Detection of various gas environments is an important security task, especially in conditions of military operations and in contaminated areas. In this case, optical gas sensors of the colorimetric type are effective, which can promptly signal the presence of toxic substances in "field conditions", do not require complex equipment or energy consumption.

The object of the study is a detector of harmful gases of the colorimetric type. The problem of improving the characteristics of colorimetric sensors by amplifying useful signals and reducing the influence of spurious radiation is being solved.

To solve the problem, a functional and mathematical model of the signal path of a pollutant detector was developed. A method for forming an optical signal of increased sensitivity due to multiple passage and reflection of light fluxes in a colorimetric sensor model was proposed.

A model of an optical gas detector based on a polyaniline sensor element was manufactured. The presence of ammonia vapors was analyzed using gas-stimulated changes in optical absorption at different wavelengths, namely, 470 ± 5, 528 ± 7 and 623 ± 5 nm. The proposed functional scheme of the detector signal path allowed to improve its sensitivity and selectivity, which is explained by the amplification of useful signals and the reduction of the influence of parasitic radiation.

The high speed of recovery of the resulting sensor to the initial values (up to 10 s) ensures its reversibility and opens up prospects for effective practical use, in particular, monitoring the state of the environment, the freshness of food products, harmful gas leaks near landfills, chemical storage sites, etc.

Keywords: optical sensor, informative detector signal, conjugated polymers, toxic gases, signal converter

FORMATION OF INFORMATIVE SIGNALS IN AN OPTICAL TOXIC GAS DETECTOR

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1. Introduction

Detection of various gas environments is an important task for the safety and survival of living organisms, especially in conditions of military operations and in contaminated areas. Chemical and biological pollutants are capable of gas emission, therefore, it is advisable to use gas sensors for their detection. At the same time, optical gas sensors of the colorimetric type are quite effective, which can promptly signal the presence of toxic substances in "field conditions", do not require complex equipment or energy consumption.

Gas-sensitive detectors (sensors, indicators) allow to detect harmful factors below the threshold of their perception by human senses. The most common technologies for creating harmful gas detectors are based on the use of semi-conductor structures, while the formation of sensor films is carried out by methods of thermal vacuum or magnetron sputtering, laser ablation, etc. [1, 2]. The disadvantages of the production of such sensors are the need to use vacuum and high temperatures, which is energy-consuming. The disadvantages of known sensors include their high cost and toxicity (the presence of chemical elements Hg, Pb, Cd, Te, etc.), since sensor sensitivity is detected only after heating to high operating temperatures (200–400°C). Significantly reduce energy consumption, increase the environmental friendliness of sensor systems and ensure the operation of active elements at room temperatures can be achieved by using new sensor substances, in particular, organic semi-conductors based on conjugated polymers and their composites [3]. Among them, polyaniline and its derivatives attract

special attention [4, 5]. In contrast to known sensor systems, new technological methods for forming polyaniline films – polymerization *in situ,* or electropolymerization, does not require vacuum or complex equipment.

For the detection of harmful gases, systems of the "electronic nose" type are being actively developed [6]. However, the use of such systems in everyday activities is problematic due to the complexity of the design, the high cost of inorganic semiconductors, which are the basis of most gas sensors. The problem is also significant energy consumption during production and imperfections in the processes of forming informative signals in the working paths of detectors and sensors. Significantly limits the operational characteristics, in particular, selectivity gas sensors, the fact that in most of them an electrical signal is generated from the primary transducer. In this case, the selectivity of the sensor is ensured by the fact that the appropriate gas-sensitive element is selected for each type of gas.

One way to improve the characteristics of an optical sensor can be to develop new gas-sensitive sensor substances and create "intelligent" colorimetric sensor systems based on them [7] using various sensor platforms. Such systems are able to quickly and reliably detect the presence of harmful gases using mathematical processing of the optical signal with appropriate software.

Existing gas sensors and gas environment analysis systems do not yet provide effective comprehensive analysis of the state of the gas atmosphere, including toxic and poisonous substances in contaminated areas and optimal adaptation to modern servers. This is due, in particular, to the presence in existing optical gas detectors of a significant level of parasitic radiation from extraneous light sources, such as solar radiation, artificial lighting sources, etc., as well as the inefficient use of informative detector signals due to the fact that the response is analyzed in only one spectral region.

Therefore, there is a need to develop new optimized methods for analyzing informative signals in optical gas detectors that will eliminate these shortcomings. This can be achieved by using a gas detector and effective sensory substances, development of mathematical models and design of more optimal signal paths of the corresponding converters. Thus, research devoted to the creation of new effective methods of controlling informative signals in optical gas detectors is relevant.

2. Literature review and problem statement

Colorimetric sensors operate on the basis of several key mechanisms. The first mechanism is based on localized surface plasmon resonance (LSPR), which is especially characteristic of gold and silver nanoparticles. When the size, shape or interparticle distance of nanoparticles changes or due to their aggregation, the absorption maximum shifts, which leads to a color change from red to blue [8]. The disadvantage of the colorimetric LSPR sensor is the complex procedure for manufacturing sensor media using high-cost materials, such as gold. In addition, the information signal is recorded mainly in the near UV region and very weakly in the visible, which does not allow visually tracking the color transformations of the sensor element.

The second mechanism involves the course of redox reactions, where enzymes or nanoenzymes catalyze the oxidation of substrates and their aggregation, which is accompanied by a color change [9]. A significant disadvantage of this type of sensor is the operation in the liquid phase, as well as the use of several reagents to carry out reactions that cause a color change, which significantly complicates the process.

Colorimetric sensors are known that operate on a color change due to electrostatic interaction between the negatively charged sulfonate group on modified silver nanoplates and europium ions (Eu^{3+}), which causes a color change [10]. The disadvantage of this type of sensor is the use of expensive materials, including rare earth elements (Eu), conducting reactions in the liquid phase, and low reproducibility of results.

Recently, the so-called "paper" sensors have been actively developed [11]. For the manufacture of sensor elements, cellulose is mainly used and its composites with various compounds and nanoparticles. Sensors can be used in different configurations: spot tests, dipsticks, lateral flow assays (LFA) and microfluidic paper devices (μPADs). The main disadvantages of paper sensors are low sensitivity and limited efficiency in conducting quantitative analysis.

In [12], a fast colorimetric humidity sensor based on a thin-film active element based on polyvinyl alcohol (PVA) with silver nanoparticles (AgNP) is described. AgNP particles are directly printed on a quartz substrate with titanium dioxide using a precision photoreduction technology. This PVA-AgNP-TiO_2 structure detects brighter colors with an extended gamut compared to the colors of a single-layer PVA film. The colorimetric sensor can quickly respond to change humidity air, and the measured rise time feedback (speed) is 87 ms. The disadvantage of the sensor is its limited use only for humidity detection, while the detection of toxic gases is not provided. Another disadvantage is the partial loss of sensor sensitivity after interaction with the sensing medium due to irreversible adsorption of moisture from the surface of the hydrophilic PVA film.

