M. E. ESHKOBILOVA

DEVELOPMENT OF HIGHLY SENSITIVE CHEMICAL SENSORS FOR METHANE DETECTION AND MONITORING

MONOGRAPH

SAMARQAND

M.E. Eshkobilova. " Development of highly sensitive chemical sensors for methane detection and monitoring

"

Monograph. 2024. 110 pages.

Reviewers:

Khalikov K.M. – Head of the Department of Biological Chemistry, Professor Samarkand State Medical University

I.E. Abdurakhmanov – Head of the Department of Chemistry, Professor Samarkand State University

INTRODUCTION

In the context of rapid industrial expansion across multiple sectors of the economy, the development of chemical sensors and alarm systems plays a critical role in ensuring fire and explosion safety in both industrial and residential environments. Among the various risks, methane explosions pose one of the most severe threats. Methane becomes explosive when its concentration in the air ranges between 5% (lower explosive limit) and 16% (upper explosive limit).

The Republic currently produces over 64 billion cubic meters of natural gas annually, with methane as its primary component. As production and consumption of natural gas continue to grow, the demand for fast-acting, reliable detection systems for methane leaks and accumulations becomes increasingly urgent. Effective monitoring of methane concentrations is vital to prevent catastrophic accidents in both domestic and industrial settings.

Globally, there is a growing focus on the design and implementation of affordable, high-performance chemical sensors capable of promptly identifying the presence of natural gas in the air. Comparative analysis of international trends highlights thermocatalytic and semiconductor-based sensors as the most effective technologies for mitigating explosion risks. With ongoing development in energy, transport, and particularly the oil and gas sectors, the standards for explosion prevention are becoming increasingly rigorous worldwide.

The growing demand for rapid, sensitive, and selective gas detection technologies highlights the critical importance of advancing research in this field. Reliable identification of explosive gas mixtures, especially in enclosed or environmentally sensitive areas, is essential for safeguarding both human lives and the environment. In this context, the Republic has made notable progress in developing domestic gas analyzers aimed at replacing imported equipment, particularly for monitoring industrial process gases. Furthermore, Uzbekistan’s national development strategy emphasizes the production of high-value-added goods through the in-depth processing of local raw materials. This includes fostering innovation and introducing new tech-

nologies to enhance the global competitiveness of local products. Within this framework, guaranteeing explosion and fire safety is a fundamental requirement—especially across key sectors such as industry, transportation, and public utilities—where the risks associated with gas use are most acute.

This monograph research to a certain extent serves to fulfill the tasks provided for in the Decree of the President of the Republic of Uzbekistan UP-4947 of February 7, 2017 "On the Strategy of Actions for the Further Development of the Republic of Uzbekistan", in the Resolutions of the President of the Republic of Uzbekistan PP-3479 of January 17, 2018 "On measures to stably provide the country's economic sectors with demanded types of products and raw materials" and PP-3983 of October 25, 2018 "On measures to accelerate the development of the chemical industry of the Republic of Uzbekistan", as well as other regulatory and legal documents adopted in this area.

The relationship of the research with the main priority areas of development of science and technology in the republic. This study was carried out in accordance with the priority direction of development of science and technology of the Republic VII “Chemical technologies and nanotechnologies”.

Across the globe, particularly in highly industrialized nations, there is ongoing, systematic research focused on the development of advanced technologies and methodologies for detecting toxic, flammable, and explosive gases. A major emphasis is placed on designing fast-responding, highly sensitive sensors capable of reliably assessing the explosive potential of gas mixtures, especially within enclosed or environmentally controlled settings.

Prominent international researchers—such as Tang M., Stamataki M., Chang J.F., Corcoran P., Shurmer H.V., Gardner J.W., Jin W., Ho H.L., Cao Y.C., Ju J., and Qi L.F.—have significantly contributed to innovations in gas mixture analysis and sensor technology.

Within the Commonwealth of Independent States (CIS), scientists like Shcherban A.N., Furman N.I., Karpov E.F., Golinko V.I., Ryazanov A.V., Molodechkin M.O., Sysoev V.V., Zyuryukin Yu.A., Lashkov A.V., and

Dobrokhotov V.V. have conducted pioneering research in environmental monitoring. Their efforts include the development of thermocatalytic sensors designed to detect combustible gases and vapors.

Uzbekistani researchers, including T.K. Khamrakulov, N.S. Zakirov, R.Kh. Dzhiyanbaeva, A.M. Gevorgyan, A.M. Nasimov, E.A. Abdurakhmanov, and Z.A. Smanova, have also made significant scientific contributions. Their work has advanced national capabilities in designing sensor systems and analytical methods for monitoring environmental conditions, supporting both ecological safety and industrial risk reduction.

With the rapid evolution of technology and advancements in analytical monitoring systems, there is a growing demand for methods that offer greater sensitivity and selectivity in detecting various chemical substances. One of the most forward-looking approaches in this area involves the development of sensors based on semiconductor and thermocatalytic technologies for monitoring concentrations of flammable, explosive, and toxic gases.

In this context, creating next-generation sensors capable of accurately identifying hazardous gases—particularly methane—remains a critical challenge. Methane detection is especially vital due to its widespread use and high explosion risk. The need for innovative, efficient detection systems is particularly acute in high-risk environments such as industrial sites, transportation networks, and public utility facilities. Consequently, advancing thermocatalytic and semiconductor-based methods for precise methane identification within complex gas mixtures continues to be a top priority in the pursuit of enhanced fire and explosion safety.

The connection of the monograph topic with the research work of the higher educational institution, whe re the monograph was completed. The Monograph research was completed within the framework of the plan of scientific research works of applied projects carried out at Samarkand State University on the topic IDT-12-07 "Development of physicochemical bases and technology of synthesis of hybrid organo-inorganic gas-sensitive nanomaterials for chemical sensors of new

generation" (2012-2014) and OT-F7-84 "Development of sensor sensors for the production of gas sensitive materials for the synthesis of natural gas" (201-2-20).

The goal works is the development of sensitive, selective thermocatalytic sensors for methane (natural gas) using nanomaterials obtained using the sol-gel process and creating highly efficient natural gas alarms and analyzers based on them.

The primary aim of this research is to investigate the oxidation mechanisms of combustible gases and to develop a catalyst composition for a selective thermocatalytic sensor that detects methane. A key focus will be identifying optimal conditions that ensure the sensor's stability, selectivity, and sensitivity for detecting explosive concentrations of natural gas in the air of enclosed ecological systems.

Another goal is to develop fast-response, reliable detection methods and alarm systems for identifying methane leaks and accumulations in both industrial and domestic environments. This includes creating sensitive and efficient techniques that can provide real-time monitoring of methane in these settings.

Further, the research will explore the sol-gel synthesis processes for producing gas-sensitive nanocomposites, which will be used in the creation of a highly responsive semiconductor methane sensor.

Additionally, the study aims to combine semiconductor and thermocatalytic sensor technologies to develop a two-channel methane analyzer capable of continuously monitoring methane in air and process gases.

The project will also involve assessing the metrological and analytical properties of the methane analyzer through laboratory tests, followed by the deployment of these sensors in industrial production environments.

Objects of research: This study focuses on catalytically active metal oxides, natural gas, propane-butane mixtures, exhaust gases from combustion systems, methane, and standardized gas mixtures.

Subject of research: The research delves into the chemistry of oxidation reactions in combustible substances, the principles behind sol-gel synthesis of gas-sensitive nanomaterials, and the analytical performance characteristics of selective thermocatalytic and semiconductor methane sensors.

Research methods. Gas chromatography, IR spectroscopy, differential thermal analysis, potentiometry, photocolorimetry, conductometry, viscometry.

Scientific novelty of the research is as follows:

- for the first time, using selected optimal conditions and selective catalysts of measuring and compensating elements of the TCS, high sensitivity and selectivity of determining CH_4 from the composition of atmospheric air in closed ecological systems has been ensured;

- for the first time, a targeted synthesis of a HFM for a semiconductor CH_4 sensor was carried out using the sol-gel technology method based on ZnO and CoO. Using a HFM based on SiO_2/ZnO+CoO, a decrease in the temperature sensitivity threshold and an increase in the selectivity of semiconductor sensors for natural gas were ensured;

- a combined analyzer has been developed, based on the use of a thermocatalytic and semiconductor sensor, ensuring the determination of methane in a wide range of its concentrations;

- the influence of various factors on the metrological, operational and other parameters of semiconductor CH_4 sensors based on SiO_2/ZnO+CoO was revealed.

