TEST Engineering & Management

May-June 2020
ISSN: 0193-4120 Page No. 477 - 482

Mathematical Modeling and Optimization of Electrochemical Gas Analyzers

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Article Info
Volume 83
Page Number: 477 - 482
Publication Issue:
May - June 2020

Article History
Article Received*: 11 August 2019*
Revised*: 18 November 2019*
Accepted*: 23 January 2020*
Publication*: 09 May 2020*

Abstract:
The results of the application of information and communication technologies for mathematical modeling and optimization of the operation of electrochemical gas analyzers for determining the concentration of carbon monoxide in industrial technological environments were presented.

A substantial statement was considered and a solution to the applied problem of optimizing the parameters of automatic compensation of temperature errors in electrochemical cells was given. An instrument implementation of the coulometric method of gas analysis of toxic substances in industrial process media was performed, which ensures high efficiency and reliability of the results of continuous monitoring of the composition of natural gas.

Keywords: *electrochemical cell, gas analysis, modeling and optimization, content of harmful substances in gas mixtures.*

INTRODUCTION

The effectiveness of the functioning of environmental monitoring systems and industrial gas emissions monitoring and control systems with increasing flows of information is determined by the completeness, reliability and speed of obtaining a large number of environmental parameters. The basis for real-time extensive information databases formed on the basis of information on the content of harmful impurities and components of the air. First of all, this applies to such components as carbon monoxide, sulfur compounds, etc., the content of which in industrial emissions is mandatory regulated in accordance with the Kyoto Agreement and the requirements of the World Health Organization (WHO).

Thus, the task of developing industrial automatic gas analyzers for measuring the content of carbon monoxide in industrial gas emissions and in the air of adjacent industrial zones is particularly relevant.

The urgency of the problem is confirmed by a wide front of scientific research and development aimed at improving the efficiency of operational monitoring of the state of the surrounding air environment, the reliability and controllability of industrial technological complexes and installations based on the operational assessment of the state of monitoring and control objects according to their functioning parameters, carried out by high-speed information-measuring control systems complex of operational parameters. The latter are, including the parameters of the content of carbon oxides in the composition of industrial gas emissions and exhausts [1-4].

In this regard, the efficiency of management and operation of industrial technological installations and complexes with complex algorithms for processing a large amount of operational measurement information, changing loads and quality indicators of the functioning of monitoring and control objects require the development of effective high-speed

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automatic meters of a complex of operational parameters.

The severity of the problem is exacerbated by a chronic and widespread lack of industrial gas analytical instruments for the selective measurement of the concentration of harmful components in gas-vapor environments.

Currently, the main directions have been formed that underlie the development of control devices for a wide class of harmful substances at the MPC level. These include, in particular: electrochemical, (coulometric, potentiostatic, amperometric) and optical measurement methods.

In theoretical terms, the study of the coulometric method for determining the concentration of the target component in the gas mixture, which provides high efficiency and selectivity for continuous monitoring of the carbon monoxide content in the gas-vapor mixture of industrial technological environments and in atmospheric air, is urgent.

The analysis of patent and technical literature testifies to the wide potential potentials of the electrochemical cells with gas diffusion hydrophobized electrodes (HE) that are not fully exhausted. The task is that it is necessary to modernize previously developed primary measuring transducers in such a way that, with the smallest overall dimensions of the sensor, it is possible to significantly expand the detection range of micro-concentrations of harmful gases.

All this requires the creation of new generations of gas analyzers for modern information management systems built on modern physical and chemical measurement methods using the latest achievements of science and technology.

The aim of the work is to study the potentiometric method for determining the concentration of carbon dioxide in the gas mixture and to develop automatic industrial gas-analytical devices on this basis, as well as mathematical modeling of the operation of flowing electrochemical cells and solving the applied problem of optimizing the parameters of the automatic thermal compensation scheme of electrochemical cells [4-6].

Mathematical modeling of flowing electrochemical cells

The development of electrochemical sensors for electrolyte analysis is an urgent task, as it opens up new possibilities for automation of control. The most promising methods are those in which electrodes of various shapes are placed in an electrolyte stream.

For analysis, an electrode device was proposed called "an electrode with a function in the vicinity of a critical point", in which part of the body of revolution in the vicinity of the point of incidence serves as an indicator electrode [1]. Expressions were obtained for the concentration of the reacting substance on the surface of the electrode and stationary "current-potential" curves for an electrode device of this type placed in a parallel laminar flow. However, for sensors operating on non-stationary methods of chronovoltammetry and chronopotentiometry, theoretical expressions do not exist.

