USE OF THERMOCATALYTIC SENSORS IN SYSTEMS FOR MONITORING WORKING CONDITIONS AT OIL AND FUEL FACILITIES

**Purpose.** To substantiate the possibility of using thermocatalytic sensors in systems for monitoring working conditions to control the content of gasoline vapours in the air of the working area of oil and fuel facilities.

**Research methods.** The paper applies analytical methods for studying the processes occurring in thermocatalytic sensors, which are based on the basic provisions of electrical engineering and the theory of heat and mass transfer, evaluation and generalisation of research results.

**Results.** The use of thermocatalytic sensors in systems for monitoring working conditions to control the content of gasoline vapours in the air of the working area of oil and fuel complex facilities is substantiated. It is shown that the sensitivity of thermocatalytic gas analyzers, which is necessary to control the content of gasoline vapours within the maximum permissible concentrations (MPC), can be ensured by selecting the sensor power mode with voltage stabilisation on the comparative element, carrying out periodic automatic checking and correcting zero readings of gas analyzers.

**Originality.** It consists in the use of a method of feeding a thermocatalytic sensor with voltage stabilization on a comparative sensing element, which ensures a stable temperature regime of thermoelements, and improving the method of monitoring and correcting zero readings of thermocatalytic gas analyzers by reducing the sensor supply voltage to the value at which the oxidation reaction of gasoline vapours does not occur on the working thermoelement of the sensor, which consists in the calculated determination of the zero displacement of the measuring bridge in the operating mode of the sensor power supply and taking into account the value of this displacement when determining the current value of the gasoline vapour content.

**Practical value.** The proposed solutions to increase the sensitivity of gas analyzers create conditions for the use of relatively simple, stable and cheap thermocatalytic sensors in the systems for monitoring working conditions to control the content of gasoline vapours in the air of the working area of oil and fuel complex facilities, which creates the prerequisites for the introduction of modern information technologies in the field of health and safety of workers.

**Key words:** working conditions, gasoline vapours, air of the working area, control, sensors, gas analyser, monitoring

**Introduction**

An important task set for employers by the International Labor Organization in the field of occupational health and safety is to create decent working conditions at every enterprise, organization or institution [1]. An important element for this is the introduction of modern information systems for monitoring working conditions, the main component of which is the systems of automatic continuous control of working conditions, emissions of harmful substances into the environment and safety of the working environment, which should be further integrated with environmental monitoring systems and information systems of technological safety [2,3].

Among the most common high-risk facilities that use chemicals that can cause harmful effects on workers and the environment are gas stations. Filling stations consist of buildings and equipment designed mainly for receiving petroleum products, storing them and issuing them to vehicles. The technological equipment of the filling station is partially located in open areas. At the same time, vapours of gasoline and other petroleum products will dissipate in the atmosphere and enter the premises of gas stations and buildings in the surrounding areas with natural air currents [4].

Gasoline is not only a flammable liquid that can form explosive mixtures with air under normal conditions, but a substance that, in the event of the inflow of gasoline vapours into the lungs of a person, has a harmful effect on his health [5]. Constant work at a concentration of gasoline vapours in the air of the working area of 250–300 mg/m³ affects the violation of the digestive system, liver, pancreas, negatively affects reproductive function, etc. Gasoline vapours, and especially their decay products, have a harmful effect on the environment [6]. In view of this, the following maximum permissible concentrations are established for gasoline vapours in Ukraine: the maximum one-time concentration of gasoline in the air of the working area and in the sanitary protection zone of oil products supply facilities is 100 mg/m³; The average daily concentration of gasoline in the air of settlements is 1.5 mg/m³. To prevent the harmful effects of gasoline vapours on gas station employees and the environment, it is necessary to constantly monitor working conditions and the state of the atmosphere in the sanitary protection zone of the
filling station. The main and most important elements of the monitoring system are the means of controlling the content of oil vapours in the air of the working area and in the sanitary protection zone of the filling station. Difficult conditions of their operation, the influence of temperature, humidity, changes in pressure, composition of the fuel-air mixture, pollution with dust and fuel components can affect the performance and stability of their operation.