Practical results of the research are as follows:

a composition of the catalyst of sensitive elements and the design of a thermocatalytic sensor providing selective control of the explosive concentration of natural gas from the composition of the atmospheric air of industrial and housing and communal facilities is proposed;

the optimal temperature-time regime, composition and ratio of the initial components of sol-gel synthesis were recommended and the production of highly sensitive GCM for a selective semiconductor sensor of CH_4 was achieved;

developed with Selective sensors are proposed for use in a methane alarm and two-channel analyzer.

Reliability of the results obtained proven by such modern physical and chemical methods as conductometry, potentiometry, gas chromatography, photocolorimetry, microscopic and differential thermal methods of analysis.

Conclusions are made on the basis of experimental results processed by methods of mathematical statistics. Scientific and practical significance of the research results**.** The scientific significance of the research results lies in finding selective catalysts and optimal conditions for thermocatalytic methane sensors; formation of selective gas-sensitive nanocomposites based on Zn oxide using the sol-gel process and with creation of selective semiconductor sensors for methane and natural gas and based on them.

The practical significance of the work lies in increasing the expressiveness and reducing the detection limit of methane from the atmospheric air of industrial and domestic premises. The created sensors as part of alarms and automatic analyzers will find wide application in solving important social, environmental and economic problems of monitoring environmental objects, and the safe operation of a number of explosive industries. Based on the results of scientific research on the development of chemical sensors for monitoring methane from atmospheric air:

Thermocatalytic sensors and methane leak and accumulation control alarm have been implemented in the practice of the analytical laboratory of Mubarek Gas Processing Plant LLC (certificate of Mubarek Gas Processing Plant LLC No. 45/GK-18-07 dated February 25, 2018). As a result, the developed sensors as part of the methane leak and accumulation control alarm have made it possible to prevent fire and explosion hazards in industrial conditions. At the same time, the developed thermocatalytic alarm is characterized by high expressivity and selectivity.

Semiconductor sensors and an automatic gas analyzer developed on their basis have been introduced into the practice of the analytical laboratory of Mubarek Gas Processing Plant LLC (certificate of Mubarek Gas Processing Plant LLC No. 45/GK-18-07 dated February 25, 2018). As a result, the developed sensors as part of the alarm ensure the detection of methane in a wide range of its concentrations in the atmospheric air of closed ecological systems (industrial and domestic premises).

I. METHODS AND INSTRUMENTS FOR METHANE DETECTION IN AIR-GAS MIXTURES

Methane, a primary component of natural gas, is one of the most commonly encountered flammable gases. Various sensors and devices have been developed for monitoring methane concentrations in the atmosphere. However, these devices often suffer from significant drawbacks, including their bulky size, inadequate measurement accuracy, and lack of selectivity. As a result, there is a pressing need to design more effective sensors capable of detecting explosive levels of methane (natural gas) in the air, particularly within residential, industrial, and domestic environments. Addressing this challenge requires the creation of advanced monitoring systems that can accurately assess the explosiveness of the surrounding atmosphere.

Existing techniques for detecting the explosive content of gas mixtures rely primarily on the distinct physical and chemical properties of the gases involved. These methods leverage variations in these properties to evaluate the concentration of hazardous gases. Some of the key properties of gases that influence measurement accuracy are summarized in table 1.1.

Table 1.1.

Physicochemical properties of gases

Name of the quantity	Unit of measurement	The value of the value for gases				
		Air	CH_4	C_2H_6	H_2	CO
Density	Kg/m3	1,293	0.717	1,357	0.0899	1.25
Specific heat of combustion	J/Kmol	-	892 106	1562 106	287 106	283 106
Thermal conductivity	W/(m K)	2.4 10^{-2}	3.1 10^{-2}	1.8 10^{-2}	17.9 10^{-2}	2.35 10^{-2}
Heat capacity	KJ/(Kmol K)	29.15	39.82	51.9	28.76	28.47
Autoignition temperature	^{0}WITH	-	645	472	510	610
Lower explosive limit	% about.	-	5	3.2	4	12.5
Upper explosive limit	% about.	-	15	12.5	75.2	74.2

One distinguishing feature of all combustible gases, setting them apart from other air contaminants, is their calorific value. Gases such as methane, hydrogen, ethane, and carbon monoxide, commonly found in mine atmospheres, are capable of undergoing oxidation when exposed to atmospheric oxygen. Of these gases,

methane has the highest ignition temperature, a characteristic attributed to the relatively strong atomic bonds within the methane molecule.

When it comes to detecting combustible gases and vapors, thermocatalytic and semiconductor sensors are the most selective and sensitive. These technologies outperform other methods, including optical, thermoconductometric, and electrochemical sensors, in terms of their ability to detect and differentiate combustible gases. While optical sensors may provide similar signals for some gas groups, they generally lack the specificity and responsiveness of thermocatalytic and semiconductor-based sensors. [3; pp. 2-10].

1.1.Optical methods and devices for determining combustible gases.

Optical methods, alongside chromatographic and electrochemical techniques, are key components of modern analytical chemistry. These methods rely on the interaction between substances and electromagnetic radiation, and they encompass various approaches for detecting hydrocarbons.

One widely applied method for monitoring methane levels in the atmosphere is the refractometric technique, which leverages the difference in the refractive indices of light in methane and air. This method has proven useful in the development of portable sensors and analyzers. One of its primary advantages is its low inertia, which allows for quick response times. However, implementing this benefit in stationary gas analyzers is challenging due to the need to protect the sensor’s optical elements from contamination. As a result, refractometric sensors have not seen widespread use in practical applications.

Among optical methods, the optical absorption technique is particularly noteworthy for its role in the development of methane sensors and gas analyzers. The selectivity of optical absorption sensors for methane is typically achieved by employing either specialized optical-acoustic beam receivers or monochromatic light sources tuned to wavelengths that correspond to methane's peak absorption. While the use of optical-acoustic beams improves selectivity, it complicates the design, making these analyzers bulky and energy-intensive, with the added drawback of increased sensor inertia due to the need for lens protection.

Fourier spectroscopy, another optical method, involves obtaining spectra by performing a Fourier transform on the interferogram of the analyzed radiation. This technique provides accurate concentration data for all gas components present. The first implementation of Fourier spectroscopy sensors utilized open-path configurations, where a light beam travels through a chamber containing the gas mixture. While effective, these systems require large chambers to achieve sufficient sensitivity, resulting in bulky setups. More modern approaches use fiber optic cables as the gas chamber, which reduces size but sacrifices sensitivity. In these systems, the gas interacts with micro-holes in the fibers, and the light absorbed at the phase boundary of the solid phase offers a less precise measurement.

A different optical method, photoacoustic spectroscopy, operates on the principle of sound emission caused by the absorption of light by a gas. This technique is advantageous because it does not produce a background signal, ensuring cleaner results. However, it comes with two main drawbacks that hinder its use in portable methane gas analyzers. Firstly, the equipment tends to be large and complex, and secondly, more accurate measurements require longer path lengths—the physical distance the light travels through the gas mixture—leading to larger, less practical devices.The portable photo-ionization gas analyzer "KOLION-1" is designed to monitor methane (natural gas) and petroleum products [14; pp. 455-467]. The device is equipped with a signaling device that generates an audio and visual signal when the measured concentration exceeds the set level [14; pp. 455-467]. The 102 FA 01M gas analyzer equipped with an optical sensor is designed to measure the volume fraction of hydrocarbons from exhaust and flue gases [15; pp. 1-5]. The operating principle of the device is based on the infrared absorption method of analysis using a solid-state radiation receiver. The limits of permissible basic absolute error for CH ± 250 ppm [16; pp. 34-39]. Due to their above-mentioned shortcomings, the existing optical sensors cannot be used as alarms for explosive methane concentrations.

