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EVALUATION OF STATIC METROLOGYCAL CHARACTERISTICS OF MEASURING CHANNEL OF IONS ACTIVITY

There had been deduced on equations of transformation of measuring channel of ions activity. There had been evaluated basic static metrological descriptions are appraised by expanding the transformation equalization into the series. There had been presented of Taylors, graphs of their changes with the to recommendation of diminishing the measuring error.

Key words: *transformation equation, static characteristic, measuring channel, activity of ions, additive error, multiplicative error, sensitiveness, nonlinear error.*

Urgency and problem statement

Soil as any natural body of biosphere, contains the products of vital activity of microorganisms which strengthen its fertility. One of such most important products is humus – a specific organic substratum which characterizes soil in respect of its potential fertility. Therefore the development of control devices of the main humus components with the increased metrological characteristics is an important for today task. Chemical activity of soils since humus holds the chemical bonds a variety of very useful to plants nutrients (ammonia nitrogen, potassium, nitrate nitrogen, fluoride), and physical properties of soils, such as water penetration, density, a moisture capacity which directly influence quality of a crop, directly depend on humus components.

Building of high-precision control devices for humus components requires to select a method which helps to be research the activity (concentration) of ions, to build on its basis the measuring channels evaluate the main static metrological characteristics for finding ways for reduction of measurement errors.

Analysis of latest research and publications

From [1, 2] it is known that high-hair accuracy of measurement of ions activity of humus components in soil is given by a straight method of potentiometry. This method is grounded on the basis of measurement of electrode potentials (EP) and electromotive forces (EMF) of galvanic elements. Values of EMF and EP depend on activity of substances – participants of electrode reactions, temperature and pressure. Electric energy of a galvanic element appears due to the reduction of energy of Gibbs during chemical reaction in it. Since *n* ions that participate in chemical reaction, the balance potential may be described by the equation:

$$\Delta U = \frac{RT}{nF} ln(K) + \frac{2{,}303RT}{nF} lg(a_A + K_S a_B), \tag{1}$$

where R –universal gas constant; T – absolute temperature; F –Faradays constant; K – constant of reaction equilibrium; K_S – selectivity factor; a_A – activity of measured ions A; a_B – activity of hindering ions B.

In expression (1) the first component $\frac{RT}{nF} ln(K)$ is named as standard potential which is equal U_{st} and is expresses in mV, the second component of the equations (1) $\frac{2{,}303RT}{nF}$ is named as angular factor of an inclination of electrode function (slope S) the value of which depends on the substance temperature which activity is being measured. For an ideal electrode in case of a positive monovalent ion, the slope S is accept as equal +59,16 mV at temperature 25 °C.

Objective of the research

Considering above the objective of the paper is to develop improved equation for transformation of ions activity which would allow to consider the temperature of researched substance by additional measurement and research of the main static metrological characteristics of the measuring channel (MC) of ions activity.

Presentation of the basic material

To consider the temperature in the environment in which measurements are being conducted, the expression of initial measuring transformer (1) will be written as:

$$\Delta U = U_{st} + \frac{\alpha(273,16 + t)}{n} lg(a_A + K_S a_B),\qquad(2)$$

where α – temperature coefficient of slope S, which is equal $198{,}4 \cdot 10^{-3}/°C$; t – temperature of the analyzed environment, ($°C$).

The static characteristic of a conversion function (2) of ionoselective electrodes of nitrates nitrogen and fluoride in a range of change of activity from 10^{-6} to 10^{-1} mol/dm^3 at temperature 20 $°C$ is represented in fig. 1, and during the change of activity of ions of ammonia nitrogen, potassium and calcium in a range of change from 10^{-5} to $0{,}3$ mol/dm^3 at the same temperature, the static characteristic varies as it is represented in fig. 2.

By the definition, ionoselective the electrode which allows to determine the activity of the necessary ions with 10 – to 100-fold surplus of hindering ions a_B [1] therefore at during the research of static characteristics of primary ionoselective measuring converters, activity of ions which hinder a_B has been accepted by some orders above the activity of ions which are subject to measurements.

The factor of selectivity K_s depends on nature of ions which activity is measured. It is established on the basis of experimental data by means of graduating characteristics (fig. 3) $\Delta U = f(a_A)$ with constant activity of hindering ions a_B.