In a known gas sensor, in particular, ammonia, polyaniline, obtained by the oxidative polymerization of aniline in an acetic acid medium [13], is used as an active sensor medium. The sensor is also sensitive to acetone, toluene, and humidity. The disadvantage of the sensor is the dependence of its parameters on the morphology of the obtained polyaniline, and insufficient speed (300 s or more). In addition, the sensor operates on a change in the resistance of polyaniline and cannot be used in colorimetric measurements.

Sensitive elements for optical gas sensors based on polyaniline and its derivatives [14, 15] are manufactured by electrochemical polymerization on the surface of optically transparent plates with a semiconductor layer of ITO or tin oxide SnO_2. Under the action of ammonia, significant changes occur in the optical spectra and, accordingly, the color of the films [14]. The speed of such a sensor is 120–180 s. The sensitivity of the sensors is almost doubled due to the simultaneous measurement of the increase in optical absorption in the visible region of the spectrum and its decrease in the near infrared region, as well as the summation of the absolute values of these opposites.

The disadvantage of known gas sensors based on polyaniline is also insufficient speed, as well as their predominant use only as primary converters, without processing the information signal. Software for the information signal processing system has not been developed, which does not allow monitoring of the gas "on-line". The influence of parasitic radiation significantly distorts the measurement results, which makes it impossible to use such a sensor in "field conditions" for direct detection of harmful gases in contaminated areas.

Currently, various approaches to quantitative measurement of colorimetric changes using smartphone cameras have been developed [16, 17]. In [17], a portable array reader for interaction with smartphones was developed. This reader can detect color changes of a colorimetric strip under the influence of toxic gases – ammonia, methylamine and trimethylamine. The array strips that react to toxic gases consist of dyes that change color according to the acidity of the environment, and the reader monitors the color change in real time to generate chromaticity (color) data. Data on the detected gas is transmitted to a smartphone, which displays the type and concentration of the harmful gas on the screen. The disadvantage of the development is the imperfect system of signal registration and processing, since instead of directly using RGB- image intensities, chromaticity values are used to construct calibration curves of analyte concentrations. A key drawback of smartphone- based measurement systems is the influence of lighting conditions on measurement accuracy. The calibration methods developed to compensate for measurement errors caused by ambient light variability are not effective enough [16, 17].

One way to overcome these shortcomings and improve the characteristics of colorimetric sensors is to use new sensor substances that respond to the action of gases by changing their color and, accordingly, their spectrum, and to improve the system for forming and processing an informative signal with the leveling (rejection) of parasitic radiation under natural lighting conditions, in particular, the action of sunlight.

All this allows to state that in order to improve the system for recording and processing an informative optical signal in a colorimetric gas detector, it is advisable to develop a functional and mathematical model of signal formation, as well as a specialized path of noise-resistant signal conversion for such a detector. To test the obtained results and analyze gas-stimulated changes in optical absorption, it is advisable to manufacture a prototype of a gas sensor with a polyaniline sensitive element and test it in real time under the influence of a harmful gas, such as ammonia.

3. The aim and objectives of the study

The aim of the study is to improve the system for recording and processing an informative optical signal in a colorimetric gas detector to amplify useful signals and reduce the influence of parasitic radiation when recording a signal in an optical gas detector.

This will increase the sensitivity of the gas sensor and provide the ability to detect harmful substances under various lighting conditions when using the detector "in the field", and to analyze the results of detecting harmful gases in the "on-line" mode.

To achieve the goal, it was necessary to complete the following tasks:

– to develop functional and mathematical models of the signal path of a colorimetric pollutant detector;

– to propose a method for generating an optical signal of increased sensitivity and to develop a specialized path for noise-resistant signal conversion;

– to test an improved signal generation and registration system in a mock-up of an optical gas sensor with a polyaniline active element, to analyze the gas-stimulated change in optical absorption at different wavelengths in online mode.

4. Materials and methods

The object of the study is a colorimetric type harmful gas detector.

The main hypothesis of the study assumes the possibility of improving the characteristics of the gas detector by improving the system of registration and processing of the informative signal. It is assumed that the improvement of the sensitivity and speed of the detector can be achieved by using new sensor substances, while the measurement of informative signals is carried out by combining the processes of passage and reflection of light fluxes with a reduction in the influence of parasitic radiation.

To test the hypothesis in an optical gas detector, it is proposed to use polyaniline as a sensor substance. A unique property of this polymer is the ability to change the optical spectrum and, accordingly, the color or intensity of the color under the influence of various external factors, especially under the influence of gases - the " gasochromic effect" [5]. A significant change in the optical properties of the sensor element under the influence of gases allows for reliable monitoring of the environment in conditions of military operations and the influence of technogenic factors. In addition, in optical sensors and detectors there is a possibility to analyze response signals at different wavelengths, which can significantly improve their selectivity.

The sensor element with a gas-sensitive polyaniline film was formed by the electropolymerization method as described in [4, 14] on the surface of optically transparent plates with an ITO or SnO_2 layer. The structure and cross-section of the sensor element are shown in Fig. 1.
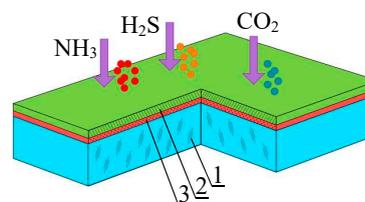

Fig. 1. Structure of the sensing element of an optical gas sensor: 1 — glass substrate; 2 — gas-sensitive polymer film; 3 — SnO_2 layer

Under the influence of harmful gases, in particular ammonia, typical changes occur in the spectral characteristics of optical absorption of polyaniline sensor films, an example of which is shown in Fig. 2.

The presented spectra are characterized by optical absorption in the visible part of the spectrum, while under the influence of gaseous media there is a change in both the absorption intensity and the position of the spectral bands (Fig. 2). Changes in the spectra are accompanied by a change in the color of the polyaniline sensor film, from yellow to green, blue and violet [4, 5, 14], which makes it a good candidate for colorimetric type detectors. Therefore, polyaniline films were chosen as the sensor element in the manufacture optical gas sensor layout.

To develop a mathematical model and design the signal path of a portable gas detector, the synthesis of spectral characteristics at selected wavelengths of light radiation using sums of Gaussian functions was envisaged.