Analysis of the latest research and publications

Methods and devices used to control the explosiveness of the environment, to determine the concentration of gasoline vapours in the premises and on the territory of gas stations, as well as in the sanitary protection zone and in the atmosphere of settlements are known [7]. Among them, optical, flame-ionisation, photo-ionisation, chromatographic [2,7], refractometric [8], thermocatalytic and semiconductor methods should be highlighted [9, 10].

Some of these methods (flame-ionisation, chromatographic, etc.) are used in relatively complex, expensive, highly sensitive devices designed to measure low concentrations of vapours of petroleum products, as a rule, in systems for monitoring air pollution of settlements, as well as for periodic monitoring of the content of harmful substances in the air of the working area, for example, when certifying workplaces for working conditions. Their use in systems of automatic control of working conditions is economically inexpedient.

Semiconductor (metal oxide) sensors are also characterised by their simple design and low cost [10]. Their advantage is high sensitivity and long service life. However, these sensors are not stable enough when exposed to high concentrations of vapours or gases. Under such conditions, there is a gradual decrease in their sensitivity. In addition, these sensors are characterised by different sensitivity to the constituents of gasoline. The latter drawback is also characteristic of the optical method, and in addition, its disadvantages include the impressive dimensions of the sensors, a significant impact on the results of measuring temperature, pressure, humidity and various gas impurities.

In the systems of automatic control of the explosion hazard of the gas environment, the thermocatalytic method of control is most often used [11]. This is due to the simple design of thermocatalytic sensors, small size, low cost, the possibility of their remote placement (remote sensors) on the territory and premises with subsequent integration with a single measuring device. Such sensors are characterised by a long service life, minimal impact on their operation of gas composition and air humidity, dust, and temperature. At low concentrations of gasoline vapours in the air, these sensors make it possible to obtain an integral characteristic of explosiveness.

Despite the above-mentioned advantages of the thermocatalytic method, it has not found use in systems of automatic continuous monitoring of working conditions. The reason lies in the relatively low stability of zero readings of analyzers when monitoring the content of gasoline vapours within the maximum permissible concentration, which necessitates periodic inspection and installation of a "zero" measuring bridge with a thermocatalytic sensor. Such a check is possible if clean air is used, which is difficult to carry out in the presence of gasoline vapours in the atmosphere of the gas station. For example, for periodic verification of the "zero" of portable multicomponent gas detectors DOZOR-S-M [12], a test gas mixture is used, which does not contain combustible gases and vapours (clean air). With the regulated frequency of checking and correcting "zero" - 30 days and monitoring the concentration of combustible gases in the range of 0 - 300 mg/m³, the normalised absolute measurement error of this analyzer is ±75 mg/m³ (for methane), which is almost comparable to the maximum permissible concentration of gasoline vapours in the air of the working area. To reduce the measurement error, it is necessary to significantly reduce the frequency of checking and correcting the "zero", which is unrealistic when using test mixtures.

In the paper [7], a scheme of a gas analyzer is proposed, which allows the use of atmospheric air to set the zero of the analyzer. This is achieved by periodic pre-oxidation of fuel vapours contained in atmospheric air in a special thermal chamber and its subsequent use as a test gas. Such a solution significantly complicates the means of control, and in addition, in this case, the influence of changes in the temperature of the gas after the thermal chamber and oxidation products on the zero of the analyzer is not excluded. Another way to solve the problem, proposed to improve the reliability of explosion protection systems, is to control and correct the zero readings of analyzers.
by reducing the supply voltage of the thermogroup to the value at which the oxidation reaction of the combustible gas on the working thermoelement does not occur [13], which allows to programatically implement the verification and correction of zero readings without complicating the sensors. However, the issue of using such a solution to control the content of gasoline vapours in the air of the working area within the maximum permissible concentration has not yet been investigated.

The purpose of the article
The purpose of the publication is to substantiate the possibility of using thermocatalytic sensors in systems for monitoring working conditions to control the content of gasoline vapours in the air of the working area of oil and fuel facilities.