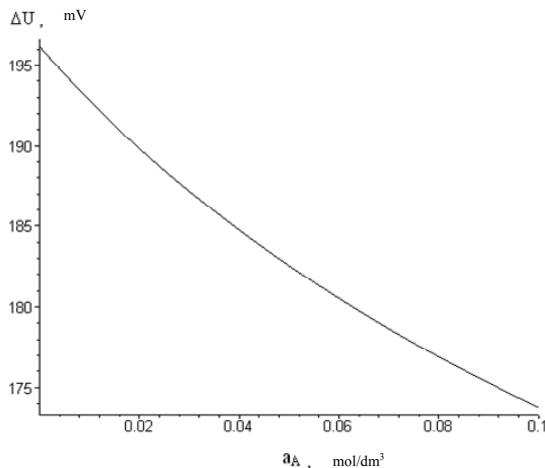The measuring channel of ions activity is the set of measuring devices and measuring apparatuses (fig. 4).

Fig. 1. Dependence of change of difference of potentials on activity of ions of nitrate nitrogen and fluorine
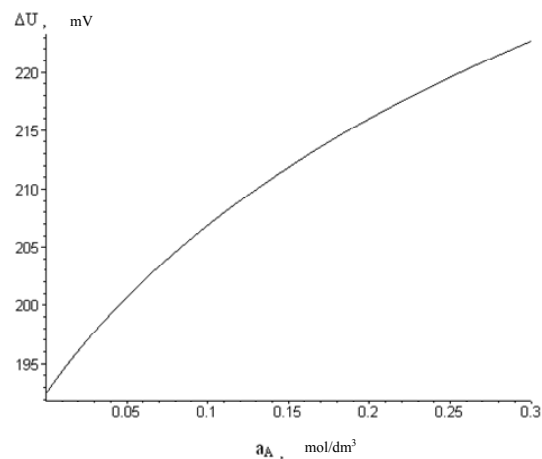
Fig.2. Dependence of change of difference of potentials on activity of ions of ammonium nitrogen and potassium

Measuring devices in this scheme are: initial ionoselective measuring converter which converters the activity of measured ions a_A to a difference of potentials ΔU and is described by the equation (2) and the measuring amplifier, which multiplies the input an entry difference of potentials and the amplification factor value k. The analog-to-digital converter (ADC) successive approximation is a
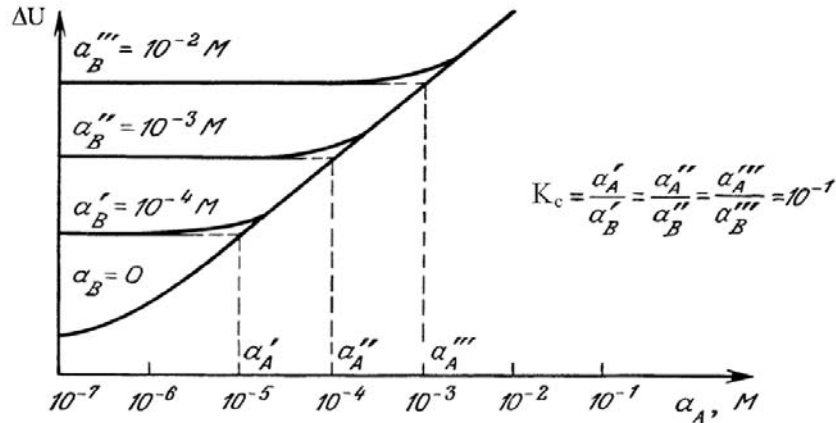
secondary measuring means.

Fig. 3. Description is experimental for determination of coefficients of selectivity

Presented MC is the main one for building the automated controlling means for such humus constituents in the soil : ammonium , nitrate nitrogen, potassium, calcium, fluorine.

