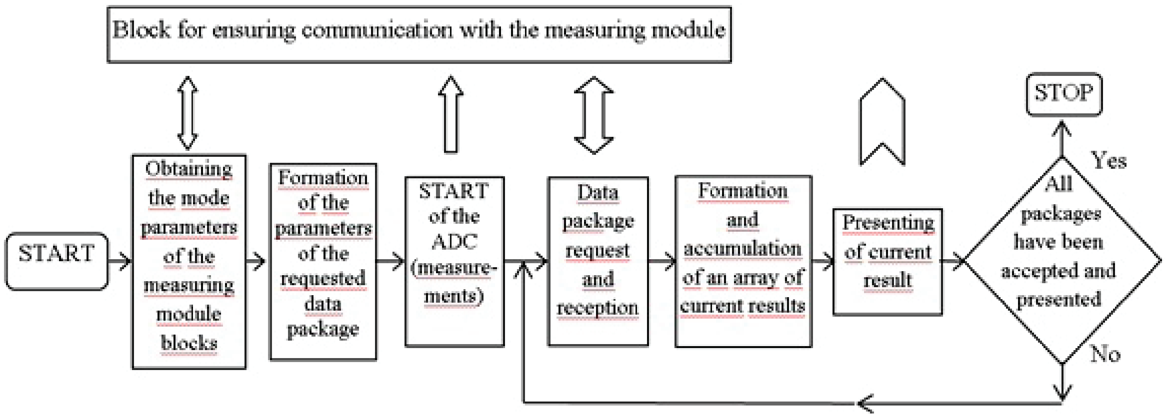


Figure 8. The basic operations sequence when working in the measurement mode in the top-level program.

Conclusion

Differential measurements using a pair of planar conductometric transducers (working and reference) included in a balanced bridge electrical circuit are a promising way to create highly sensitive analytical systems and, in particular, the development of biosensors. Their wide application for solving practical problems is limited by a significant increase in the additive error from changes in the background electrical conductivity during measurements, if the electrical parameters of the conductometric transducers differ significantly, which occurs during their operation. The solution to this problem can be based on preliminary balancing of the bridge into a state of quasi-equilibrium, at which the minimum value is reached not of its residual output signal, but of its response to changes in the background electrical conductivity. This state is set by additional rotation of the signal phase in the reference transducer by the difference in the phase angles of the transducers. Theoretical and experimental studies have established that for a sufficiently deep suppression of the influence of changes in the background electrical conductivity, in addition, it is necessary to correct the amplitude of this signal, taking into account the difference of the actives and the difference of the reactives components of the two-element equivalent circuits of the impedance of the converters. It is shown that the degree of suppression of the effect of background electrical conductivity also worsens in the presence of a difference in charge transfer resistances in the near-electrode region. The developed method for determining and considering them when correcting the amplitude of the reference signal makes it possible to maintain a high degree of suppression of the effect of background electrical conductivity in this case as well. As a result of the development, a hardware-software complex was created for a conductometric biosensor analyzer with high metrological reliability of measurement results under the parameters of a differential conductometric sensor transducers typical for practical conditions, what was confirmed experimentally by using conductometric enzyme biosensor [30].

The work was carried out with the support of the National Academy of Sciences of Ukraine within the framework of the State Budget Program "Support for the Development of Priority Areas of Scientific Research" (KPKVK: 6541030), the target program of scientific research of the National Academy of Sciences of Ukraine "Smart" sensor devices of the new generation based on modern materials and technologies". The project "Development and optimization of the electronic module of the conductometric biosensor analyzer for the determination of arginine".

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Стаття надійшла до редакції 25.08.2023 р.
UDC621.317

DOI: https://doi.org/10.18524/1815–7459.2023.3.288160

HARDWARE AND SOFTWARE COMPLEX FOR CONDUCTOMETRIC MEASUREMENTS WITH HIGH METROLOGICAL RELIABILITY

V. G. Melnyk[1], S. V. Dzyadevych[2], P. I. Borshchov[1], V. K. Beliaev [1], O. D. Vasylenko[1], Nicole Jaffrezic-Renault[3]

[1] Institute of Electrodynamics National Academy of Sciences of Ukraine, Peremohy ave., 56, Kyiv, 03057, Ukraine. E-mail: melnik@ied.org.ua
[2] Institute of Molecular Biology and Genetics National Academy of Sciences of Ukraine, Zabolotnoho st., 150, Kyiv, 03680, Ukraine. E-mail: dzyad@yahoo.com
[3] Institut des Sciences Analytiques, Université Claude Bernard Lyon 1, 5 Rue de La Doua, F69100 Villeurbanne FRANCE