1.2. Thermal conductometric methods and gas analyzers.

Thermal conductivity sensors are commonly used in methane detection systems and typically consist of a gas-permeable working chamber and a sealed comparison chamber containing a reference gas. These chambers are equipped with thermoelements connected to bridge measuring circuits. When monitoring mixtures with significantly differing molecular weights or polarities, deviations from the additive law of thermal conductivity are commonly observed. Under standard operating conditions, errors in methane concentration measurements caused by the presence of oxygen (O_2) can reach up to 0.5 vol.%. In emergency situations, such as fires, where O_2 levels may be significantly higher, the impact of this gas on methane readings becomes more pronounced, potentially leading to inaccurate or ambiguous results.

In early methane gas analyzers, the sensitive components of the thermal conductivity sensors were often made from platinum microwires, arranged as threads or glass-fused spirals. These thermoelements function as both resistance thermometers and heating elements. The thermal conductivity of gases is largely unaffected by atmospheric pressure but increases with temperature.

Unlike thermocatalytic sensors, thermoconductometric methane sensors use a reference thermistor in a sealed chamber to help compensate for minor changes in certain environmental parameters, such as the power source. However, these sensors are not capable of compensating for other atmospheric fluctuations, and such factors can influence their performance. This limitation has led to interest in developing thermoconductometric sensors that use a non-insulated reference thermoelement, which differs from the working thermoelement in its electro-thermal properties.

Starting in the 1980s, efforts were made to combine both thermocatalytic and thermoconductometric methods into versatile, wide-range methane meters. One such example is a methane detector that employs two bridge circuits to measure both low and high concentrations of methane.

However, thermal conductivity gas analyzers, which are typically used to monitor methane concentrations at the brink of explosiveness, suffer from significant measurement errors. These errors arise due to the impact of humidity and

gas composition variations in the monitored environment. Additionally, these analyzers are prone to "zero drift," which compromises their reliability for detecting pre-explosive methane concentrations in gas mixtures.

1.3.Electrochemical analyzers for monitoring gas-air mixture

Electrochemical methane sensors are devices that generate an analytical signal through electrochemical reactions. These sensors are designed for both qualitative and quantitative analysis of gases and liquids, including methane. At the core of modern electrochemical sensors is a galvanic cell, where two electrodes and an electrolyte are separated from the analyzed medium by a semipermeable membrane. These sensors can detect a range of gases, such as methane (CH_4), oxygen (O_2), hydrogen (H_2), chlorine (Cl_2), and hydrogen sulfide (H_2S), making them highly versatile.

One of the key advantages of electrochemical sensors is their ability to measure gases at trace concentrations, making them particularly valuable for monitoring air quality and ensuring compliance with sanitary standards in both industrial and residential settings. Compared to traditional analytical instruments, electrochemical methane sensors are compact, easy to use, and cost-efficient. They are among the most widely utilized types of devices where the analytical signal results from chemical interactions within the analyzed medium.

There are several types of electrochemical sensors, including potentiometric, amperometric, conductometric, and impedance-metric sensors, each based on different analytical signals:

- Potentiometric sensors: Measure the potential of the indicator electrode when no current is flowing through the electrochemical cell.
- Amperometric sensors: Measure the current flowing through the cell when the electrode potential is set at a fixed value.
- Conductometric sensors: Measure the electrical conductivity of the electrolyte solution.
- Impedance-metric sensors: Measure the electrochemical impedance, which represents the combined resistances and capacitances in the system.

These sensors are most commonly used to detect electroactive substances that can undergo oxidation or reduction reactions at the indicator electrode. The electrodes themselves can be made from inert materials like platinum (Pt), palladium (Pd), gold (Au), or silver (Ag), or from chemically active materials like copper (Cu), indium (In), or tin (Sn). Additionally, electrodes may be modified with complex compounds or feature thin-film nanocomposites to enhance sensitivity.

The electrolyte in these sensors can be liquid, such as potassium chloride (KCl) or sulfuric acid (H_2SO_4), or solid, such as zirconium oxide (ZrO_2), aluminum oxide (Al_2O_3), or antimony pentoxide (Sb_2O_5). This electrolyte is kept separate from the gas being analyzed by the semipermeable membrane.

While electrochemical sensors offer excellent selectivity for detecting specific gases, they are generally not suitable for assessing the explosiveness of complex gas mixtures on their own. However, they are frequently employed as part of multisensory systems, where they work in conjunction with other sensors to provide a comprehensive analysis.

1.4. Thermocatalytic method and sensors for monitoring methane-air mixtures

Thermocatalytic methane sensors operate based on the flameless oxidation of combustible gases over a catalyst, typically a platinum-coated thermistor. The oxidation process releases heat, which causes the platinum wire to heat up, leading to a change in the sensor's resistance. These sensors are known for their simplicity in manufacturing, compact size, low power consumption, and nearly linear output signal. To measure methane concentrations, two sensitive elements (SE) are commonly used: a working element and a compensatory (reference) element. Both elements are connected in a Wheatstone bridge circuit, with two fixed resistors in the second branch. The sensors are placed in the environment under examination, with the working and reference elements helping to detect changes in methane levels.

Catalytic sensors are particularly effective in detecting combustible gases, offering good selectivity for methane. However, they are typically calibrated for

methane, requiring recalibration when used for other gases. These sensors perform well in detecting pre-explosive concentrations of gases and vapors, making their selectivity for combustible gases a significant advantage. Their affordability and ease of maintenance make them widely used for monitoring explosion hazards in various environments.

Earlier versions of thermocatalytic sensors had a reaction chamber constructed from double metal mesh, with an internal diameter of around 15 mm and a height of 15-20 mm. Today's sensors have much more compact designs, with reaction chambers made of ceramic or metal-ceramic materials, typically with an internal diameter of 5-6 mm. The working and compensating elements are usually connected within one branch of the Wheatstone bridge.

The oxidation of combustible gases on the catalyst can proceed in either the kinetic or diffusion region. In the kinetic region, the rate of the oxidation reaction is typically a function of the molar concentrations of methane and oxygen. For methane concentrations above 9%, the limiting factor in the reaction rate is the availability of oxygen. Therefore, the main application of this sensor type is in detecting pre-explosive methane concentrations, typically in the 0-5 vol.% CH_4 range. Studies have shown that for methane concentrations between 40 and 100 vol.%, the output signal shifts negatively when the sensor is calibrated for 0 and 100 vol.% concentrations, indicating that the catalytic activity of the reference element exceeds that of the working element.

In a broad-spectrum combustible gas analyzer [28; pp. 189-193], only a single Wheatstone bridge circuit integrated with a thermocatalytic methane sensor is employed. Researchers are continually focusing on improving the performance of thermocatalytic methane sensors. This includes developing innovative design concepts, incorporating new materials, and exploring advanced manufacturing techniques to broaden their potential applications [29; pp. 51-55]. The primary performance criteria for thermocatalytic methane sensors include high sensitivity, selectivity, rapid response, and stability [30; pp. 20-28, 31; pp. 53-57]. A widely recognized method for fabricating the sensitive components of these sensors is the

sol-gel technique [32; pp. 51-58]. Oxides such as titanium, zinc, and cobalt are commonly used as active materials in catalytic thermosensors. Titanium oxide-based sensors, in particular, are sensitive to target gases at temperatures exceeding 500 ºC [33; pp. 17-27], which imposes specific design challenges. The manufacturing process for these sensors relies on the sol-gel method as outlined in [34; pp. 81-87]. To enhance the sensitivity of these sensors, effective catalysts, especially precious metals like platinum and palladium, are incorporated into the gas-sensitive layers [35; pp. 37-41]. Research has shown that catalytic thermosensors with titanium dioxide powder in their sensitive layers exhibit strong responses to methane. The highest sensitivity to methane is achieved using anatase titanium dioxide powder synthesized through a sol-gel process [36; pp. 68-72].