Research Methods
The paper applies analytical methods for studying the processes occurring in thermocatalytic sensors, which are based on the basic provisions of electrical engineering and the theory of heat and mass transfer, evaluation and generalisation of research results.

Statement of the main material
In gas analyzers, thermocatalytic sensors are usually included in the bridge measuring circuit. In practice, bridge measuring circuits are more often used with a sequential arrangement of the working and comparative elements in one branch of the measuring bridge [11], as well as with the inclusion of sensitive elements in different branches of the measuring bridge [7]. Setting the "zero" of the measuring bridge is carried out by balancing it when it is supplied to the clean air sensor.

Ideally, with the careful manufacture of thermocatalytic sensors, which ensures the identity of the characteristics of the catalytically active and compensating elements, the method has high sensitivity; The measurement results are not affected by temperature, pressure, atmospheric composition, as well as voltage fluctuations that feed the thermogroup (within small limits). However, in the practical implementation of the method, it is very difficult to achieve the identity of the characteristics of the elements and therefore all manufactured technical means have a relatively large measurement error.

The theoretical dependence of the voltage value on the thermoelements of thermocatalytic sensor on the current value in the absence of combustible vapours and gases in the air is as follows [11]

\[ U_e = I_e R_{e2} + \beta b_e R_{0e} I_e^3. \]  

where \( U_e \) - is the voltage across the thermoelement, V; \( I_e \) - is current through the thermoelement, A; \( R_{e2} \) - is resistance of the thermoelement at air temperature, Ohm; \( \beta \) - temperature coefficient of resistance, \( 1/\circ C \); \( b_e \) - thermosteresistive coefficient of the thermoelement, \( \circ C/A^2 \); \( R_{0e} \) - thermoelement resistance at \( 0 \circ C \), Ohm;

The resistance of a thermoelement at air temperature for a platinum resistor is given by the well-known expression

\[ R_{e2} = R_{0e} (1 + \beta t_e), \]  

where \( t_e \) - is the air temperature, \( 0 \circ C \).

Taking into account the expressions (1) and (2), the voltage on the series-connected working \( p \) and comparative \( n \) elements, respectively, is:

\[ U_p = I_e R_{0p} (1 + \beta t_e) + \beta b_p R_{0p} I_e^3, \]  
\[ U_n = I_e R_{0n} (1 + \beta t_e) + \beta b_n R_{0n} I_e^3. \]

At the value of the current through the thermoelements \( I_e \), which corresponds to the operating mode of the sensor, due to the non-identity of the voltage characteristics of the elements, the voltage difference between them is \( \Delta U \). Based on equations (3) and (4), in this case, it is

\[ \Delta U = U_p - U_n = I_e (R_{0p} - R_{0n}) \times \] \[ \times (1 + \beta t_e) + \beta b_e R_{0p} - b_n R_{0n}. \]  

In existing thermocatalytic gas analyzers, measuring circuits with thermocatalytic sensors are usually supplied with a stable voltage. However, with such switching schemes, a change in ambient temperature leads to a change in the temperature regimes of thermoelements, which causes a significant measurement error. It is possible to reduce this error by using switching circuits that ensure a stable temperature regime of thermoelements when the
temperature of the gas medium changes. In this regard, the circuits for switching on sensors with voltage stabilization on a comparative thermoelement, which ensures the invariability of its temperature regime under operating conditions, are of interest [11].

When using modern microcontrollers to store information and process it, the procedure for setting "zero" is carried out, as a rule, by software according to commands from the analyzer display when supplied to the clean air sensor [12]. The determined value $\Delta U$ is remembered and, in operating mode, is taken into account when determining the concentration of fuel vapours in the air.

Analysis of expression (5) shows that the change $\Delta U$ can occur when the magnitude of the current changes due to the elements, fluctuations in air temperature, as well as due to the instability of the value of the resistance of thermoelements or their thermoresistive coefficients.