Considering the function of transformation of iono-selective measuring the converter (2), amplification factor k of the measuring amplifier and the function of transformation of ADC of consecutive approximation,

the final the equation of MC transformation of ions activity will look like

$$N = \frac{k 2^m}{U_{on}} \left(U_{cm} + \frac{\alpha(273,16 + t)}{n} lg\left(a_A + K_C a_B\right) \right), \qquad (3)$$

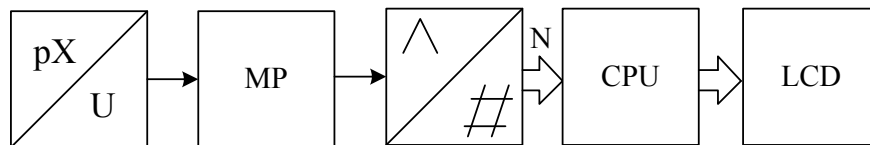where m – bit of ADC (16); U_{on} – values of supporting voltage of ADC (5 V).

Fig. 4. Flow diagram of measuring channel of activity of ions

In operating conditions MC of ions activity carries out the functional transformations of informative parameter a_A in to a binary code N. Except for an informative signal, it is acted upon by influencing values, which belong all the other constituents with direct relation to the value N which favor to appearance of non informative constituent of transformation. The analysis of the received equation of transformation (3) shows that process of transformation of informative parameter into the output signal is influenced by a considerable number of influencing values.

Having accepted all constituents (influencing values) of the equations (3), except for the informative parameter, constants, we will receive the nominal factor of transformation (sensitivity) MC (fig. 5). For this purpose we will find the first derivative of function of transformation (3) on a_A which will take a form

$$S_a = \frac{\partial N}{\partial a_A} = \frac{\alpha(273,16 + t)k 2^m}{U_{on} n \left(a_A + K_s a_B\right) ln(10)} . \qquad (4)$$

Nominal function of MS transformation of ions activity we will determine from the equation of decomposition in the row of Taylors [3], considering the equation (3) and (4), after a formula

$$N_{nom} = S_a a_A + \frac{1}{2}\frac{\partial S_a}{\partial a_A}a_A^2 + \frac{1}{6}\frac{\partial^2 S_a}{\partial a_A^2}a_A^3 = S_a\left(a_A - \frac{a_A^2}{2\left(a_A + K_s a_B\right)} + \frac{a_A^3}{6\left(a_A + K_s a_B\right)^2}\right). \qquad (5)$$
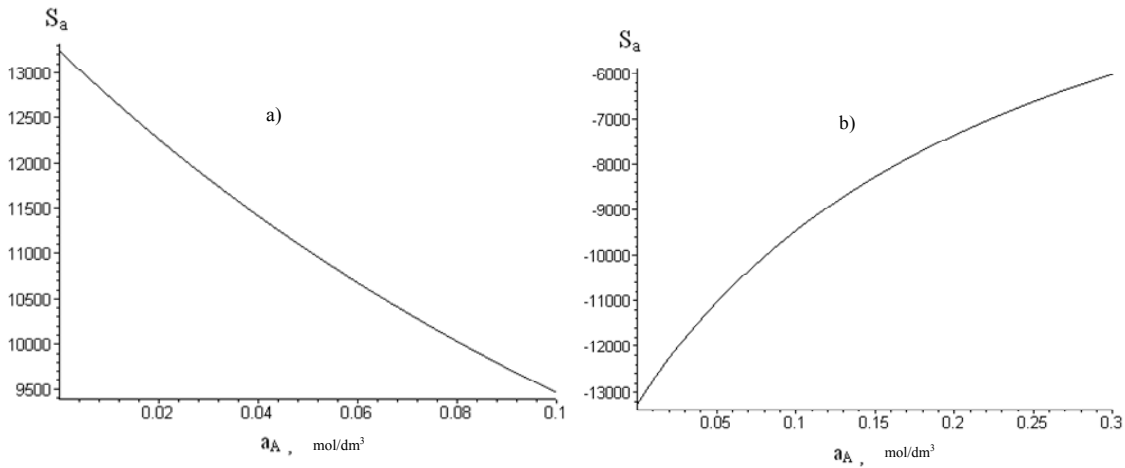
Fig. 5. Characteristics change of sensitiveness MC to activity of ions: a) – for nitrate nitrogen and fluoride; б) – for ammonium nitrogen, potassium and calcium