In the field of gas analysis, thermocatalytic sensors are employed not only for detecting methane but also for monitoring other combustible substances like CO, H_2, and hydrocarbon vapors [37; p.21, 38; p.12]. Studies [39; 1-5, 40; p.513] have led to the development of thermocatalytic sensors for carbon monoxide, which, when integrated into automatic gas analyzers like the GA-SO [41; pp. 19-25, 42; pp. 3-26], successfully passed the State Standard acceptance test in the Republic of Uzbekistan. The GA-SO automatic gas analyzer, which is designed to measure CO levels in vehicle exhaust gases, has been certified under several standards, including TU RUz 64-16096982-01-97, and has received certification from Uzbekistan, Kazakhstan, and Kyrgyzstan. The device measures carbon monoxide concentrations in the range of 0-5 vol.%, with a permissible error margin of ±0.25 vol.% within this range. The GA-SO also has a warm-up time of no more than 10 minutes [43; pp. 1-8]. The Automatic Alarm 123TX 05, manufactured by ZAO UKRANALIT, is designed for continuous detection of methane leaks in the engine, gas cylinder compartments, and passenger areas of gas-powered and gas-diesel buses. The device tracks methane levels and, when necessary, triggers audible or visual alarms when the methane concentration exceeds predefined thresholds [44; p. 1-14]. These thresholds range from 0-50% of the Lower Explosion Limit (LEL), with an allowable absolute error of ±0.25 vol.% (5% LEL). The error margin for the

threshold devices' response is ±0.05 vol.%. Alarm activation (indicated by a red light) occurs at methane concentrations as low as 1 vol.% (20% LEL). The system operates continuously for a year or up to 25,000 km of bus mileage without the need for re-calibration [44; pp. 1-14]. The methane leak alarm (MLA) is specifically used for constant monitoring of natural gas and carbon monoxide levels in places such as basements, underground garages, parking lots, and within vehicle engine and gas cylinder compartments. It operates alongside the LMA-20 system.

A stationary thermocatalytic gas analyzer has been developed to measure the mass concentration of hazardous and flammable gases, such as carbon monoxide (CO), methane (CH4), gasoline vapors, and others [45; pp. 1-7]. The analyzer's gas selection and measurement range can be tailored based on customer specifications. The system consists of a sensor module (SM) and an information processing unit. The SM is suitable for installation in hazardous environments, such as vehicle interiors or industrial spaces, to monitor the air quality in workplaces. The methane measurement range of this analyzer is 0–2.5 vol.%, with a permissible relative error of ±20%.

The portable hydrocarbon gas analyzer FP11.2K is designed for continuous and automatic measurement of hydrocarbon concentrations in the ambient air of populated areas, industrial settings, and process gases. It can also be used to monitor hydrocarbon levels within vehicle cabins [46; pp. 1-6]. This analyzer is widely employed by environmental agencies, labor protection, and sanitary oversight bodies. Additionally, the authors of [47; pp. 44-49] have developed a thermocatalytic sensor aimed at early detection of methane at pre-explosive concentrations, with an integrated methane concentration monitoring alarm system.

Given that some time is required for the sensor to stabilize after activation, the device includes a light indicator to signal its readiness for operation. To improve methane concentration accuracy, the alarm system is equipped with a pointer device calibrated in % vol. CH4. Once the device is powered on, an LED indicator (HL2) confirms that it's ready to function. The system features two methane concentration thresholds: 1.5 vol.% and 2.0 vol.%. If either of these thresholds is exceeded, LEDs

HL4 and HL6 light up, and a voltage signal triggers an audible alarm, reinforcing the visual alarm indicating the presence of 2.0 vol.% methane.

Since the 1980s, a multisensory approach to gas analysis devices has been gaining traction [48; pp. 352-355, 49; pp. 24-28]. This technique integrates non-selective sensors into a cohesive system that can selectively detect a broad spectrum of gases and gas mixtures [50; pp. 111-119]. Semiconductor and thermocatalytic sensors are among the most commonly used gas-sensitive components in both single-sensor gas alarms and multisensory systems.

The catalytic thermo-sensor design incorporates a gas-sensitive layer of Al2O3 granules functionalized with PdCl2 and H2PtCl6 solutions, deposited over a crystalline SiO2/Si substrate. This layer is divided by Pt electrodes to form four distinct sensor elements [51; pp. 14-18]. The developed cylindrical sensor element measures 0.6 mm in diameter and 0.85 mm in length [52; pp. 146-149]. Its resistance at 20 ºC is (6.3 ± 0.4) Ohms. With a supply voltage of 2.4 V, the sensor's temperature in air ranges from 370 to 408 ºC, which supports the catalytic oxidation of methane in the diffusion region [53; pp. 113-118]. This process minimizes interference from external factors, ensuring that the sensor remains stable and operates predictably. In the measurement range of 0 to 2.5% methane by volume, the sensor's basic absolute error is within ±0.15%, with an inertia of no more than 4 seconds. Initially, the catalytic process operates in the kinetic region, where the catalytic activity is highly temperature-dependent, before eventually ceasing altogether.

One of the ways to ensure the selectivity of these sensors is to carry out measurements at several points with different temperatures [54; pp. 426-428]. Since different gases have different temperatures of the onset of the catalytic reaction, it is possible to selectively determine the influencing gases based on the sensor response at different temperatures. However, this method has a significant drawback: the temperature of the onset of oxidation is unstable and a reaction of combustible components at a lower temperature is possible, which leads to measurement errors. In the work [55; 432-441] it is shown that the explosiveness of a gas mixture or one combustible gas depends linearly on the heat released during its combustion. Thus,

it becomes possible to integrally assess the degree of explosiveness of the analyzed gas on the % LEL (Lower Concentration Limit of Propagation) scale. The principle of measurement is as follows. First, measurements of clean air are taken, calculating a certain heat Q_0 corresponding to the absence of combustible gases, then the gas to be measured is supplied and the heat Q is calculated. Having calculated the difference $Q-Q_0$, the heat released during gas combustion is obtained. Then, using the necessary calculations, the desired value is obtained [56; pp. 121-131, 57; pp. 1-10]. This method makes it easy to calculate the degree of explosiveness of any gas mixture, without requiring additional calculations (the LEL of the mixture does not directly depend on the sum of the concentrations of the gases included in the mixture). The true composition of the influencing mixture remains unknown [58; pp. 78-88, 59; pp. 25-26].

The creation of energy-saving thermocatalytic sensors using porous substrates made of anodic aluminum oxide has become possible thanks to the development and widespread use of planar technologies such as photo- and electron lithography and all kinds of methods of vacuum deposition of thin films [60; pp. 1-14].

Analysis of existing literature data on the control of explosive methane concentrations allows us to draw the following conclusions:

- existing thermocatalytic gas analyzers, which provide reliable control of the explosiveness of a gas mixture at pre-explosive concentrations of methane, after prolonged operation of the sensors in a gas environment with a methane concentration of more than 10 vol.%, significantly change their characteristics;

- it is necessary to study how the parameters of thermocatalytic methane sensors change during their long-term operation under real conditions;

Preventing accidents and explosions that result in the destruction of material assets and human casualties has a significant economic effect.

1.5. Semiconductor gas sensors

The operating principle of the semiconductor methane sensor is based on the change in the electrical conductivity of the semiconductor film due to the adsorption

of methane on its surface [33; pp. 17-27]. The operating principle of the semiconductor gas sensor is based on the change in the electrical conductivity of the semiconductor film due to the adsorption of the monitored gas on its surface. A thin layer of tin oxide (SnO_2) doped with elements with catalytic properties (Pt, Cu, Ni, Pd) is applied to an aluminum oxide substrate to provide higher sensitivity of the semiconductor to a specific type of impurity gas. When the sensor is heated to the operating temperature (about 400 °C) using a heating element made in a single design with the sensor, methane is absorbed on the surface of the sensitive layer of the sensor. The degree of absorption depends on the concentration of the impurity gas. As a result of surface effects, the electrical conductivity of the sensor changes, i.e. the sensor response is expressed through a change in its resistance depending on the concentration of the gas, which changes the degree of absorption on the sensor material. The response speed depends on the sensor model and the specific gas impurity. The advantages of semiconductor sensors include their low cost and simple connection circuit. The disadvantages include a short period of continuous operation (about 1 year) due to the consumption of the working layer interacting with the controlled substance.

The use of semiconductors to determine methane concentration is based on the change in conductivity of these substances during reversible chemisorption of methane. The change in conductivity due to chemisorption of methane molecules is due to the change in the concentration of electrons in the conduction band due to charge exchange with chemisorbed particles of the gaseous medium. In this regard, the use of semiconductor metal oxides, which are active and selective catalysts for chemical reactions, is preferable from the point of view of their high chemical and thermal stability, as well as high specific resistance. Processes on the surface of a metal oxide semiconductor can be characterized as heterogeneous catalytic oxidation-reduction reactions of gases with the participation of chemisorbed atmospheric oxygen, which is converted into an electronegative ion [61 p.233-236].