The informative signal of such a gas sensor is due to the significant absorption of the optical medium interacting with the gas. Therefore, to obtain the spectral characteristics of

informative signals in the optical gas detector, optocouplers were used, which consist of controlled sources of optical radiation and photosensitive elements [9, 10].
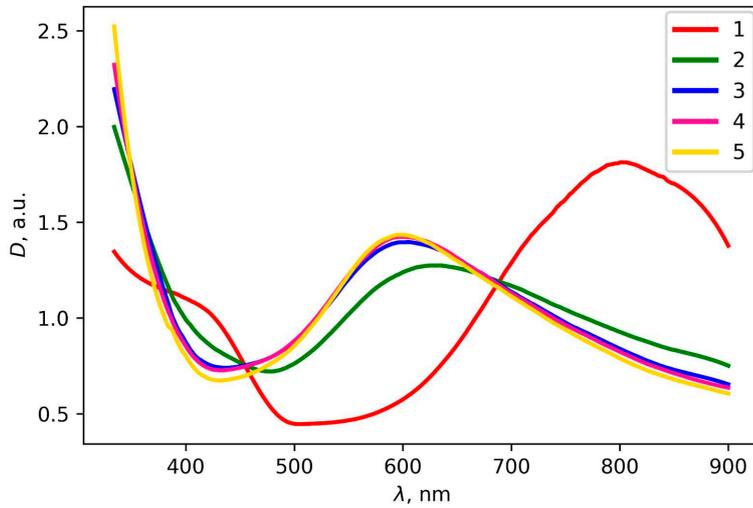

Fig. 2. Absorption spectra of polyaniline film obtained by electropolymerization: 1 — without gas; 2 — under the action of ammonia for 1 minute; 3 — 3 minutes; 4 — 6 minutes; 5 — 25 minutes

The simplifications adopted in our study consist in the use of a simplified functional diagram of the SPICE signal path model used for functional analysis, which does not include components of analog switches, operational amplifiers, active filters, etc. In addition, to simplify the calculation of signal values by the method of integrating the product of the spectra of the sensitive films and the light-emitting diode (LED), the spectral characteristic of the photodiode is not taken into account.

5. Results of research into ways to improve the formation of informative signals in an optical gas detector

5. 1. Functional and mathematical models of signal formation in an optical toxic gas detector

The construction of the optical sensors (detectors) studied in this work is based on the colorimetric measurement method. To create a system for generating informative signals of the detector, it was necessary to develop a functional and mathematical model of generating informative signals, on the basis of which it is possible to determine the quantitative parameters of the change in the spectral characteristics of the sensitive film of the sensor device.

The functional model is a structured description of the system and defines the functions and interaction of its components. The paper proposes a functional model of the formation of a family of informative signals in a gas detector, which is implemented by multispectral optocouplers, shown in Fig. 3.

The structure of such optocouplers includes a matrix of LEDs LED Array (Light Emitting Diode Array) with different emission spectra and a photodiode array with a corresponding set of spectral filters PD & CL Array (Photodiode and Color Filter Array). The family of

informative signals is formed as a result of modulation of the intensity of light fluxes, which is caused by a change in the spectral characteristics of the medium. In this work, such a medium is a colorimetric sensor film, the absorption spectrum of which is modulated by the substances under study, in particular, harmful gases.

The mathematical model of the formation of a family of informative signals uses the basis of Gaussian functions in a simplified form – Gaussian

$$F_G(x) = ae^{\frac{(x-b)^2}{\tilde{n}}}, \tag{1}$$

where x is the argument of the function, a, b, c are the coefficients, $e \approx 2.718$ is Euler's number.

The mathematical model involves the synthesis of the spectral characteristics of the actuator $S_A(\lambda)$, medium $S_M(\lambda)$ and sensor $S_S(\lambda)$ by the argument of the wavelength of light radiation λ using the sums of Gaussian functions:

$$S_A(\lambda) = \sum_{n=1}^{N} A_A^n e^{-\frac{\left(\lambda - B_A^n\right)^2}{C_A^n}}, \tag{2}$$

$$S_M(\lambda) = \sum_{n=1}^{N} A_M^n e^{-\frac{\left(\lambda - B_M^n\right)^2}{C_M^n}}, \tag{3}$$

$$S_S(\lambda) = \sum_{n=1}^{N} A_S^n e^{-\frac{\left(\lambda - B_S^n\right)^2}{C_S^n}}, \tag{4}$$

where n – the number of Gaussian components that synthesize the spectral characteristic; A_A^n – actuator matrix components light radiation, which are LEDs with different emission spectra; A_M^n – components of the matrix of the medium, which is the colorimetric film; A_S^n – components of the light radiation sensor matrix, which are photodiodes with different filter spectra.

Examples of spectral characteristic synthesis are shown in Fig. 4.
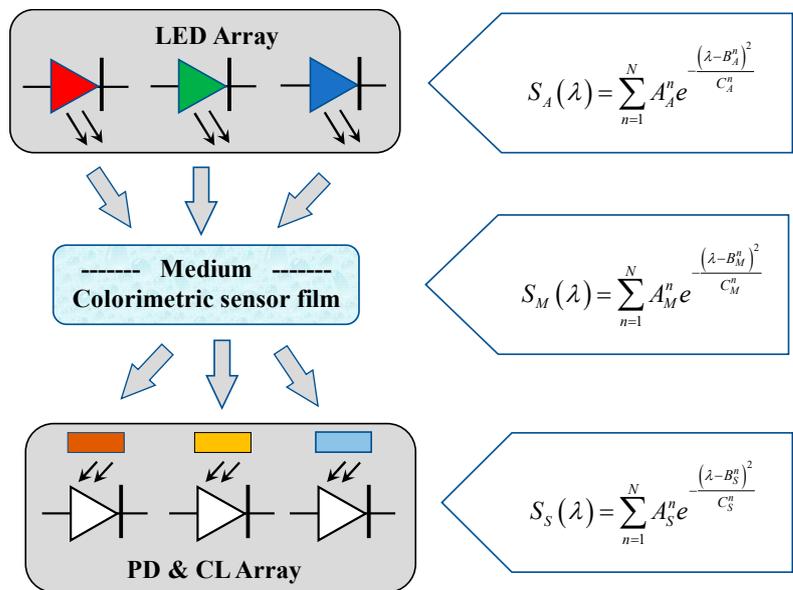