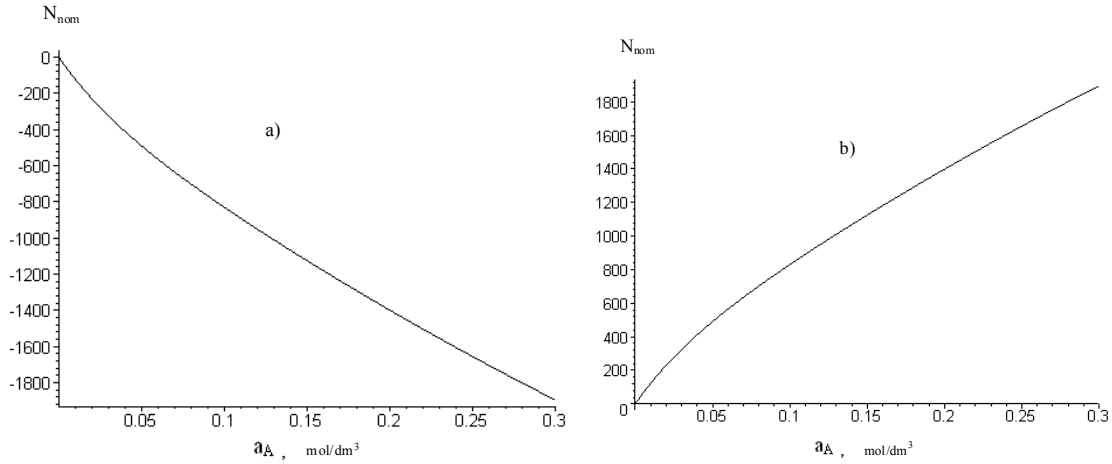Characteristics of change of the nominal function of transformation (5) is shown in fig. 6.

Fig. 6. Dependence of change of nominal characteristics MC of activity of ions: a) – for nitrate nitrogen and fluoride; б) – for to ammonia nitrogen, potassium and calcium

We will determine the absolute nonlinear error ΔN_{nom} of nominal function of transformation from the expression

$$\Delta N_{nom} = \frac{1}{2}\frac{\partial S_a}{\partial a_A}\left(a_A - a_{Anom}\right)^2 + \frac{1}{6}\frac{\partial^2 S_a}{\partial a_A{}^2}\left(a_A - a_{Anom}\right)^3, \tag{6}$$

where a_{Anom} – nominal values of the measured activity of ions (10^{-6}).

We will determine the relative error $\delta_н$ of non-linearity of nominal function of transformation (5) as follows [4]:

$$\delta_н = \frac{\Delta N_{nom}}{S_a\left(a_A - a_{Anom}\right)} = \frac{\left(a_A - a_{Anom}\right)\left[\left(a_A - a_{Anom}\right) - 3\left(a_A + K_s a_B\right)\right]}{6\left(a_A + K_s a_B\right)^2}. \tag{7}$$

Characteristics of change of absolute (6) and relative (7) errors of non-linearity are represented on fig. 7 and fig. 8.
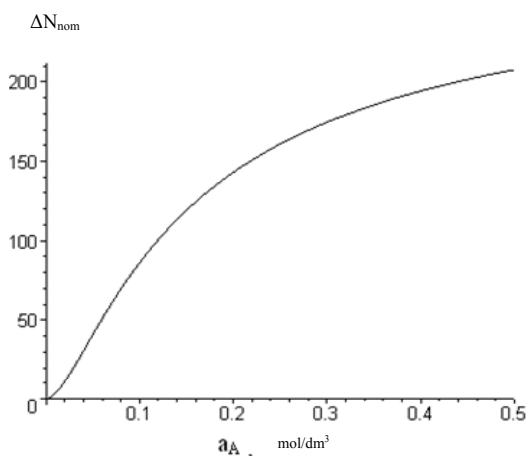
Fig. 7. Description of change of absolute error
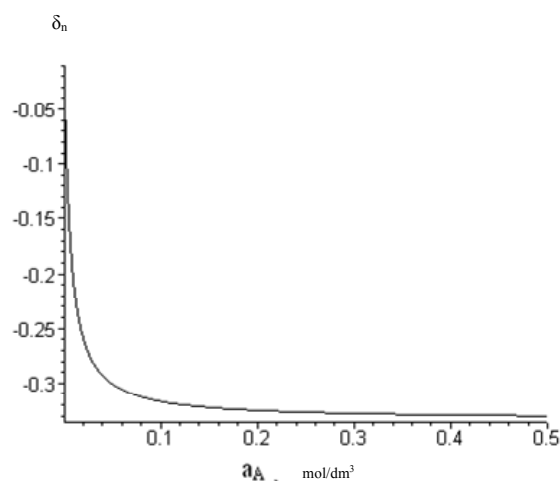of non-linearity MC of activity of ions

