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RESEARCHING OF IONS ACTIVITY MEASUREMENT UNCERTAINTY USING MEANS OF MEASUREMENT BASED ON ANALOG-DIGITAL CONVERTER

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The paper represents the method that has been proposed for evaluating the uncertainty by means of ions concentration measuring. The reference data and previous studies information enable the researches to identify the algorithm for estimating the uncertainty introduced by means of measurement.

To begin with, converter equation of ion-selective transmitter can be introduced as [1]:

$$\Delta U = U_0 + \frac{2,3RT}{n_A F} \lg\left(a_A + K_c (a_B)^{n_A/n_B}\right) \tag{1}$$

where ΔU – difference of potentials on the transmitter output; U_0 – standard constant potential of the sensor (reference electrode $U_0 = 201 \pm 3\,\text{mV}$); R – a gas constant; T – an absolute temperature of the investigated concentration; F – Faraday constant; n_A, n_B – ion charge A and B correspondingly; a_A – activity of A-ions to be determined; a_B – activity of B-ions interfering the determination of A-ions; K_c – selectivity coefficient (maximal value 10^{-1} in the determining of Fluoride ions activity).

Since measuring the ions activity in humus it is necessary to determine the content of such substances as a monovalent fluoride, nitrate nitrogen, ammonia nitrogen, potassium in the equation (1) ratio $\frac{2,3RT}{n_A F}$ is constant which shows the sensitivity of ion-selective transmitter relative to A-ions that equals S=59,16 mV and calibrating temperature $25\,°\text{C}$.

The changes in the ions activity result in the changes in the difference of potentials. For amplifying low differences of potentials in the means of measurement we will use measuring amplifier that has to satisfy the following conditions:

 – differential input for decrease of the cophased noise affect;
 – low level of zero signal;
 – large coefficient of decreasing cophased noise.

After being amplified the measuring signal is supplied to analog-digital converter (ADC), where it is converted in binary code N.

Taking into account the constituent elements of the secondary measuring means the converter equation (1) has the form:

$$N = \left[U_0 + S\lg\left(a_A + 0{,}1a_B\right)\right]\frac{K2^m}{U_{REF}} \tag{2}$$

where U_{Ref} – ADC voltage reference (5 V); m – ADC bit width (m=16); K – the gain of the measuring amplifier.

The previous studies reveal that limits of non-excluded remnants of systematic errors are the following:

 – standard potential U_0 of sensor $\theta_{U0} = \pm 3\,\text{mV}$;

 – absolute error of ions activity measuring $\theta_a = 5 \cdot 10^{-6}\,\frac{\text{mol}}{\text{dm}^3}$

 – maximum temperature coefficient of the measuring amplifier shift is $0.25\,\text{mV}/°\text{C}$;
 – temperature coefficient of the reference voltage of the ADC is $k_t = 10^{-5}/°\text{C}$;
 – the reference voltage deviation from the nominal value does not exceed $\theta_{U_{REF}} = \pm 0{,}02\,\text{V}$.

Under the assumption of a uniform distribution law [2, 3] the standard uncertainty of the potential sensor is defined as:

$$u_{U0} = \frac{\theta_{U0}}{\sqrt{3}} \approx 1{,}73\,\text{mV} \tag{3}$$

The standard uncertainty, caused by an absolute error of measuring the ions activity on the assumption of normal distribution of errors within the limits [6, 7] is calculated by the formula:

$$u_a = \frac{\theta_a}{k} \approx 2,55 \cdot 10^{-3} \frac{mmol}{dm^3} \qquad (4)$$

where k – enrollment ratio for the normal distribution, equal to 1.96 to 95% [3].