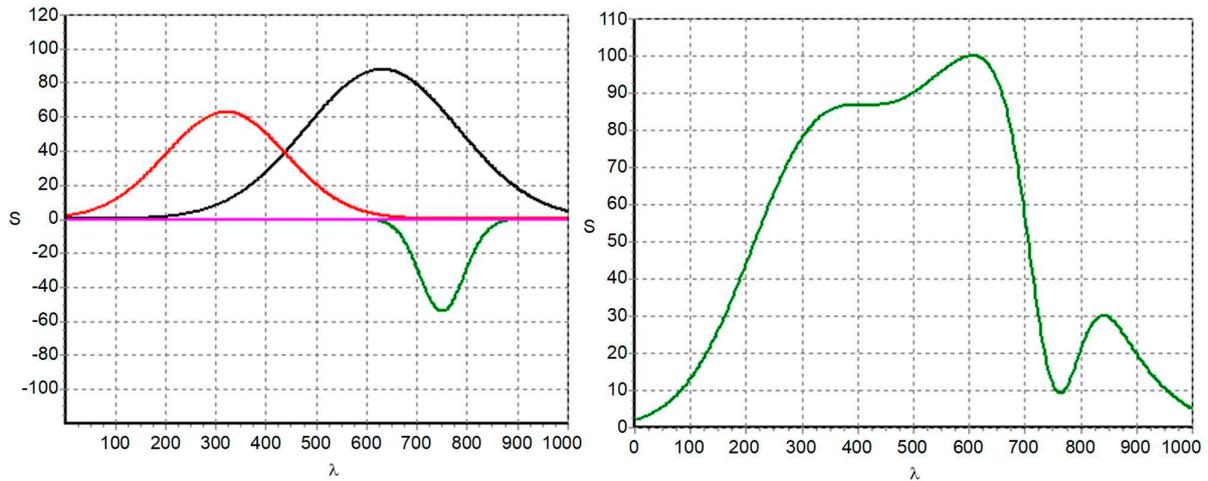Fig. 3. Functional model of the formation of informative signals

Fig. 4. Example of synthesis of spectral characteristics at $n = 3$

The nominal value of the signals S_{SP} is calculated in a normalized and dimensionless form based on the integration of the product of the synthesized spectra

$$S_{SP} = \int_{\lambda_{MIN}}^{\lambda_{MAX}} \left(S_A(\lambda) \cdot S_M(\lambda) \cdot S_S(\lambda) \right), \qquad (5)$$

where λ_{MIN} and λ_{MAX} are the minimum and maximum wavelengths.

The informative signals of the measurement process are changes in the values of ΔS_{SP}, which are caused by the modulation of the spectral characteristics of the medium $S_{M1}(\lambda)$, $S_{M2}(\lambda)$, $S_{Mi}(\lambda)$

$$\Delta S_{SP} = \int_{\lambda_{MIN}}^{\lambda_{MAX}} \left(S_A(\lambda) \cdot S_{M2}(\lambda) \cdot S_S(\lambda) \right) -$$
$$- \int_{\lambda_{MIN}}^{\lambda_{MAX}} \left(S_A(\lambda) \cdot S_{M1}(\lambda) \cdot S_S(\lambda) \right). \qquad (6)$$

The sensitivity of the measurement transformation in relative units is determined by the partial derivative

$$K_{SREF} = \frac{d(S_{SP})}{dc}, \qquad (7)$$

where c – the measured value of the concentration of pollutants.

The sensitivity of the measurement conversion in absolute units is determined by the ratio of the change in the signal ΔS_{SP} to the sum of its initial (nominal) value S_{SPN} and the interference (parasitic offset) S_{OFF} caused by external light sources

$$K_{SABS} = \frac{\Delta S_{SP}}{S_{SPN} + S_{OFF}}. \qquad (8)$$

Typical examples of the results of model studies of the formation of spectral characteristics SP and informative signals (Signal) of express indicators of the concentration of substances (gases) are presented in Fig. 5, 6, where λ is the wavelength of electromagnetic radiation. For example, the signal values are calculated by the above method by integrating the product of the spectra of sensitive films (Film) and LED. For simplicity, the spectral characteristic of the photodiode is not taken into account. Two cases are given, which present the formation of signals in the middle part (Fig. 5) and at the boundary (Fig. 6) of the spectrum of optical transparency of the sensitive film.
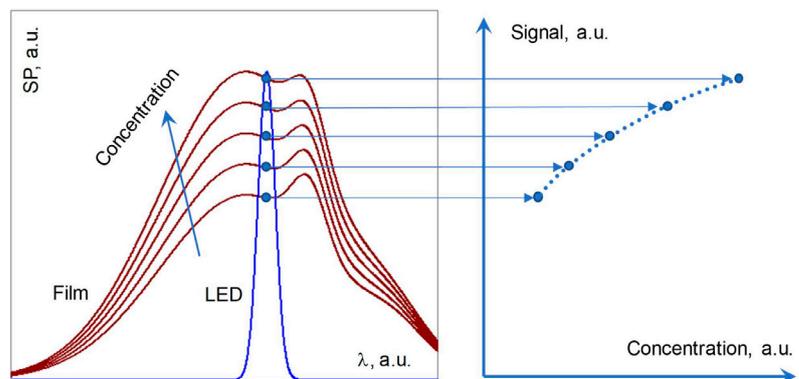

Fig. 5. Model studies of signal formation in the middle part of the optical transparency spectrum of a sensitive film
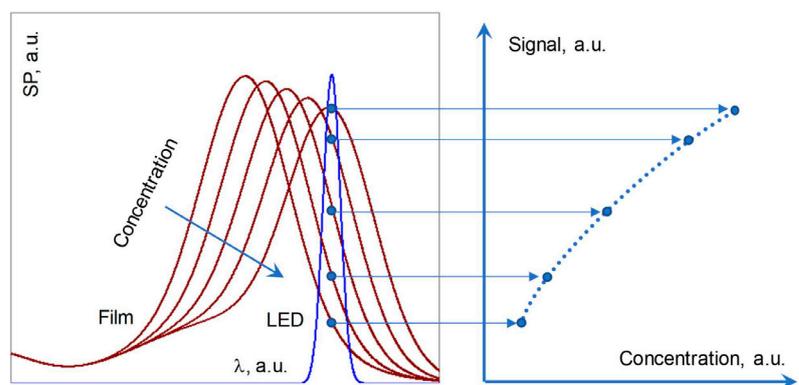

Fig. 6. Model studies of signal formation at the optical transparency spectrum boundary of a sensitive film

As can be seen from the examples given, the spectral characteristics in different parts of the spectrum significantly depend on the concentration of the analyte (the gas under study), which allows to construct calibration curves and determine their content in the environment.

5. 2. Method for forming an optical signal of increased sensitivity and development of a specialized noise-resistant signal conversion path

In the development of the colorimetric measurement method, a combined method for determining the quantitative parameters of changes in the spectral characteristics of a sensitive film is proposed. The peculiarity of this method, the model representation of which is shown in Fig. 7, is the measurement of informative signals when combining the processes of transmission and reflection of light fluxes. In such a structural model, the LED Array LED matrix and the PD & CL Array photodiode matrix are located in the same plane.
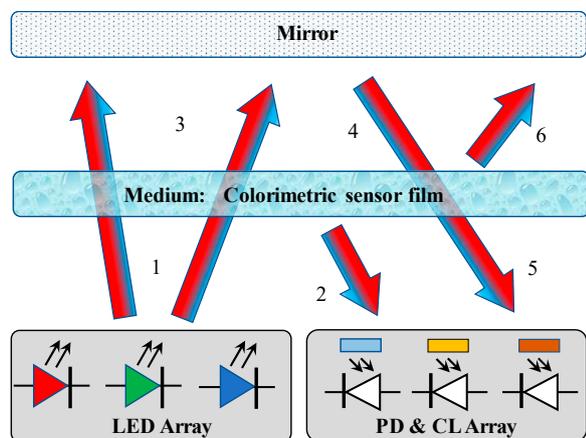

Fig. 7. Model of formation of informative signals with a combination of the processes of passage and reflection of light fluxes

The light fluxes emitted by the LED matrix (1) are partially reflected (2) from the Colorimetric sensor film. sensor film, and also partially penetrate (3) through the film and are reflected (4) from the mirror surface Mirror placed behind it. Then there is a re-penetration (5) of these light fluxes into the sensor film. There are reflection processes (6) from the back side of the film with subsequent secondary reflection from the mirror surface. Thus, the processes of penetration and reflection occur repeatedly. The proposed combined method is characterized by increased sensitivity of determining the quantitative parameters of changes in the spectral characteristics of the sensitive film, which is explained by the multiple process of passage and reflection. In addition, this method expands the functionality of the measurement method, because sensitive films can be oriented both to penetration and reflection of rays.