Let us analyze the nature of the change of the first component in expression (5) for the case of a change in the temperature of the medium, for example, for the case when the setting of zero was carried out at an air temperature of $0^\circ$C, and the measurement is carried out at a temperature of $10^\circ$C. When using a traditional thermoelements power supply scheme from a stable voltage source, such a temperature change will result in a multiplier increase $(1 + \beta t_e)$ of 4% (given that for platinum $\beta = 0.0039$), and also, given the quadratic nature of the dependence of heat dissipation on the magnitude of current, this will lead to a decrease in current by 2%. The multidirectional nature of the change in these factors testifies to certain autostabilisation properties of this power supply scheme, however, despite this, a change in the temperature of the medium under such conditions leads to a change in the value of this component of expression (5) of about 0.2% for every $0^\circ$C. When using the thermoelements power supply scheme from a stable current source, such a temperature change will lead to a change in the value of this component of about 0.4% for every $0^\circ$C. It is possible to minimise the effect of temperature changes on the value of the first component by using the sensor power mode with voltage stabilisation on the comparative thermoelement, which is recommended in [11] for powering thermoconductivity sensors. In this case, the increase in the multiplier $(1 + \beta t_e)$ with an increase in temperature is actually completely compensated by a corresponding decrease in the magnitude of the current through the thermoelements.

The second component in expression (5) depends on the magnitude of the current and the difference between the products of the resistances of the elements and their thermoresistive coefficients. The thermally resistive coefficient determines the relationship between the electrical, thermal, and geometric characteristics of a thermoelement and is often taken as a constant value when analysing thermal processes within certain temperature ranges [11]. At first glance, when thermoelements are powered from a stable current source, this component will not depend on temperature. This assumption is generally acceptable when using thermocatalytic sensors in explosion protection systems. In our case, it is unacceptable to neglect the change in the value of the thermally resistive coefficients when the temperature of the medium changes.

In small-sized thermocatalytic sensors, the heat released in the thermoelement is dissipated into the environment mainly due to the thermal conductivity of air and radiation [11]. With an increase in the temperature of the thermoelement, both the thermal conductivity of the air and the radiation component of heat transfer increase, which, in turn, reduces the increase in temperature per unit of power consumption and, accordingly, reduces the values of thermal-resistive coefficients. Therefore, when thermoelements are powered both from a stable current source and from a constant voltage source, the invariability of the second component of expression (5) is not ensured.

When using the power supply mode of the sensor with voltage stabilisation on the comparative thermoelement, with an increase in air temperature, the value of the current through the thermoelement $I_e$ decreases and at the same time the temperature difference between the thermoelement and the gaseous diffusion filter decreases, and this, in turn, leads to an increase in temperature per unit of power consumption and, accordingly, increases the value of the thermoresistive coefficient.

As for such reasons as the instability of the resistance value of thermoelements or their thermally resistive coefficients, they can manifest themselves during long-term operation of sensors at high concentrations of fuel vapours due to the evaporation of platinum during overheating of sensitive elements and the
accumulation of products of thermal destruction of hydrocarbons on the surface of sensitive elements [13]. When controlling the content of gasoline vapours within the maximum permissible concentration, these factors practically do not affect the measurement results.

Another way to solve the problem, proposed to improve the reliability of explosion protection systems, is to control and correct the zero readings of analyzers by reducing the supply voltage of the thermogroup to the value at which the oxidation reaction of the combustible gas on the working thermoelement does not occur [14], which allows you to programmatically implement the verification and correction of zero readings without complicating the sensors.