Fig. 8. Description of change of relative error
of non-linearity MC of activity of ions

Multiplicative error ΔN_M MC of ions activity with the influence of hindering ions a_B on the sensitiveness of S_a is described by an expression

$$\Delta N_M\left(a_A, a_B\right) = \frac{\partial S_a}{\partial a_B} a_A\left(a_B - a_{Bnom}\right) = \frac{-S_a K_s a_A\left(a_B - a_{Bnom}\right)}{a_A + K_s a_B}, \tag{8}$$

where a_{Bnom} − nominal values of activity of hindering ions (10^{-6}).

Multiplicative error ΔN_{Mt} MC of ions activity with the influence of temperature of the analysed substance on the sensitiveness of S_a is described by the expression

$$\Delta N_{Mt}\left(a_A, t\right) = \frac{\partial S_a}{\partial t} a_A\left(t - t_{nom}\right) = \frac{\alpha k 2^m a_A\left(t - t_{nom}\right)}{U_{on} n\left(a_A + K_C a_B\right) ln(10)}, \tag{9}$$

where t_{nom} − nominal values of temperature.

Characteristics of change of a multiplicative error $\Delta N_M\left(a_A, a_B\right)$ with influence of activity of hindering ions a_B on the nominal sensitiveness of S_a MC is shown in fig. 9, and the changes of a multiplicative error $\Delta N_{Mt}\left(a_A, t\right)$ with the influencing value in the kind of temperature of the analyzed substance is shown in fig. 10.
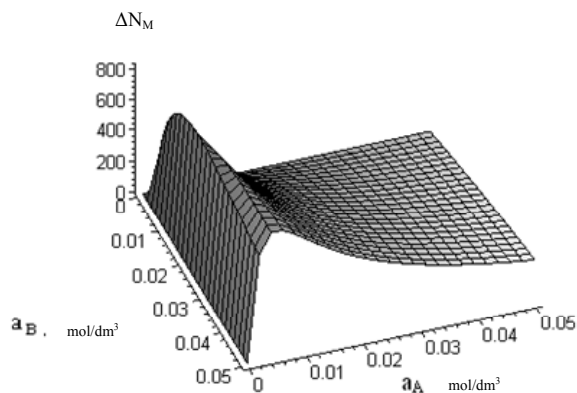

Fig. 9. Change of multiplicative
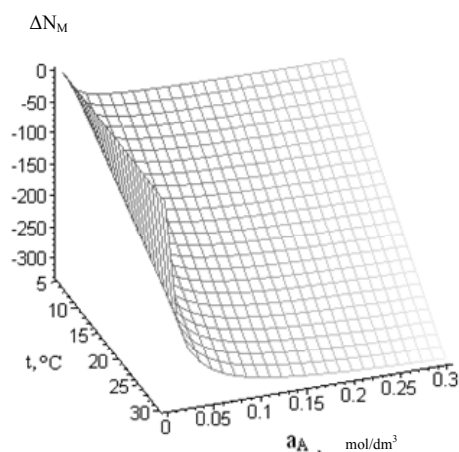error $\Delta N_M(a_A, a_B)$

Fig. 10. Change of multiplicative
error $\Delta N_{Mt}(a_A, t)$

We will determine the additive error of transformation in the conditions of change of activity of hindering ions a_B as follows:

$$\Delta N_a = \frac{\partial N}{\partial a_B}(a_B - a_{Bnom}) + \frac{1}{2}\frac{\partial^2 N}{\partial a_B^2}(a_B - a_{Bnom})^2 = S_a K_s (a_B - a_{Bnom})\left[1 - \frac{K_s(a_B - a_{Bnom})}{a_A + K_s a_B}\right]. \quad (10)$$