Atmospheric oxygen, chemisorbing on the surface of the gas-sensitive metal oxide layer (for an n-type semiconductor), accepts electrons from the conductivity

zone, thereby increasing the layer resistance. Foreign reducing gases contained in the atmosphere (methane, hydrogen, etc.) interact with the chemisorbed oxygen ions, reducing their surface concentration. The electrons released in this process return to the conductivity zone.

1.5.1. Semiconductor sensors of combustible gases based on metal oxides

The first industrial semiconductor gas sensors were created in 1962 by the Japanese inventor Nao Yoshi Taguchi, after whom the first three letters TGS (Taguchi Gas Sensor) in the name of the gas sensors were named [62; 34-36].

Zinc oxide is widely used as a gas-sensitive oxide. The operating principle of semiconductor sensors (SSS) of methane is based on the property of ZnO to change its electrical parameters upon adsorption of CH_4 [63; pp. 1-6]. When adsorbed on the surface of metal oxides, oxygen molecules act as an acceptor, and methane molecules act as an electron donor. Therefore, when oxygen molecules are adsorbed, the conductivity decreases, and when methane is adsorbed, the conductivity of materials based on metal oxides increases [64; pp. 80-87, 65; pp. 66-71]. The mechanism of gas sensitivity during adsorption is based on the presence of surface states in the metal oxide, forming near-surface local energy levels that can be occupied by electrons and holes, thereby forming a surface electric charge [67; pp. 22-31, 68; p. 67]. In this case, a charge equal in magnitude and opposite in sign is formed in the near-surface layer. Thus, enriched and depleted charge regions are formed, changing the electric potential and conductivity of the near-surface region of the film [69; p.340, 70; pp.24-27]. The paper [71; pp.258-264] presents the results of studies of a gas sensor based on a nanocrystalline ZnO film. The film was deposited on a SiO2 substrate using magnetron sputtering. It is shown that with a decrease in the film thickness from 390 nm to 65 nm, the gas sensitivity at 400 °C increases from 20% to 60%. With an increase in temperature from 100 °C to 400 °C, the gas sensitivity of a film 65 nm thick increases by 1% to 60%.

The authors [72; pp. 1326-1331] present the results of studies of a methane sensor based on a nanocrystalline ZnO film obtained by magnetron sputtering on a SiO_2/Si substrate.

The properties of a methane gas sensor based on a nanocrystalline ZnO film are presented and described in [73; pp. 4428–4434] depending on the thickness of the gas-sensitive layer. It is shown that the gas sensitivity of the sensor decreases with an increase in the film thickness. The highest gas sensitivity is achieved at a thickness of less than 100 nm, at a temperature of 300 °C. In [74; pp. 6–12], studies are presented of the effect of deviation from the stoichiometry of a 300 nm thick ZnO film on the dynamics of the response to various gases. The effect of the oxidation time of metallic zinc on the gas sensitivity of the resulting ZnO film is described in [75; pp. 472–478]. In the semiconductor sensor, the gas-sensitive layer was a nanocrystalline ZnO film with grain sizes of (20–40) nm [76; pp. 3817–3819]. The operating temperature of the sensor was 150 °C. The author of [77; [pp. 80-87], the dependence of the semiconductor sensor signal on various parameters was investigated and it was shown that:

- the gas sensitivity of the film sensitive element is affected by the film thickness and grain size. Therefore, to develop promising gas sensors based on ZnO, it is necessary to use nanostructured films whose thickness and grain size do not exceed the thickness of the depleted layer during gas adsorption;

- the technology for forming nanocrystalline ZnO films for sensitive elements of methane sensors is compatible with silicon microelectronics technology, while the formation of nano-sized monocrystalline ZnO films requires special substrates (Al_2O_3, MgO, etc.);

- to ensure maximum gas sensitivity for methane, the operating temperatures of the sensors are 200-400°C, which places demands on the films for the stability of the dependence of the electrophysical parameters on temperature during thermal cycling in the temperature range from room temperature to operating temperature;

- to ensure the possibility of measuring the resistance of the ZnO film as part of the electrical measuring circuit of the gas sensor without involving complex measuring circuits, it is necessary to controllably obtain films with a resistance in the range of (104-106) Ohm [78; pp. 4995-4998, 79; pp. 284-295]. In order to promptly detect the leakage of even small amounts of explosive gases (especially

methane), semiconductor chemical sensors capable of identifying small concentrations of explosive gases with high speed and high sensitivity are finding increasingly wider application [80; pp. 24-27, 81; pp. 1-6. SnO_2, TiO_2 and some others have proven themselves to be good gas-sensitive oxides, but currently preference is given to tin dioxide [82; pp. 45-49, 83; pp. 20-22].

In the work [84; pp. 116-121] three-component nanostructures in the $SnO_2/In_2O_3/TiO_2$ system were manufactured and their sensitivity and selectivity to methane were studied. Prevention of emergency situations and explosions leading to the destruction of material assets and human casualties provides a significant economic effect. As is known, almost all semiconductor systems have sensor activity, but semiconductors based on tin oxide are characterized by record high gas sensitivity. The main disadvantage of standard sensors based on tin oxide is a very significant dependence of the output signal on changes in the humidity of the measured gas mixture [85; pp. 11-16]. Almost all manufacturers of gas sensors note a high dependence of the signal of the sensitive element on the temperature and humidity of the environment [86; pp. 14-18].

As already noted, the magnitude of the signal generated by the semiconductor sensor can differ by 2 times or more when the humidity changes from 10 to 100%, which inevitably leads to false alarms when the concentration of the detected gas is erroneously determined. To construct the measuring circuit, the authors of [87; pp. 1-6] used the ATMEL ATMEGA-8 controller [88; pp. 11, 89; pp. 44-47] with the corresponding program reducing the resistance of the gas-sensitive layer [90; pp. 18-22, 91; pp. 237-243].

Direct experiments have shown that the temperature zone of maximum sensitivity of the tin dioxide layer with the addition of platinum is quite narrow and is in the region of 500˚C. At this temperature, the influence of humidity can be neglected and, what is valuable, the response for the component being determined (methane) significantly exceeds the response for any other component of the gas mixture [92; pp. 20-22, 93; pp. 56-63]. Based on the synthesis of SnO_2:Pt oxide sensors, an alarm for pre-explosive methane concentrations was developed. The

results of the development of sensors for the early detection of pre-explosive methane concentrations are presented [94; pp. 44-49].

Semiconductor sensors are currently widely used in the field of measuring pre-explosive methane concentrations [95; pp.12-17, 96; pp.32-37]. In addition to methane, there are semiconductor sensors for a large number of gases [97; pp.389, 98; pp.741-759]. The first works on multicomponent analysis on semiconductor sensors appeared on the basis of an array of sensors tuned to different gases [99; pp.370-380, 100; pp.251-254]. Unfortunately, like multisensory systems, an array of semiconductor sensors has a drawback: if the mixture contains a gas to which the sensors were not tuned, a large measurement error will occur. Making systems for a large number of gases is extremely difficult and inefficient. In laboratory conditions, such a system will give good results, but in real conditions its efficiency is significantly lower.

In the work [101; pp.12-14] the pulse mode of operation of the semiconductor sensor was investigated. For all industrially produced semiconductor sensors there is a serious problem of signal stability when detecting sufficiently high threshold concentrations of combustible gases (0.5-2.0% vol. CH_4) under conditions of changing humidity of the surrounding air. As already noted, the magnitude of the signal generated by the semiconductor sensor can differ by 2 times or more when the humidity changes from 10 to 100%, which inevitably leads to false alarms when the concentration of the detected gas is erroneously determined.

Thus, a comprehensive solution to the problem allows manufacturing gas analyzers that fit well into gas safety systems used in places where natural gas (methane) may appear, with detection thresholds whose values are minimally affected by ambient humidity and temperature. The upgraded sensors, in which a full range of optimization measures have been carried out, have shown a slight dependence on the humidity of the detected environment. The relative error of these devices does not exceed 10%.