In the case of redox reactions on the electrode, limited by diffusion, the equation for the transfer of the reactant to the surface of the electrode, immersed in a laminar flow of electrolyte, with a steady flow of a viscous liquid has the form:

$$\partial C/\partial t + u(x,y)\partial C/\partial x + v(x,y)\partial C/\partial y = D\partial^2 C/\partial y^2, \quad (1)$$

where $C(x,y,t)$, D is the concentration and diffusion coefficient of the reacting substance; u,v - tangential and normal to the body of rotation components of the fluid velocity.

The boundary conditions for equation (1) in the case of the most commonly used methods of electrochemical analysis - chronoamperometry and chronovoltammetry are written as:

$$C(x,y,t) = C_0, \text{ at } x > 0,\ y \to \infty,$$
$$C(x,y,t) = C_e(t), \text{ at } x > 0,\ y = 0. \quad (2)$$

In the particular case for chronoamperometry $C_e = const$.

Using the curvilinear coordinate system associated with the surface of the body of revolution

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[2], we express the velocity components in terms of the current function and change the variables

$$y^* = y/D;\ x^* = \ln x/\alpha, \qquad (3)$$

where $\alpha = 1{,}312(\rho u_0{}^3/\mu L^3)$; ρ, μ - density and dynamic viscosity of the solution; u_0 - speed at an infinite distance from the electrode; L - characteristic size of the electrode.

The differential equation thus obtained is solved using the double Laplace transform with respect to t and x^*, and for the inversion of x^* it is necessary to use the two-sided Laplace transform.

Assuming that the initial conditions are homogeneous and denoting $W = C - C_0$ after the double Laplace transform, we obtain the equation

$$(\lambda + py^*)\tilde{W} - \alpha y^* \partial\tilde{W}/\partial y^* - \partial^2\tilde{W}/\partial y^{*2} = 0 \qquad (4)$$

with boundary conditions:

$$\tilde{W} = 0, \text{ at } y^* \to \infty;$$

$$\tilde{W} = (L_t C_e(t) - C_0/\lambda)/p, \text{ at } y^* = 0, \qquad (5)$$

where $\tilde{W} = L_2 W$.

After elimination by replacing the term with the first derivative, we obtain the equation

$$(\lambda + (p+\alpha)y^* + \alpha^2 y^{*4}/4)\tilde{\Psi} - \partial^2\tilde{\Psi}/\partial y^{*2} = 0. \qquad (6)$$

The solution to equation (6) are some special functions. However, in this case, for $\alpha << 1$ and $y^{*2} << 1$, the Airy $Ai(z)$ function can be taken as an approximate solution. Then the solution of equation (4) can be written as

$$\tilde{W} = \frac{\Phi(\lambda) - C_0/\lambda)(Ai((\lambda + (\alpha+p)y^*)}{(\alpha+p)^{2/3})/(Ai(\lambda/(\alpha+p)^{2/3})p)\exp(-\alpha y^{*3/6})}, \qquad (7)$$

where $\Phi(\lambda) = L_t C_e(t)$.

Solution (7) is divergent at $x \to 0$, that is, at the point of incidence on the electrode. To exclude this feature, we will seek a solution in the form of a series in α.

In an analytical form, it is impossible to record originals from the obtained images (7) in the general case. Therefore, for an approximate calculation of the originals, we use the interpolation function for the logarithmic derivative of the Airy function

$$Ai(z)/Ai'(z) \approx -(1+z)/\sqrt{1{,}887 + z}. \qquad (8)$$

For simplicity, put $C_e(t) = C_e = const$. Then

$$C(t, x^*, y^*) = C_0 + L_2^{-1}\frac{(Ai(\lambda + py^*)/p^{2/3}}{(\lambda/p^{2/3})(C_e - C_0)}. \qquad (9)$$

Finding the original of such an image for arbitrary y^* is difficult. However, for practice, the most interesting is the dependence of the current density $i(x^*, t)$ on time. Since $i \sim \partial C/\partial y^*$, we calculate the derivative

$$\partial C/\partial y^*\big|_{y^*=0} = \frac{C_e - C_0}{\sqrt{D}} L_2^{-1}\frac{(Ai'(\lambda/p^{2/3})}{\lambda p Ai(\lambda/p^{2/3})}. \qquad (10)$$

Using (8) and performing the inverse Laplace transform with respect to λ, we obtain the original of equation (10) in the form

$$\partial C/\partial y^*\big|_{y^*=0} = \frac{C_e - C_0}{\sqrt{D}} L_{x^*}^{-1}(\exp(-1{,}887\,p^{2/3})/\sqrt{\pi t} + \\ + p^{2/3} erf(\sqrt{1{,}887\,p^{2/3}t}/\sqrt{1{,}887\,p^{2/3}})/p). \qquad (11)$$