To build the characteristics of change of additive error in the conditions of change of temperature of the measured substance, we use formula

$$\Delta N_{at} = \frac{\partial N}{\partial t}(t - t_{nom}) + \frac{1}{2}\frac{\partial^2 N}{\partial t^2}(t - t_{nom})^2 = \frac{\alpha k 2^m \ln(a_A + K_s a_B)}{nU_{on}\ln(10)}(t - t_{nom}). \quad (11)$$

Dependences of change of additive errors (10) and (11) on influencing of the proper external values of a_B and t is shown in fig. 11 and fig. 12.
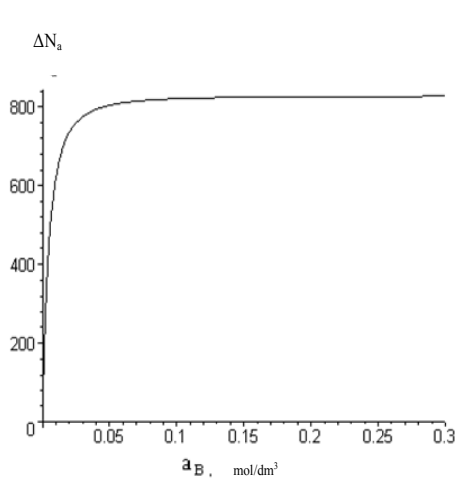

Fig. 11. Dependence of additive error
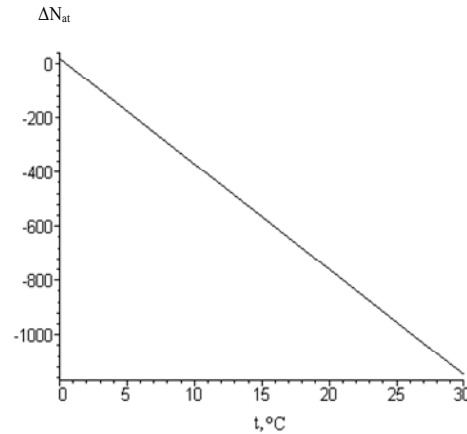on influence of activity of mixing ions

Fig. 12. Dependence of additive error
on influence of temperature of analyzed substance

Analysing the obtained results of basic static descriptions, we see that the equalization of transformation MC of ions activity is nonlinear, and inclination of static description MC depends on the charge of ions, the activity of which is measured. With measuring of activity of such humus constituents as ammonium nitrogen and potassium – the coefficient of inclination of electrode function is positive and values of difference of potentials on the output MC increases with the increase of activity of the indicated ions, and during the determination of such humus constituents as fluoride and nitrate nitrogen, - coefficient of inclination of electrode function is negative and values of difference of potentials on the output MC diminish with the increase of activity of ions. Relative value of error of non-linearity of nominal function of transformation MC to activity of ions, as be seen from a fig. 8 does not exceed 0,35 % in the range of measuring from 10^{-6} to 0,5 mol/dm^3.

Conclusions

The suggested equation of transformation(2) shows that the temperature of the environment substantially influences the additive and multiplicative errors of ionoselektiv electrodes. The relative value of temperature error makes up near 0,34%/$^\circ C$. Therefore the diminishing of total error of measuring of ions activity requires to measure the temperature of the analyzed substance, that is to enter the additional MC of the temperatures and to substitute the measured value of temperature in the improved equation of transformation of MC of ions activity.

The coefficient of sensitiveness of ionselective electrodes directly depends on the temperature of the analyzed substance, and for univalent cations, such as ammonium nitrogen and potassium, makes up +58,16 mV, and for bivalent, such as a calcium - 29,08 mM at a temperature $20\,^\circ C$.

As a result of evaluation of the basic static metrology descriptions of measuring channel of ions activity there had been received the analytical dependences are got for the function of transformation MC sensitiveness, nominal function of transformation, error of non-linearity, multiplicative and additive errors in the conditions of change of activity of hindering ions and change of temperature of analyzed substance. Software environment of Maple helped simulate the basic static metrology characteristics MC of ions activity, which allows to synthesize the microprocessor facilities of measurings with the previously set rationed metrologic characteristic and enter corrections on deviation from linearity on the additive constituents of errors, and also to correct the multiplicative constituents of errors.

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