The combined standard uncertainty, introduced by ion-selective electrodes $u_{ГГs}$, calculated by type B, taking into account the equations (3) and (4) is defined by the formula:

$$u_{ГГs}^2 = \left(\frac{\partial \Delta U}{\partial U_0}\right)^2 u_{U0}^2 + \left(\frac{\partial \Delta U}{\partial a_A}\right)^2 u_a^2 + \left(\frac{\partial \Delta U}{\partial a_B}\right)^2 u_a^2 \qquad (5)$$

where $\frac{\partial \Delta U}{\partial U_0} = 1$ – sensitivity coefficient of standard potential; $\frac{\partial \Delta U}{\partial a_A} = \frac{S}{2,3(a_A + K_c a_B)}$ – sensitivity coefficient of A-ion activity measured which at the lower measuring range ($D_{min} = 10^{-6} mol/dm^3$) equals 23383,4 Vdm^3/mol; $\frac{\partial \Delta U}{\partial a_B} = \frac{K_c S}{2,3(a_A + K_c a_B)}$ – sensitivity coefficient of B-ion activity that interferes the determination of the A-ions measured which on the lower measurement range ($D_{min} = 10^{-6} mol/dm^3$) equals 23383,4 Vdm^3/mol.

Substituting the calculated values of sensitivity coefficients in the equation (1), the combined standard uncertainty introduced by ion-selective electrodes equals $u_{ГГs} \approx 60$ mV.

Since the measurements are carried out at the ambient temperature from 5 to 40 °C the maximum change in temperature in this case is $\Delta t = 35°C$. Taking into account the temperature coefficient of the amplifier shift $0,25 mV/°C$, the offset voltage will be $U_{os} = 35°C \cdot 0,25 mV/°C = 8,75$ mV. With the known gain K=10, maximum offset voltage is equal to $U_{osmax} = U_{os} \cdot K = = 87,5$ mV. Taking into account the maximum output voltage of the amplifier $U_{out} = \pm 5$ V maximum relative error can be calculated by the formula:

$$\delta_K = \frac{U_{osmax}}{2U_{out}} = 8,75 \cdot 10^{-3} \qquad (6)$$

Calculating the maximum relative amplifier error, standard uncertainty, introduced by the amplifier, measuring the concentration of ions in the assumption of the normal distribution can be calculated by the formula:

$$u_K = \frac{\Delta U_{max} \delta_K}{k} \approx 0,83 \, mV \qquad (7)$$

where ΔU_{max} - the maximum potential difference, which corresponds to the maximum ion activity of nitrate nitrogen (maximum measuring range is $D_{max} = 0,5 \, mol/dm^3$) at the highest possible activity of interfering B-ions.

The uncertainty Uref (Δt), caused by changes in the reference voltage source when the ambient temperature from 25 °C (temperature calibration reference voltage source ADC t_1) to 35 °C (the maximum possible ambient temperature changes Δt) calculated by the temperature coefficient, in the assumption of uniform distribution law of the limits will be equal to:

$$u_{REF}(\Delta t) = \frac{k_t (\Delta t - t_1)}{\sqrt{3}} U_{REF} \approx 0,43 \, mV \qquad (8)$$

The uncertainty Uref (), caused by the deviation of the reference voltage from the nominal value, on the assumption of a uniform distribution law will be equal to:

$$u_{U0} = \frac{\theta_{U_{ОП}}}{\sqrt{3}} \approx 11,55 \, mV \qquad (9)$$

Thus, the combined standard uncertainty of the ADC voltage reference, which consists of the uncertainty calculated using the formula (8) and (9) is equal to:

$$u_{REFs} = \sqrt{(u_{REF}(t))^2 + (u_{U0})^2} \approx 11,56 mV \qquad (10)$$

The standard uncertainty u_h introduced by the process of the voltage quantization that on the ADC input, in the assumption of a uniform distribution law is defined as follows:

$$u_h = \frac{h}{\sqrt{3}} = \frac{U_{ОП}}{2^m \sqrt{3}} \approx 44{,}05 \, \mu V \tag{11}$$

Taking into account calculated by formulas (5), (7), (10) and (11) the standard uncertainty at each stage of transformation, the combined standard uncertainty of type B is calculated by the formula:

$$u_S = \sqrt{u_{ПТs}^2 + u_K^2 + u_{REFs}^2 + u_h^2} \approx 61{,}11 \, mV \tag{12}$$

Thus, analyzing the results we can see that the maximum uncertainty of 60 mV is entered by primary ion selective converter, and the total uncertainty of type B does not exceed 61.11 mV.

Conclusions. On the basis of reference and previous studies data there has been suggested a method of uncertainty estimation introduced by means of ions concentration measuring. Ranging from 10^{-6} to $5 \cdot 10^{-1} \, mol/dm^3$ it equals to 61,11mV with maximum activity of interfering ions.

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