1.6. Conclusions and justification of the direction of experimental research.

As is known, rapid determination of the degree of danger of methane (natural gas) in the air is possible only with the help of express and sensitive methods, since long-term sampling and subsequent analysis exclude the possibility of timely detection of hazardous concentrations of methane in the air. From the reviewed literary data it follows that most of the existing methods for determining CH_4 require the use of bulky equipment and, accordingly, have a stationary (not portable) nature of application. In some cases, the process of determination by these devices is multi-stage, lengthy and very complex. One of the promising methods for determining methane from gas mixtures may be thermocatalytic and semiconductor methods, which are characterized by rapidity and have a high degree of automation, which, in turn, allows you to quickly receive accurate information in the required period of time for their subsequent transfer to the database. In this regard, the determination of CH_4 using thermocatalytic and semiconductor sensors, the development of automatic analyzers and alarms on their basis with a wide range of detectable concentrations and a high degree of automation are promising in connection with the need to ensure explosion safety of closed ecological systems, the creation of a new generation of highly efficient thermocatalytic and semiconductor methane (natural gas) sensors is a pressing problem in analytical chemistry, which is the subject of this Monograph. The main objective of the work is the development and study of analytical parameters of semiconductor and thermocatalytic sensors for monitoring methane

Analysis of available literature data has shown that additional research aimed at improving the analytical and metrological parameters of semiconductor and thermocatalytic methane sensors is required to ensure effective control of leakage and accumulation of natural gas in closed ecological systems. In this regard, the main objectives of this work can be formulated as follows:

1. To study the analytical capabilities of the method for measuring the concentration of sensors. To study the physical and chemical processes on the surface of gas-sensitive elements of sensors when determining methane. To establish a linear methane based on the use of a thermocatalytic and semiconductor sensor.

To determine the composition of the catalyst and gas-sensitive material, the region of dependence of the signal on the concentration of methane and to conduct its experimental verification. To determine the measurement range, dynamic characteristics and measurement error of methane caused by changes in environmental parameters.

2. Develop and study the analytical capabilities of a method for measuring methane (natural gas) concentration based on the use of a thermocatalytic sensor. Create a household alarm on its basis to monitor methane leakage and accumulation in household premises and vehicle interiors. Determine the main metrological and analytical characteristics of the thermocatalytic methane alarm. Conduct an error analysis of the measurement method.

II.DEVELOPMENT AND RESEARCH OF METROLOGICAL CHARACTERISTICS OF A SELECTIVE THERMOCATALYTIC SENSOR FOR METHANE (NATURAL GAS)

2.1. Preparation and certification of standard gas mixtures of methane and natural gas with air

In our study, gas-air mixtures were prepared using the manometric method in accordance with the CMEA standard 4981-86 (group B 19). This method involves the gradual addition of individual combustible gas components into a pre-evacuated cylinder. The concentration of each component in the mixture is directly proportional to the pressure change observed after introducing the corresponding component, relative to the total pressure of the mixture.

To create the mixture, methane is first introduced into the evacuated cylinder as the initial component for calibration. The subsequent components are added one by one. The dosing process is carried out at a pressure higher than the cylinder's internal pressure to prevent any leakage of components from the mixture. After each component is added, the pressure is measured once it stabilizes and no longer fluctuates.

The concentration of each component in the gas mixture (Xi) is then calculated using the appropriate formula.

$$X_i = \frac{P_i}{\sum_{i=1}^{n} P_i} \cdot 100 = \frac{P_i}{P} \cdot 100 \qquad (2.1)$$

where *Pi* is the partial pressure of the 1st component.

P is the total pressure of the mixture.

To achieve a more precise determination of methane content, the gas chromatographic method was employed in addition to the monometric method. The details of the prepared gas mixture (PGS) used for testing the TKS-CH4 sensor, with a measurement range of 0.1 to 5% by volume and 0.1 to 50 mg/m³, are provided in Tables 2.1 and 2.2 (Appendices 1 and 2).

Gas-air mixtures were diluted using the 823 GR-03 gas mixture generator, manufactured by the All-Russian Research Institute of AP KNPO "Analitpribor," and the 926 GC-02 clean air generator from KNPO "Analitpribor." The GR-03 generator is designed to prepare gas mixtures with specified error limits by dynamically diluting certified gas mixtures with certified diluent gases. The GC-02 clean air generator purifies atmospheric air from flammable substances to produce zero gas, which is used for calibrating and adjusting gas analyzers, as well as serving as a diluent gas for creating gas mixtures with the GR-03 generator. The GC-02 also removes nitrogen oxides, hydrogen sulfide, and sulfur dioxide from the air.

The generator works through a two-stage adsorption-catalytic process, purifying atmospheric air of hydrocarbons, including methane. Initially, dust-free and dried air is passed through a carbon sorbent to remove heavy hydrocarbons and catalytic poisons. Then, deep purification of air from hydrocarbons, including methane, is achieved using a palladium catalyst at approximately 300°C. The results of methane-air mixture dilution using the GR-03 generator are presented in Table 2.3 (Appendix 3).

For this study, standard mixtures of natural gas in air were prepared (Table 2.4, Appendix 4). The required low concentrations of natural gas were achieved by diluting gas-air mixtures with the gas mixture generator (GR-03) and the clean air generator (GC-02), both manufactured by KNPO "Analitpribor."

During the experiments involving natural gas-air mixtures, the composition of the natural gas used was first determined using a Crystal chromatograph (Table 2.5, Appendix 5). According to the data in Table 2.5, the main components of the gas mixture studied were methane (94.33 mol%), ethane (2.88 mol%), and propane (0.485 mol%).

2.2. Study of the activity of metal oxides in the process of oxidation of combustible gases and selection of a catalyst for a selective thermocatalytic methane sensor

The selectivity index is one of the key metrological parameters for gas analysis instruments. In practice, no sensor is entirely selective; therefore, each method

inevitably involves the influence of unmeasured components on the measurement results. Sensor selectivity refers to the instrument's ability to isolate and measure the target component from a complex gas mixture, minimizing the interference from other components in the mixture. Essentially, the effect of unmeasured components on the measurement result should be lower than the maximum allowable error for the instrument. An instrument and method that meet this criterion are considered selective.

Traditionally, it has been believed that commonly used thermochemical sensors do not ensure selectivity in measuring specific components of a gas mixture [102; pp. 44-49]. These sensors were primarily used for indicating and signaling the presence of flammable gases and vapors [2; p. 227]. Therefore, the challenge of transitioning thermocatalytic sensors from merely indicating to measuring with selectivity is an important issue. One approach to achieving selectivity in thermocatalytic sensors for combustible gases involves using temperature-sensitive elements with varying activity levels toward different gas components. This variation in activity is achieved by carefully selecting the catalyst composition [103; p. 242, 104; pp. 165-169] or by adjusting the oxidation conditions (such as temperature) for individual components in the mixture [105; pp. 317-320].

Atmospheric air, which often requires continuous methane content monitoring, is a complex multi-component mixture containing CO, H2, H2O, CO2, and others. Thus, developing a selective methane sensor necessitates selecting catalytic systems with temperature-sensitive elements tailored to the gas components involved.

To develop a highly sensitive and selective sensor for continuous automatic methane (or natural gas) detection, oxidation patterns of combustible substances on various catalysts were studied. The extent of oxidation of the target component was chosen as the criterion for selecting a catalyst for creating the sensor's sensitive element. Since the completeness of oxidation depends on various factors, such as composition, process temperature, reactant concentration, and component ratios in the gas mixture, these factors were also explored.

According to the literature [102; p. 44, 106; pp. 164-187], catalysts for hydrocarbon oxidation can be made from metal oxides, noble metals, or mixed systems of metal oxides and platinum group metals. Metal oxides exhibit relatively high catalytic activity for the oxidation of combustible substances, making them widely applicable in gas masks and catalytic devices for neutralizing industrial and automotive exhaust gases. The development of a catalyst for a highly sensitive natural gas sensor was carried out using a flow-type system with a fixed catalyst bed.