A significant problem in the implementation of the signal path of optoelectronic sensor devices is the high level of parasitic radiation from extraneous light sources. In particular, these are solar radiation or artificial lighting sources. The level of their radiation is variable in time and can significantly exceed the level of radiation from the LEDs of the signal path. Traditional methods of rejecting parasitic radiation and selecting informative signals based on frequency filters are not effective enough. Therefore, in order to solve this problem, research has been conducted within the framework of this work to develop a specialized noise-resistant signal conversion path.

The operation of the signal path is based on the synchronous detection method and is implemented in the modern concept of a mixed signal front- end (Mixed Signal Front-End).

The functional diagram (Fig. 8) of such a signal path contains: LED – light-emitting diode, MD – medium (sensor film), PD – photodiode, LDR – LED power driver, TIA – trans-impedance amplifier, BPF – bandpass filter. Also required are CNT – measurement process controller, SHD – synchronous detector, LPF – low-pass filter or integrator, PGA – program-controlled amplifier, ADC – analog-to-digital converter.
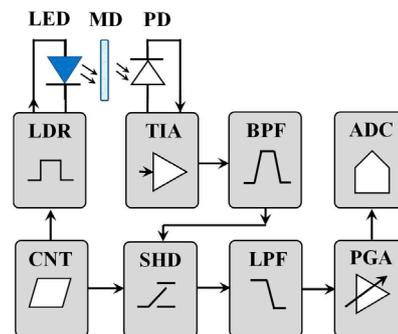

Fig. 8. Functional diagram of the signal path

The signal path operates in a pulsed mode with a certain frequency of LED power pulses. Most often, the pulse frequency is several kilohertz. The pulse duration is within 0.01...1 ms and is determined by a compromise between the speed and power consumption of the optoelectronic sensor device. The primary signal conversion of the photocurrent of the photodiode PD into voltage is carried out by a transimpedance amplifier TIA, which provides high linearity and speed of the measurement process.

Next, the first stage of spurious radiation rejection is performed using a bandpass filter BPF. As already noted, the efficiency of such rejection is not sufficient. Therefore, the second stage of rejection is used using a synchronous detector SHD and subsequent low-pass filtering LPF or signal integration.

Synchronous detection is implemented by one of two methods. The first method involves multiplying the instantaneous values of the input signal and the pulses of the CNT measurement process controller. The second method involves switching the polarity of the input pulses with control from the CNT. Operation in a wide range of signal amplitudes is provided by an amplifier with a software-controlled gain coefficient PGA, which normalizes the ADC input voltage level.

In order to perform functional analysis and optimize measurement conversion modes, models of the analog front-end AFE were developed within the framework of this work. They are based on SPICE simulation models [11], which are used in most modern computer-aided design systems.

A simplified functional diagram of the SPICE model of the signal path used for functional analysis is shown in Fig. 9. The SPICE model diagram consists of the following components: IPB – source of the useful component of the photocurrent; IPS – source of parasitic low-frequency components of the photocurrent; XN – source of parasitic high-frequency components of the photocurrent; VC – source of control pulses; R1, C1 – input filtering circuits; XM – synchronous detector multiplier; R2, C2 – input filtering circuits. In the optimization problems of measurement conversion modes, more complex SPICE models are used, which use a significantly wider set of

components, in particular – components of analog switches, operational amplifiers, active filters, etc. Illumination these models is not within the scope of this work.

For each of the functional blocks of this circuit, the output signal plots are analyzed. Example of informative and parasitic DC (Direct Current) AC (Alternative Current) signal components are presented in Fig. 10, and examples of signals in the process of their conversion are shown in Fig. 11, 12.

Analysis of the shapes of these signals forms the basis for further parametric optimization of the signal path. In particular, Fig. 13 shows an example of signal formation at the output of an LPF or integrator. The duration of signal settling is determined by the reactive properties of the filter or integrator.
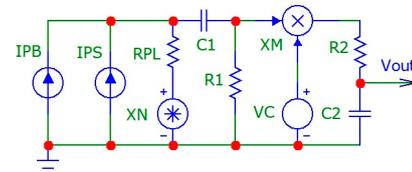

Fig. 9. Simplified functional diagram of the SPICE model of the signal path: IPB — sources of the useful component of the photocurrent; IPS — sources of parasitic low-frequency components of the photocurrent; XN — sources of parasitic high-frequency components of the photocurrent; VC — sources of control pulses; R1, C1 — input filtering circuits; XM — synchronous detector multiplier ; R2, C2 — output filtering circuits
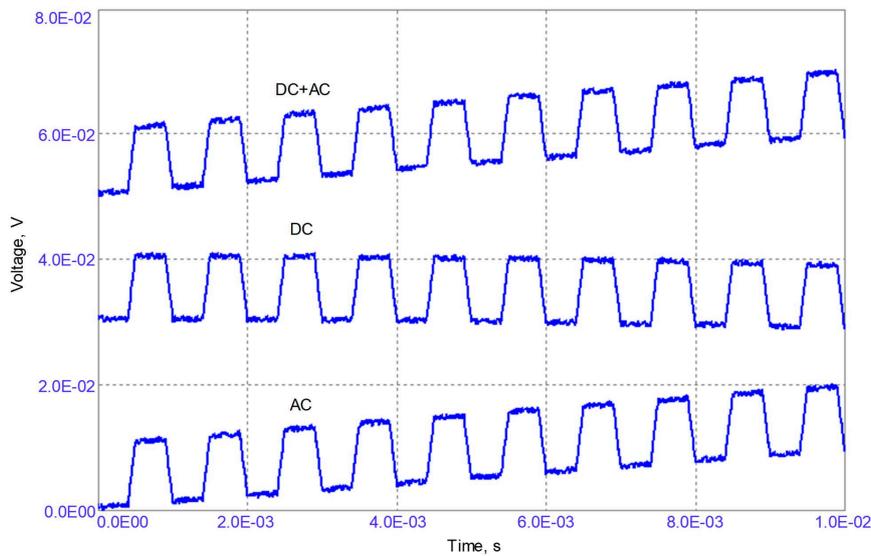