Further, using the asymptotic expansion for the functions exp and erf, we obtain the originals in the form of series

$$\partial C/\partial y^*\big|_{y^*=0} = \frac{C_e - C_0}{\sqrt{D\pi t}}(1 + \sum_{k=0}^{\infty} a_k (t/x^{*2/3})^k), \qquad (12)$$

where are the expansion coefficients

$$a_0 = 0; \quad a_k = (-1)^k (1{,}887)^k/(k!\Gamma(1-(2/3)k)) - \\ -(2(-1)^k (1{,}887)^{k-1})/((k-1)!(2k-1)\Gamma(-2/3(k-3/2))). \qquad (13)$$

The expressions found make it possible to obtain theoretical equations for current-potential curves and use flow-through electrochemical cells to analyze technological mixtures of electrolytes of complex composition [5].

Optimization of parameters of the scheme of thermal compensation of electrochemical cells.

Electrochemical cells with a polymer diffusion membrane are widely used in small-sized individual analyzers for monitoring the oxygen concentration of carbon oxides and analyzing the composition and other gases in the air of industrial premises and the environment. The output signal of such sensors is proportional to the concentration of the detected component and the diffusion flow of the substance

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through the polymer gas-permeable membrane separating the analyzed medium from the electrochemical cell.

One of the main tasks that need to be solved with the release of such devices is the compensation of the temperature dependence of the diffusion coefficient of the polymer membrane, which is more than 0.3% per Kelvin [2]. Typically, for this, a thermistor is placed inside the electrochemical cell, which is included in the ECC output signal circuit. The same circuit includes two adjustable resistances in parallel and in series with a thermistor. The values of their resistances are chosen so that in the entire range of operating ambient temperatures (0 ÷ 40 ° C) the temperature error of the output signal is minimal. Based on preliminary temperature tests for each cell, its basic parameters I_{20}, R_{20} are determined - the cell current at the nominal concentration C_0 and the resistance of the thermistor at a temperature of 20° C, α, β - temperature coefficients of the membrane and thermistor. The output of the electrochemical cell signal is determined by the equation

$$U(C_0T) = I(C_0T)[R_t R_s /(R_t + R_s) + R_d];$$

$$I(C_0, T) = I_{20}e^{\alpha\Delta T};\ \ R_t = R_{20}e^{-\beta\Delta T};\ \ \beta > \alpha \quad (14)$$

or

$$U(T, R_d, R_s) = I_{20}R_{20}e^{\alpha\Delta T}\left[\frac{1}{e^{\beta\Delta T} + R_{20}/R_s} + \frac{R_d}{R_0}\right]. \quad (15)$$
$$= I_{20}R_{20}\varphi(T, R_d, R_s).$$

The values of temperature coefficients α and β are calculated according to the results of preliminary temperature tests. Tests are carried out at 4 ÷ 5 points within the temperature range of the electrochemical cell (0÷40 °C) [3]. The series of voltage values thus obtained on the thermistor R_t and the additional resistance R_d are approximated by exponential dependences (14) by the least squares method. The parameters of the obtained curves determine the values of the temperature coefficients a, the current of the detector I_{20} and the resistance of the thermistor R_{20}. The mean square relative error of approximation is in the range of 0.5 - 1.5% (Fig.1).

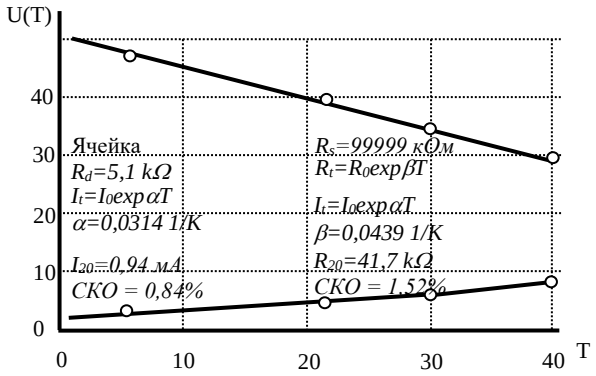

Fig. 1. Temperature curves of an electrochemical cell

The task of optimizing ECC parameters is formulated as follows [4]:

For the given cell parameters α, β, R_{20}, determine the values of the parameters R_d, R_s that provide the minimum change in the $\varphi(T, R_d, R_s)$ function in the temperature range $\pm\Delta T$. An analysis of function (15) in the range of variation of the $\pm\Delta T$ argument shows that for certain values of the parameters it can have two extrema for the values of the argument T_1 and T_2 and two extrema at the boundaries of the range at the points $-\Delta T$ and $+\Delta T$ (Fig. 2.).