Let's consider the possibility of implementing such diagnostics when using modern microcontrollers to store information and process it. Figure 1 shows the voltage characteristics of the comparative 1 and working 2 thermoelements in the absence of fuel in the gas mixture, as well as the voltage characteristics of the working thermoelement in the presence of fuel vapours in the air 3. For the sake of clarity, these characteristics are chosen to be significantly different, although in reality the displacement of characteristics is orders of magnitude smaller. At the value of the current through the thermoelements \( I_e \), which corresponds to the operating mode of the sensor and the absence of fuel vapours, due to the non-identity of the voltage characteristics of the elements, the voltage difference between them is determined based on equation (5).

\[
\Delta U' = U'_p - U'_n = I'_e (R_{0p} - R_{0n}) \times (1 + \beta e) + \beta e^3 (b_p R_{0p} - b_n R_{0n}). \tag{6}
\]

In the latter case (6), this voltage difference does not depend on the presence of fuel vapours in the air and its value can be used to calculate the value of \( \Delta U \) in the operating mode of the sensor in the presence of fuel vapours (curve 3, Fig. 1).

To simplify the verification procedure, we select the preheating temperature of the thermoelements to check "zero" when setting such that the value of \( \Delta U = 2\Delta U' \), and remember the value of the voltage value on the comparative element for this case (the value of the voltage on the comparative element is uniquely related to its heating temperature). In this case, the procedure for checking and correcting "zero" in the presence of gasoline vapours in the air is reduced to reducing the value of the current through the thermoelements to the value at which the value is set \( U'_n \) on the comparable element, the value \( \Delta U' \) is determined in the test mode and the calculation \( \Delta U = 2\Delta U' \).

Provided that the preheating temperature of the thermoelements is reduced to the value at which the catalytic oxidation reaction of the fuel does not occur on the working element, the value of the current is \( I'_e \), and the voltage difference across the elements is

\[ \Delta U' = U'_p - U'_n = I'_e (R_{0p} - R_{0n}) \times (1 + \beta e) + \beta e^3 (b_p R_{0p} - b_n R_{0n}). \]

Based on the research, we made a mock-up of a gas analyzer with the function of automatic diagnostics of zero readings and developed an algorithm and a program for its operation. There are no elements in the gas analyzer to adjust the "zero" and sensitivity of the analyzer. The analyzer has two modes of operation: debug mode and operating mode. All adjustment and verification operations are carried out without operator intervention according to the developed analyzer operation program. In the debugging mode, the remote sensor of the analyzer is installed in a small-sized chamber, which, on command from the analyzer display, is alternately filled with atmospheric air or a calibration mixture of air and hexane. When fresh air is supplied by the analyzer, the set temperature of the comparative element is set, the voltage values on the elements and their difference are determined and recorded in the analyzer's memory, the value of the current through the elements is reduced, the voltage on
the comparative element is determined and remembered, at which the voltage difference of the sensing elements is halved. When the calibration mixture is fed to the remote analyzer sensor, the voltage value on the comparison element predetermined for clean air is determined and set, the voltage on the working element is determined and the sensitivity of the analyzer sensor is calculated, taking into account the previously determined voltage difference, mV/mg.

In the operating mode, the operations of measuring the voltage on the elements, maintaining the value of the voltage on the comparable element determined during regulation, determining the voltage difference on the elements, calculating and transmitting information about the content of fuel vapours are continuously performed. Periodically, according to the time analyzer defined by the work program, the zero readings of the analyzer are checked and corrected. At the same time, the magnitude of the current through the thermoelements is reduced until the voltage is set on the comparable element, at which the voltage difference of the sensitive elements in clean air is halved. At the end of the transient process, the stresses on the elements and their difference are determined, calculated ∆V and estimated the degree of displacement of the "zero" of the sensors in the absence of an oxidation reaction of fuel vapours on the working element, and a decision is made on the need to notify the operator about the need to check and adjust the analyzer readings or correct the zero readings of the analyzer. Then the operating value of the current through the thermoelements is set, and at the end of the transient process, the operations of measuring the voltage on the elements and adjusting the voltage value on the comparative element are performed, the voltage difference across the elements is determined, the zero readings of the analyzer are corrected based on the results of the test, and the calculation and transmission of information about the content of gasoline vapours in the air is calculated.