Fig. 10. Diagrams of informative and parasitic signal components
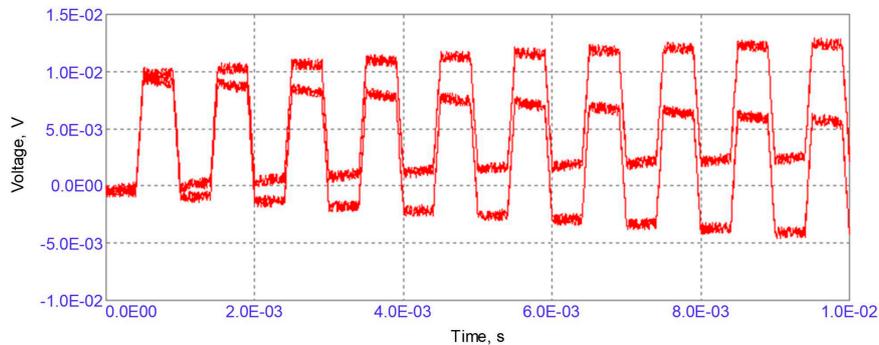

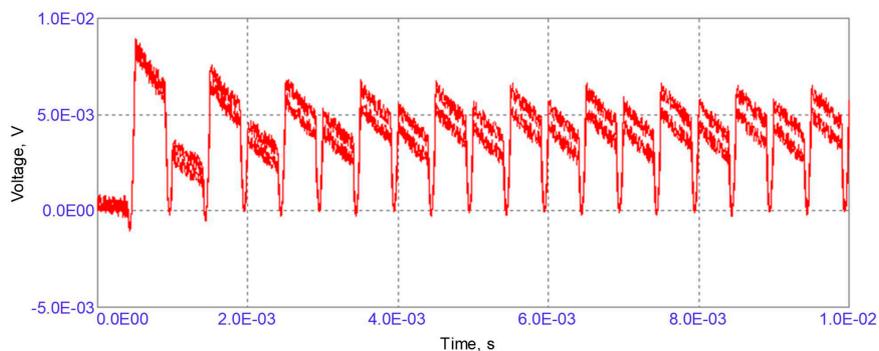Fig. 11. Signal diagrams at the output of a transimpedance amplifier

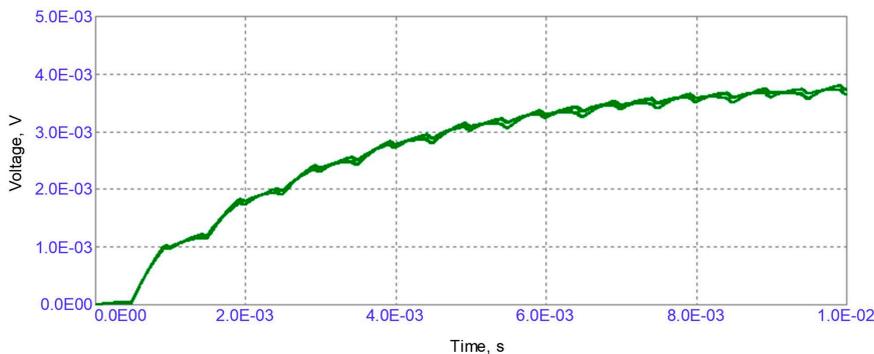Fig. 12. Signal diagrams at the output of the synchronous detector

Fig. 13. Signal diagrams at the output of an LPF or integrator

5. 3. Development of an optical gas sensor prototype for analyzing gas-stimulated changes in optical absorption at different wavelengths

To test the signal generation and registration system, a prototype of an optical gas detector based on a polyaniline sensor element with a microcontroller USB module was manufactured. The design of the optical gas sensor is shown in Fig. 14, and an image of the prototype of the internal part of the signal converter is shown in Fig. 15. The structure of the sensor element with an active polyaniline layer is shown in Fig. 1.

Using this sensor, ammonia vapors were analyzed online using the change in optical absorption under the influence of ammonia at different wavelengths (respectively, for red, green, and blue LEDs). The difference in the change in optical absorption for different combinations of these colors was also analyzed. Fig. 16, 17 shows the computerized results of

the analysis of ammonia content in the environment in real time. The magnitude of the optical response extrema available on the monitor for different wavelengths and selected combinations of their differences corresponds to the concentration of ammonia in relative units. These results can be described in percentage, pressure units, ppm or other units, using appropriate calibration.

The repeatability of such measurements exceeds 10^2 times. From Fig. 16, 17 shows that the time of recovery of optical transmission to the initial values does not exceed 10 s. This is 5 or more times less than the recovery rate of known sensors [4, 15]. Such a high recovery rate of the sensor can ensure its multiple reversibility and opens up prospects for effective practical use.

The presented layout of an optical gas sensor allows the practical use of the proposed functional diagram of the signal path of a portable toxic gas detector.
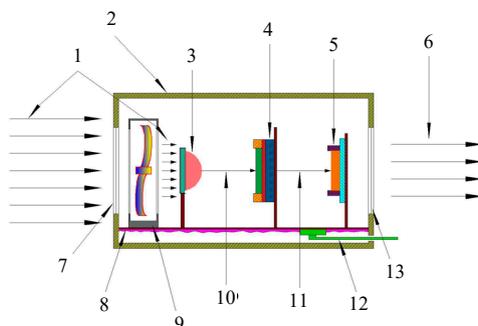

Fig. 14. Design of an optical gas sensor: 1 — air flow with analyte ; 2 — gas sensor housing; 3 — LED; 4 — sensor element; 5 — photodiode; 6 — air outlet with analyte ; 7 — analyte inlet window ; 8 — control board; 9 — fan; 10 — polychromatic radiation; 11 — sensor film transmission; 12 — connecting bus; 13 — analyte outlet window