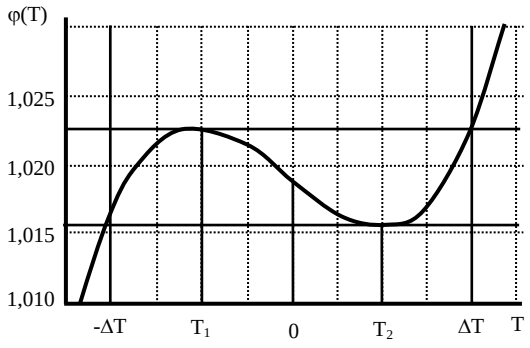

Fig. 2. Function Behavior (7).

In this case, the condition for the minimum change in the $\varphi(T, R_d, R_s)$ function can be expressed by equations for determining the parameters R_d and R_s

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$$\varphi(-\Delta T) = T_2;\ \ \varphi(T_1) = \varphi(\Delta T), \qquad (16)$$

where T_1 and T_2 are the roots of the equation $\varphi_T(T) = 0$.

The solution of these equations for the parameters R_d and R_s by methods associated with finding extremums cause certain difficulties. Therefore, it was proposed to slightly modify and simplify the task. The extremum points T_1 and T_2 at optimal parameters are near the values of $\pm\Delta T/2$. Therefore, (16) can be replaced by approximate equations

$$\varphi(-\Delta T) = \varphi(\Delta T/2);\ \ \varphi(\Delta T) = \varphi(-\Delta T/2). \qquad (17)$$

Introducing the notation in (15): $e^{\alpha\Delta T/2} = a$; $e^{\beta\Delta T/2} = b$; $R_d/R_{20} = A$; $R_{20}/R_s = B$, we obtain the equations in the form

$$a^{-2}[1/(b^{-2}+B)+A] = a[1/(b+B)+A];$$
$$a^{-1}[1/(b^{-1}+B)+A] = a^2[1/(b^2+B)+A]. \qquad (18)$$

Excluding A, after simple transformations we get

$$\frac{1}{b^{-1}+B} - 1(b^{-2}+B) + \frac{a^3}{b+B} - \frac{a^3}{b^2+B} = 0. \qquad (19)$$

Solving the equation by numerical methods (for example, Newton's method), we find the values of A and B as well as the associated R_d and R_s. With these resistance values, the minimum error of the instrument readings is achieved when the temperature changes in the $\pm\Delta T$ range. With the parameters of the electrochemical cell $\alpha = 0{,}03$ *град*$^{-1}$, $\beta = 0{,}04$ *град*$^{-1}$, the maximum error at the optimal parameters of the fitting resistances was 0.3 - 0.4% rel. in the temperature range from 0 to 40 °C [7-9].

An analysis of equation (19) shows that the minimum temperature error for the optimal selection of parameters is determined by the values of $a = \exp(\alpha\Delta T/2)$ and $b = \exp(\beta\Delta T/2)$. It increases with increasing temperature interval ΔT and the difference in temperature coefficients α and β. Optimum values of fitting resistances are achieved in the region where the $R_d/R_{20} = R_{20}/R_s$ relation is satisfied. This ratio can be used in the selection of real resistances.

The solution of equation (19) gives the calculated optimal value of the resistances R_d and R_s, however, in order to achieve real thermal compensation, it is necessary to select the maximum resistance values from a number of ratings [10].

There are two ways to do this. The first is a parallel connection of the second resistor in order to obtain the desired resistance value. Perhaps the use of standard resistors of variable resistance. However, this method can be applied with sufficient free space on the electronic board of the electrochemical cell, which is not always possible. The second method is that from the standard series of resistances, the closest to the calculated value of R_d is selected. The value of R_s is adjusted based on the ratio of $R_d R_s = R_0^{\,2}$. This way is more preferable, and the error of thermal compensation will increase no more than 1.5 times in comparison with the optimal value obtained from the solution of equation (19).

CONCLUSION

A substantive statement was considered and a solution to the applied problem of optimizing the parameters of automatic compensation circuits for temperature errors in electrochemical cells was given. The metrological characteristics of the designs of electrochemical cells were developed and investigated. In addition, mathematical modeling of the flow of electrochemical cells was performed. The obtained analytical expressions make it possible to obtain adequate theoretical equations for the "current-potential" curves and calculate the parameters of electrochemical cells to determine the concentration of harmful components in the composition of para-gas technological mixtures [11]. Static, dynamic, and other characteristics of electrochemical cells based on gas diffusion, hydrophobized electrodes were investigated, and the possibilities of implementing optimal options for their structural design were found.

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