Summary

The article summarizes and supplements the results of the development of methods and tools for determining local changes in the electrical conductivity of electrolyte solutions, which can significantly reduce the influence of additive error sources under conditions of changes in the background electrical conductivity in the measurement environment. This is relevant for biosensor and other measuring systems based on a differential pair of conductometric transducers when their electrical parameters are not identical. The aim of the work is to provide a deep suppression of the influence of background changes under these conditions. The essence of the issue, the causes and mechanism of this type of error, as well as previously developed methods and means of reducing it are briefly considered. A diagram is shown and a description of the structure of a computer biosensor system with an intelligent module for a differential conductometric channel based on an alternating current bridge is given. The algorithm of a bridge balancing operations by adjusting the module and phase of the test voltage on the converters is described. A vector model of currents and voltages in the circuit during this process is considered, as well as mathematical expressions that explain bringing the bridge to a special quasi-equilibrium state, in which a change in the background electrical conductivity does not change its output informative signal under the above conditions. Additional operations are determined to balance the bridge to achieve such a state with significant differences in both near-electrode capacitances and active resistances, and inter-electrode resistances of solution in the impedances of a pair of conductometric transducers of a differential sensor. The interaction of an intelligent module with a personal computer is described, which performs a more complete processing, accumulation and presentation of research results. The results of experimental studies of the suppression of the influence of changes in the background electrical conductivity of a solution in a differential conductometric channel carried out on its computer model and on an experimental sample of a conductometric device with an electrical equivalent of a differential sensor, are presented. A comparison of the results obtained and the corresponding data for balancing bridge circuits by previously used methods is given.

Keywords: Conductometry, AC Bridge, balancing, differential sensor
УДК 621.317

DOI: https://doi.org/10.18524/1815–7459.2023.3.288160

АПАРАТНО-ПРОГРАМНИЙ КОМПЛЕКС ДЛЯ КОНДУКТОМЕТРИЧНИХ ВИМІРЮВАНЬ З ВИСОКОЮ МЕТРОЛОГІЧНОЮ НАДІЙНІСТЮ

В.Г. Мельник[1], С.В. Дзядевич[2], П.И. Борщев[1], В.К. Беляев[1], А.Д. Василенко[1], Ніколь Жаффрезік-Рено[3]

[1]Інститут електродинаміки Національної Академії наук України,
просп. Перемоги 56, Київ, 03057, Україна.
E-mail: melnik@ied.org.ua
[2] Інститут молекулярної біології і генетики Національної Академії наук України, вул. Заболотного 150, Київ, 03680, Україна.
E-mail: dzyad@yahoo.com;
[3] Інститут аналітичних наук, Університет Клода-Бернара Ліон 1,
вул. Дуа,5 Віллербан, Франція

Реферат

У статті узагальнено та доповнено результати розробок методів та засобів визначення локальних змін електропровідності розчинів електролітів, що дозволяють суттєво зменшити вплив джерел адитивної похибки в умовах зміни фонової електропровідності у середовищі вимірювань. Це є актуальним для біосенсорних та інших вимірювальних систем на основі диференціальної пари кондуктометричних перетворювачів, коли їх електричні параметри недостатньо ідентичні. Метою роботи є забезпечення глибокого придушення впливу фонових змін у цих умовах. Коротко розглянуто суть питання, причини та механізм даного виду похибки, а також розроблені раніше методи та засоби її зниження. Показано схему та дано опис структури комп'ютерної біосенсорної системи з інтелектуальним модулем диференціального кондуктометричного каналу на основі моста змінного струму. Описано алгоритм операцій балансування моста шляхом регулювання модуля та фази тестової напруги на перетворювачах. Розглянуто векторну модель струмів і напруг у вимірювальному колі при цьому процесі, а також математичні вирази, що пояснюють приведення моста в особливий квазирівноважний стан, при якому зміна фонової електропровідності не змінює його вихідний інформативний сигнал у зазначених вище умовах. Визначено додаткові операції з урівноваження мосту для досягнення такого стану при значних відмінностях як приелектродних ємностей та активних опорів, так і міжелектродних опорів розчину в імпедансах пари кондуктометричних перетворювачів диференціального датчика. Описано взаємодію інтелектуального модуля з персональним комп'ютером, який виконує більш повну обробку, накопичення та представлення результатів досліджень. Наведено результати експериментальних досліджень придушення впливу змін фонової електропровідності розчину в диференціальному кондуктометричному каналі, виконаних на його комп'ютерній моделі та експериментальному зразку кондуктометричного приладу з електричним еквівалентом диференціального датчика. Дано порівняння отриманих результатів і відповідних даних для балансування мостових схем методами, що раніше застосовували.

Ключові слова: Кондуктометрія, мост змінного струму, балансування, дифференциальный сенсор