Catalyst selectivity was determined in the presence of combustible gases like CO and H2, which are often found together with hydrocarbons in industrial emissions, automotive exhausts, etc. The oxidation degree of the target component was monitored by recording a chromatogram of the gas mixture before and after passing through the catalyst bed. During the monitoring of oxidation processes for carbon monoxide, hydrogen, and natural gas, a Crystal 500 chromatograph and LHM-8MD system were used. The individual component concentrations in the mixture were determined using a pre-established calibration curve (Figure 2.1, Appendix 6).

To further assess the oxidation process of natural gas, additional control was performed by determining the amount of carbon dioxide in the reaction products. Carbon dioxide was measured using a titrimetric method with potentiometric indication (KTT). A 0.2 M potassium hydroxide solution was used for absorption. The quantity of potassium hydroxide consumed in absorbing the carbon dioxide was determined by comparing titration results (before and after the gas mixture passed through). The mass of carbon dioxide formed during methane oxidation was then calculated. The completeness of methane oxidation was evaluated using the coefficient "K," which represents the ratio of the observed carbon dioxide mass to the theoretically expected amount. This coefficient was used to evaluate the catalyst's activity.

In the conducted experiments, the catalytic properties of various individual metal oxides were analyzed. The catalyst selection and the optimization of conditions for the oxidation of combustible substances were performed within a

temperature range of 100-350 ºC, with a gas-air mixture flow rate of 2.5 l/hour. The combustible components in the mixture (% vol.) were: H_2-2.5; CO-2.4; methane-2.5. When catalysts were present, the oxidation of H_2, CO, and methane primarily occurred in the thermodynamically most favorable direction, leading to the formation of carbon dioxide and water vapor. This process is accompanied by a substantial thermal effect, with the specific heat of combustion (J/Kcal) for CH_4, H_2, CO, and C_2H_6 being $892 \cdot 10^{-6}$, $286 \cdot 10^{-6}$, $283 \cdot 10^{-6}$, and $1562 \cdot 10^{-6}$, respectively, and is nearly irreversible [1; p. 117].

Experiments to identify sensitive and selective catalysts for methane sensors were conducted using a range of metal oxides, including Ga, In, Ag, Cr, Mn, Fe, Co, Ni, Cu, and Zn, which are known to be highly active in the oxidation of combustible substances. The results of these studies on the catalytic activity of individual metal oxides in the oxidation of combustible substances are presented in Table 2.6 (Appendix 7).

The data in Table 2.6 indicate that all of the studied catalysts showed significant hydrogen oxidation activity at 100 ºC. Among these, the most active oxides for hydrogen oxidation were silver, iron, nickel, and cobalt oxides. At 200 ºC, hydrogen conversion reached 90-100% on these catalysts. Moderate activity in hydrogen oxidation was observed with manganese, copper, and zinc oxides, with hydrogen conversion reaching 44-83% at 200 ºC. Chromium and gallium oxides were less active, with hydrogen conversion at 200 ºC being only 26% and 36%, respectively.

Further experiments conducted in the temperature range of 100-350 ºC allowed for the ranking of metal oxides based on their catalytic activity in hydrogen oxidation by atmospheric oxygen. The order of activity for hydrogen oxidation was: Ag_2O > In_2O_3 > Fe_3O_4 > Ni_2O_3 > Co_2O_3 > MnO_2 > CuO > ZnO > Ga_2O_3 > Cr_2O_3. Additionally, a similar analysis of the catalysts for carbon monoxide oxidation revealed the following order of catalytic activity: Ag_2O > In_2O_3 > MnO_2 > Ni_2O_3 > Cr_2O_3 > Fe_3O_4 > CuO > Co_2O_3 > ZnO > Ga_2O_3. Silver, indium, manganese, nickel, and chromium oxides showed the highest activity, with 90-100% CO conversion at 200 ºC. Copper and cobalt oxides displayed moderate activity, with CO conversion

rates of 50% and 68%, respectively. Catalysts based on zinc and gallium oxides exhibited the lowest CO oxidation activity, with conversion rates of 31% and 41%, respectively.

The data from Table 2.6 also indicate that methane conversion on all the studied catalysts at 200 ºC was significantly lower compared to hydrogen and carbon monoxide oxidation. The highest methane conversion rates were observed with catalysts based on In_2O_3 and Ag_2O, which achieved conversions of 90% and 100%, respectively, at 200 ºC.

In further experiments on natural gas oxidation conducted between 100 and 350 ºC, the catalytic activity of metal oxides was again studied. Catalysts selected for the natural gas sensor included metal oxides of In, Ag, Cr, Mn, Fe, Co, and Ni, all of which are highly effective in methane oxidation. The comparative data on the activity of individual metal oxides in the oxidation of hydrogen, carbon monoxide, and natural gas are presented in Table 2.7. The findings from Table 2.7 reveal that at 200 ºC, the conversion of natural gas is notably lower than the oxidation rates of hydrogen and carbon monoxide. The highest conversion of natural gas was observed on catalysts based on Ag_2O and In_2O_3, with conversions of 86% and 98%, respectively.

Table 2.7

Results of the study of the activity of metal oxides in the catalytic oxidation of H_2, CO and natural gas with atmospheric oxygen (CH_2-2.5% vol., CCO-2.4% vol., SPG - 2.5% vol.)

№	Composition of the catalyst						
1	In_2O_3	Ag_2O	Cr_2O_3	MnO_2	Fe_3O_4	Co_2O_3	Ni_2O_3
Oxidation state of hydrogen (x Δ±X), %							
2	96.1±0.5	100.0±0.6	28.4±0.2	83±0.4	93.5±0.4	90.3±1.5	90.8±0.8
Oxidation state of carbon monoxide (x Δ± X), %							
3	97.2±0.3	100.0±0.5	93.5±0.3	96.1±0.5	90.3±0.3	50.4±0.5	95.1±0.3
Oxidation degree of natural gas (xΔ ±X), %							
4	85.7±0.3	88.2±0.3	7.3±0.5	18.9±0.1	4.2±0.3	39.9±0.3	1.7±0.1

*Journal "Chemical Industry" 2015. No. 5. P. 263

Experiments conducted within a temperature range of 100-350 ºC revealed a series of metal oxides ordered by their decreasing catalytic activity for the oxidation of natural gas in the presence of atmospheric oxygen. These metal oxides include: $Ag_2O > In_2O_3 > Co_2O_3 > Cr_2O_3 > MnO_2 > Fe_3O_4 > Ni_2O_3$. The results demonstrated that Ag_2O and In_2O_3 are the most active catalysts for natural gas oxidation, achieving a conversion rate of 86-98% at 200 ºC. Under these conditions, the extent of deep oxidation for natural gas across all the studied catalysts was 2-5% lower than the oxidation of methane.

The research identified that the most effective catalysts for a highly sensitive natural gas sensor are individual metal oxides such as Ag and In. A significant degree of oxidation for hydrogen and carbon monoxide was observed in these selected active catalysts for methane (natural gas) oxidation. However, catalysts based on Ag and In oxides do not provide selective thermocatalytic detection of individual components within a mixture of hydrogen, carbon monoxide, and hydrocarbons—substances often found together in various natural and industrial environments.

While individual oxide catalysts demonstrated less pronounced catalytic activity and selectivity compared to complex mixtures, the latter often exhibited enhanced catalytic properties, as experimental data have shown [106; pp. 256-278; 107; pp. 123-134]. Consequently, further studies focused on such systems, with particular attention given to the selectivity of the studied catalytic mixtures.

In experiments conducted at temperatures ranging from 100-250 ºC, the performance characteristics of mixtures of the most active and selective oxides, such as In_2O_3, Ag_2O, Fe_3O_4, and Ni_2O_3, were explored across a broad range of their ratios. The results of studying the effects of component ratios at a temperature of 150 ºC on the selectivity of the In_2O_3-Ag_2O and Fe_3O_4-Ni_2O_3 catalysts for the oxidation of combustible gases are presented

Table 2.8.