Conclusion.
The carried out studies made it possible to substantiate the possibility of using thermocatalytic sensors in systems for monitoring working conditions to control the content of gasoline vapours within the maximum permissible concentrations (MPC), can be ensured by selecting the sensor power mode with voltage stabilisation on the comparative element and carrying out periodic automatic checking and correction of zero readings of gas analyzers. The proposed solutions to increase the sensitivity of gas analyzers create conditions for the use of relatively simple, stable and cheap thermocatalytic sensors in the systems for monitoring working conditions to control the content of gasoline vapours in the air of the working area of oil and fuel complex facilities, which creates the prerequisites for the introduction of modern information technologies in the field of health and safety of workers.

References
"Orion". https://optima-shop.com.ua/uk/zavantagenny (in Ukrainian)


Список літератури

VIKORISTANНЯ ТЕРМОКАТАЛІТИЧНИХ ДАТЧИКІВ В СИСТЕМАХ МОНІТОРІНГУ УМОВ ПРАЦІ НА ОБ’ЄКТАХ НАФТОПАЛИВНОГО КОМПЛЕКСУ

Мета. Обґрунтувати можливість використання термокаталітичних датчиків в системах моніторингу умов праці для контролю вмісту парів бензину в повітрі робочої зони об’єктів нафтопаливного комплексу.

Методи дослідження. В роботі застосовані аналітичні методи досліджень процесів, що протікають в термокаталітичних датчиках, які базуються на основних положеннях електротехніки та теорії тепломасопереносу, оцінка і узагальнення результатів досліджень.

Результати. Обґрунтовано використання термокаталітичних датчиків в системах моніторингу умов праці для контролю вмісту парів бензину в повітрі робочої зони об’єктів нафтопаливного комплексу. Показано, що чутливість термокатализаторів газоаналізаторів, яка необхідна для контролю вмісту парів бензину в межах гранично допустимих концентрацій (ГДК), може бути забезпечена шляхом вибору режиму живлення датчика з урахуванням пристосування робочих датчиків до високого температурного режиму термоелементів, що забезпечує стабільний температурний режим термоелементів.

Надійшла до редакції 18.04.2024
Рецензент д-р. техн. наук, проф. Сергій ЧЕБЕРЯЧКО

Holinko Vasyl, Doctor of Technical Sciences, Professor, Head of the Department of Labour Protection and Civil Security, Dnipro University of Technology, 49005 Dnipro, 19 Dmytro Yavornytskoho Ave
E-mail: golinkongu@gmail.com
ORCID: 0000-0001-6069-0515

Zabelina Valentyna, graduate student, Department of Labour Protection and Civil Safety, Dnipro University of Technology, 49005 Dnipro, 19 Dmytro Yavornytskoho Ave
E-mail: vprotysyk@gmail.com
ORCID: 0000-0002-7678-7917
та вдосконалені методу контролю і коригування нульових показань термокаталітичних газоаналізаторів шляхом зниження напруги живлення датчика до величини, за якої не протікає реакція окислення парів бензину на робочому термоелементі датчика, що полягає в розрахунковому визначенні зміщення нуля вимірювального моста за робочого режиму живлення датчика та врахування величины цього зміщення при визначенні поточного значення вмісту парів бензину.

Практична цінність. Запропоновані рішення щодо підвищення чутливості газоаналізаторів створюють умови для використання відносно простих, стабільних і дешевих термокаталітичних датчиків в системах моніторингу об'єктів нафтопаливного комплексу, що створює передумови впровадження сучасних інформаційних технологій в сфері охорони здоров’я та безпеки працівників.

Ключові слова: умови праці, пари бензину, повітря робочої зони, контроль, датчики, газоаналізатор, моніторинг

Голінько Василь Іванович, професор, доктор технічних наук, завідувач кафедри охорони праці та цивільної безпеки Національного технічного університету «Дніпровська політехніка» 49005 м. Дніпро, пр. Дмитра Яворницького, 19
E-mail: golinkongu@gmail.com
ORCID: 0000-0001-6069-0515

Забєліна Валентина Андріївна, аспірант кафедри охорони праці та цивільної безпеки Національного технічного університету "Дніпровська політехніка"
E-mail: vprotsyuk@gmail.com
ORCID: 0000-0002-7678-7917