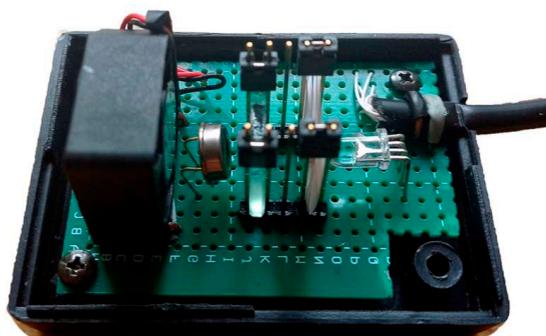
Fig. 15. Photo of the layout of the internal part of the signal converter of the optical gas sensor. The dimensions of the signal converter are 6 × 4 × 3 cm
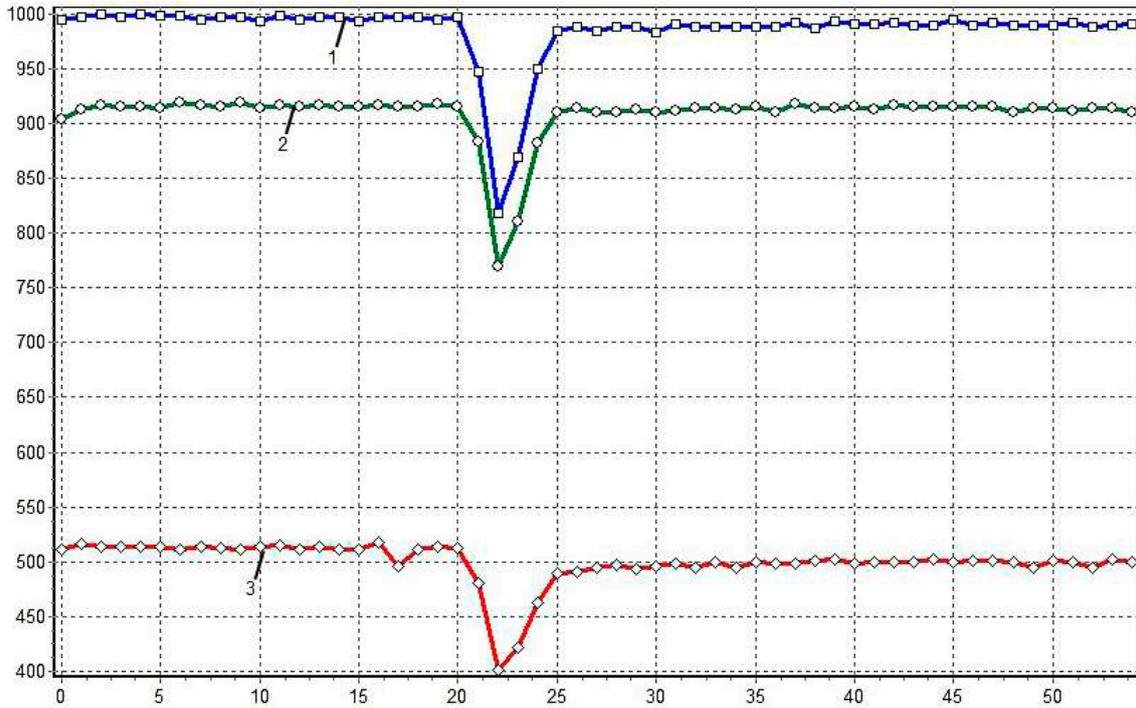
Fig. 16. Screenshot of the image on the computer monitor of the extremes of the optical response when ammonia acts on a polyaniline sensor element for different wavelengths: $1 - \lambda_B = 470 \pm 5$ nm; $2 - \lambda_G = 528 \pm 7$ nm; $3 - \lambda_R = 623 \pm 5$ nm

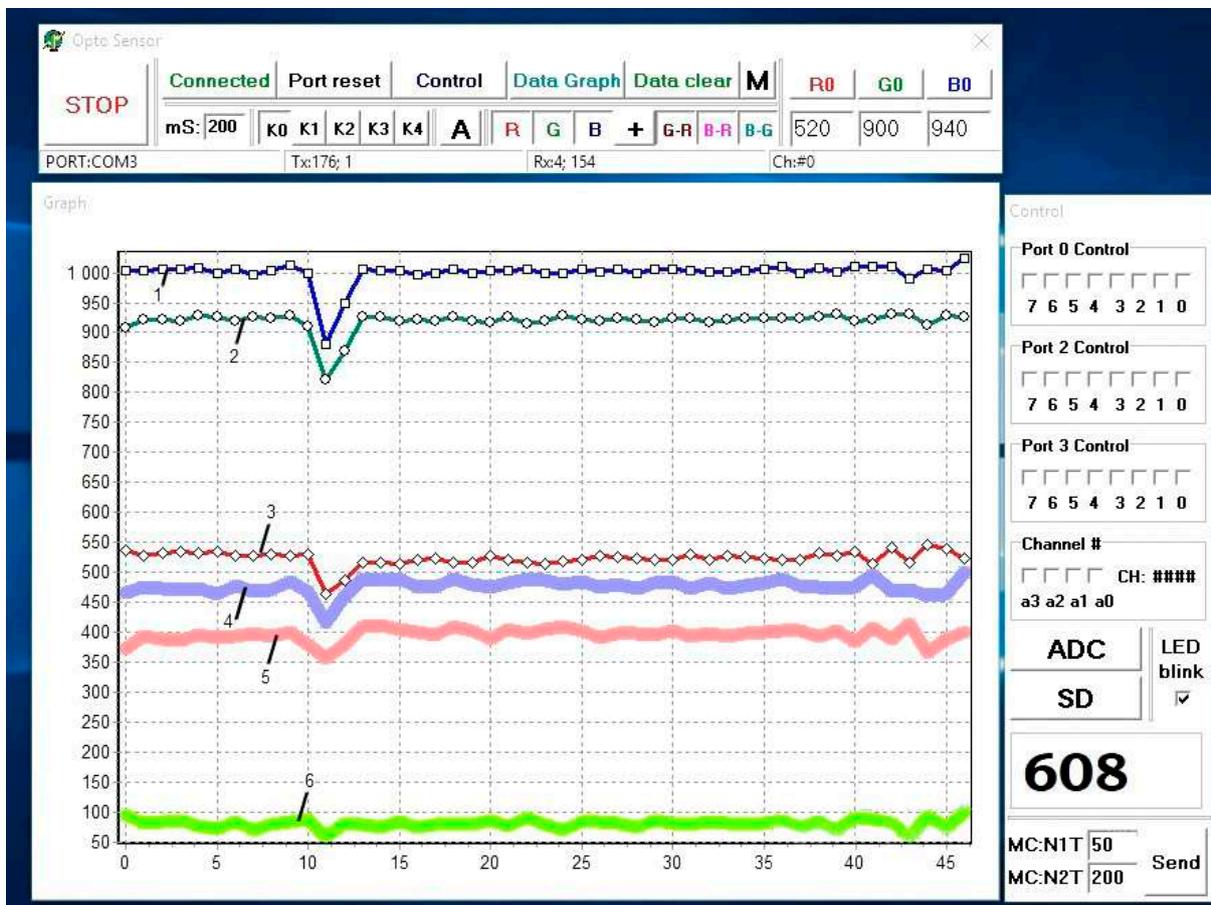Fig. 17. Screenshot of the image on the computer monitor of the extremes of the optical response for different wavelengths and the difference in response for their selected combinations when ammonia acts on the polyaniline sensor element: $1 - \lambda_B = 470 \pm 5$ nm; $2 - \lambda_G = 528 \pm 7$ nm; $3 - \lambda_R = 623 \pm 5$ nm; $4 - \Delta\lambda_{G\text{-}R}$; $5 - \Delta\lambda_{B\text{-}R}$; $6 - \Delta\lambda_{B\text{-}G}$

6. Discussion of the results of research into the ways of forming information signals in an optical gas detector

A hardware-software optoelectronic sensor device has been developed, the informative signals of which are used for express indication of volatile components of pollutants. As a result of the research conducted in this work, the optical signal registration and processing systems in a colorimetric gas detector have been improved and this system has been tested in a mock-up of an optical gas sensor with an active element based on an electrically conductive conjugated polymer – polyaniline.

For this purpose, a functional and mathematical model of the signal path of a portable pollutant detector has been developed. Their construction is based on a colorimetric measurement method with the formation of a family of informative signals, on the basis of which quantitative parameters of experimental changes under the influence of gases are determined. The proposed functional model, shown in Fig. 3, is implemented by multispectral optocouplers, the structure of which includes a matrix of LEDs with different emission spectra and a matrix of photodiodes with a corresponding set of spectral filters. The family of informative signals is formed as a result of modulation of the intensity of light fluxes, which is due to a change in the spectral characteristics of the colorimetric sensor film. The developed mathematical model of the formation of informative signals uses the basis of Gaussian functions and is described by equations (2)–(4). Typical examples of the results of model studies of the formation of spectral characteristics and informative signals of express indicators are presented in Fig. 5, 6 for different spectral ranges of optical transparency of the sensitive film. As can be seen from the examples given, the spectral characteristics in different parts of the spectrum significantly depend on the gas concentration, which allows to construct calibration curves and determine the gas content in the environment.

A method for forming an optical signal with enhanced sensitivity is proposed is proposed (Fig. 7). Increased sensitivity in determining the quantitative characteristics of changes in the spectral properties of the sensor element is due to the multiple process of passage and reflection of light fluxes. The novelty of such a solution is the measurement of informative signals with a combination of the processes of passage and reflection of light fluxes, which is ensured by placing the LED Array matrix and the PD & CL Array photodiode matrix in the same plane. Additionally, this approach expands the capabilities of the measurement method, since sensitive films can operate both in the transmission mode and in the reflection mode of light rays. The built-in interface allows to easily integrate the sensor into various electronic systems. The device has a programmable threshold function and generates hardware interrupts when the set illumination values are exceeded, which allows to reduce the load on the processor and reduce power consumption.

A specialized noise-resistant signal conversion path has been developed, the high efficiency of which is based on a combination of frequency selection and synchronous detection methods. The functional diagram of the signal path and a simplified functional diagram of the SPICE model of the signal path are shown in Fig. 8, 9. The functioning of the signal path occurs in the pulse mode of operation with a given frequency of LED power pulses. In known colorimetric sensor systems [8, 10, 12], in particular, with indicator substances based on thin films of electrically conductive conjugated polymers and their composites [4, 14, 15], such use was not. The diagrams of the output signals of individual functional blocks of the developed circuit (Fig. 10–12) allowed perform parametric optimization of the signal path. The duration of the establishment and periodicity of these signals was determined by the reactive properties of the filter or integrator.

An improved signal generation and registration system was tested in a mock-up of an optical gas sensor with a polyaniline active element, and the gas-stimulated change in optical absorption at different wavelengths was analyzed online.

A design (Fig. 13) and a model of a gas detector (Fig. 14) were developed, which belongs to portable colorimetric devices with appropriate software for generating an informative signal.

The fact that informative signals are formed by modulation of the intensity of light fluxes at different wavelengths allows to provide improved selectivity of the gas detector. After all, different gases differently change the optical absorption of the sensor film in different regions of the optical spectrum. From Fig. 15 it is seen that the optical absorption in the presented gas sensor under the action of ammonia for different wavelengths, as well as for their various combinations, differs by 2 times or more. The repeatability of such measurements exceeds 10^2 times. When analyzing in the online mode of gas-stimulated changes in optical absorption at different wavelengths (Fig. 16, 17) it is seen that the time of recovery of optical transmission to the initial values does not exceed 10 s. This is 5 or more times less than the recovery rate of known sensors. Such a high recovery rate of the sensor can ensure its multiple reversibility and opens up prospects for effective practical use.

Therefore, the results of this study demonstrate the advantages of using the proposed methods by amplifying useful signals and reducing the impact of spurious radiation. to improve the performance of optical gas detectors.

However, when using the developed gas detector, it is not advisable to carry out measurements at temperatures higher than 100°C due to the possibility of some decrease in the sensitivity of the sensor film under the influence of high temperatures. The disadvantage of the conducted study is the lack of specific examples of toxic gas recognition when using the manufactured sensor element, which was not part of the task of the work and will be the subject of further work.

The development of this study involves the development of new nanomaterials and composites for active layers of optical sensors. use in sensor devices of the Internet of Things (IoT), including with the use of artificial intelligence technologies [18, 19]. Provided that the developed sensor and the corresponding software are equipped with an IoT card, a corresponding platform and a network for connecting the device to the platform, the process of data transmission between the detector and any physical devices will become possible, in particular, recorders for monitoring the state of the ambient atmosphere and production premises, the freshness of food products, harmful gas leaks near landfills, chemical storage sites, etc.

7. Conclusions

1. Functionality developed and mathematical models of the signal path of a colorimetric pollutant detector. Model studies of the formation of spectral characteristics and infor-

mative signals were carried out for different spectral ranges of the optical transparency sensitive films. It has been shown that spectral characteristics in different parts of the spectrum significantly depend on gas concentration, which allows determining the content of gases in the environment.

2. A method of forming an optical signal of increased sensitivity due to multiple passage and reflection of light fluxes has been proposed, and a specialized path of noise-resistant signal conversion has been developed. This allowed improving the characteristics of the gas detector, its sensitivity and speed, and provided the possibility of detecting harmful substances under various lighting conditions "in the field", and analyzing the results of detecting harmful gases in the "on-line " mode.

3. A prototype of an optical gas sensor was developed and its testing was carried out – analysis of ammonia vapors in online mode, using gas-stimulated change in optical absorption at different wavelengths, namely, 470, 528 and 623 nm. The obtained plots of the output signals of individual functional blocks of the developed circuit allow perform parametric optimization of the signal path.

Conflict of interest

The authors declare that they have no conflict of interest regarding this study, including financial, personal, authorship, or other, that could influence the study and its results presented in this article.

Financing

Data availability

The manuscript has no associated data.

Use of artificial intelligence

The authors confirm that they did not use artificial intelligence technologies when creating the presented work.

Authors' contribution

Olena Aksimentyeva: conceptualization, resources, data curation, **writing, supervision,** project administration, fundraising; **Roman Holyaka:** terminology, conceptualization, methodology, software, investigation, writing – draft preparation; **Bohdan Tsizh:** formal analysis, investigation, writing – review and editing, project administration; **Grygoriy Barylo:** methodology, verification, investigation, resources.

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