Results of studying the influence of the ratio of components on the selectivity of In_2O_3-Ag_2O and Fe_3O_4-Ni_2O_3 catalysts in the oxidation of

combustible gases (temperature 150 ºC, n=5; P=0.95)

№	Ratio of catalyst components, in moles	Oxidation state (xΔ±X), %		
		Hydrogen	Carbon monoxide	Natural gas
1	$0.10In_2O_3$-$0.90Ag_2O$	100.0±0.4	100.0±2.2	100.0±2.0
2	$0.25In_2O_3$-$0.75Ag_2O$	100.0±1.5	100.0±1.4	100.0±1.0
3	$0.50In_2O_3$-$0.50Ag_2O$	100.0±0.5	100.0±0.5	98.0±1.0
4	$0.75In_2O_3$-$0.25Ag_2O$	100.0±0.9	100.0±0.8	96.0±0.3
5	0.90In2O3-0.10Ag2O	100.0±0.1	98.5±0.3	92.7±0.6
6	$0.10Fe_3O_4$-$0.90Ni_2O_3$	100.0±0.6	99.0±0.5	3.0±0.1

*Journal "Chemical Industry" 2015. No. 5. P. 264

As shown in the data presented in Table 2.8, at a temperature of 150 ºC, both In_2O_3-Ag_2O and Fe_3O_4-Ni_2O_3 exhibit high catalytic activity across a wide range of component ratios. The most effective catalyst for the measuring sensitive element of a natural gas thermocatalytic sensor is a mixture of 0.75 In_2O_3-$0.25Ag_2O$. Any deviation from this optimal ratio, either an increase or decrease in the concentration of the catalyst components, leads to a reduction in the selectivity of the reaction. For the comparative element, it is recommended to use 0.25 Fe_3O_4-$0.75Ni_2O_3$ as the catalyst. This combination provides excellent selectivity for the oxidation of CO and H_2 in the presence of methane gas. The catalysts used in this study were synthesized via sol-gel technology [108; pp. 176-186].

In summary, the experimental findings suggest that the 0.75 In_2O_3-0.25 Ag_2O and 0.25 Fe_3O_4-0.75 Ni_2O_3 catalysts are viable candidates for the measuring and comparative elements in the development of a selective thermocatalytic sensor. This sensor is particularly useful for detecting natural gas in environments containing hydrogen and carbon monoxide, substances commonly found alongside natural gas in atmospheric air in mines, process gases, and vehicle exhausts.

2.3. Design, operating principle, and assembly of a selective thermocatalytic methane sensor

The thermocatalytic method is widely employed for the development of methane analyzers and alarms. The basic operating principle behind this method involves the flameless combustion of methane on the catalyst's surface, followed by

the measurement of the heat released during the process [109; p.42-45, 110; p.256]. A thermocatalytic methane sensor consists of two sensitive elements (as shown in Fig. 2.2). These elements are classified into measuring or working (A) and compensating or comparative (B) types, based on their function. Both elements are placed within the reaction chamber.

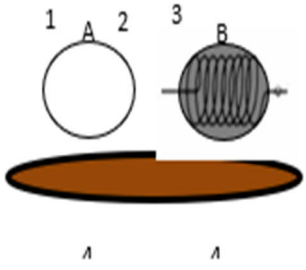

Fig.2.2. Schematic diagram of the temperature-sensitive elements of the methane sensor.A - Measuring and B - compensating sensitive elements, 1 - platinum microwire spiral, 2 - aluminum oxide ball, 3 - aluminum oxide ball with catalyst, 4 - metal posts).

The sensitive components of the catalytic thermo-sensor resemble a miniature spherical structure made from γ-aluminum oxide, within which a platinum wire coil is embedded. This coil serves dual functions, acting both as a heating element and as a resistance thermometer (refer to Fig. 2.2). The common design feature across both types of elements is the platinum wire coil, encased in glass insulation, with an identical number of turns, meaning the same resistance value (1). The coil itself is crafted from cast platinum wire and is insulated with quartz, with a core diameter of 10 μm and a quartz insulation thickness of 2 μm. The catalytically active surface of the element is coated with a catalyst. The aluminum oxide layer (2) acts as a porous support for the catalyst (3).

The spiral of the comparative sensor element shares nearly identical thermo-physical properties with the measuring element; however, it is not coated with a catalyst, meaning no oxidation reaction occurs on it. Typically, these elements, which have matching geometric dimensions and electrical parameters, are placed in separate reaction chambers. This design helps minimize the impact of changes in the parameters of the analyzed medium on measurement errors. The measuring and compensation elements are connected by a metal stand (4).

Under standard operating conditions, the flow of gases reacting with the working element’s surface and the removal of reaction products are determined by the presence of a gas concentration gradient between the element's surface and the

volume of the reaction chamber. A photograph of the sensor's sensitive elements is shown in Fig. 2.3.

A commonly used circuit to connect the sensitive elements of a sensor is a Wheatstone bridge. The comparison (R1) and measuring (R2) elements are typically positioned in one arm of the bridge circuit [2; p.167, 109; p.42-45]. Additional resistors (R3 and R4) are included in the opposite arm of the bridge (see Fig. 2.4).

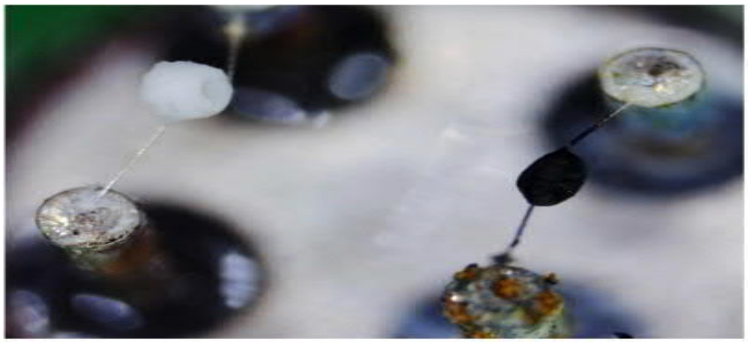

Fig. 2.3. Photograph of the sensitive elements of the catalytic thermo-sensor (on the left – comparative SE, on the right – measuring SE.

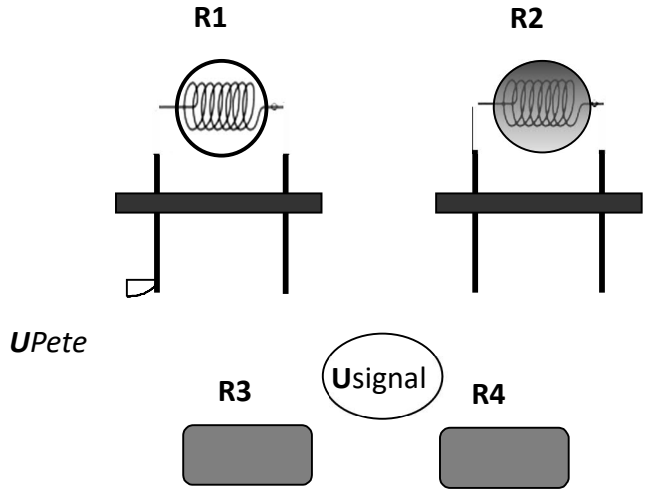

Fig.2.4. Connection diagram of sensitive elements of the thermocatalytic methane sensor

During operation, the platinum coil is heated by the flowing current, reaching the oxidation temperature for methane (approximately 450°C). The functioning of the methane sensor relies on the principle that when methane enters the reaction chamber, it undergoes oxidation on the active sensing element. This oxidation process generates heat, which leads to a change in the element's resistance. For

example, when methane molecules come into contact with the catalyst surface of the measuring element, a chemical reaction occurs, releasing heat and altering the element's resistance. Meanwhile, the resistance of the comparison element remains unaffected because methane oxidation does not occur on it due to the absence of a deep oxidation catalyst. Consequently, an imbalance arises in the bridge, and the output voltage, which represents the analytical signal of the sensor, becomes proportional to the methane concentration in the sample mixture. In this way, the sensor calculates the concentration of the combustible component in the analyzed atmosphere based on the imbalance value. Since the measuring element is coated with deep oxidation catalysts, the reaction proceeds similarly to normal combustion, following the reaction:

$$CH_4 + 2O_2 = CO_2 + 2H_2O + 805.2 \text{ kJ/mol} \quad (2.2)$$

As heat is released, the resistance (R) of the spiral changes by ΔR. The resistance of the coil is given by the formula:

$$R = R_0(1 + \alpha\Delta T) \quad (2.3)$$

Where R_0 is the resistance of the coil at 25°C, α is the temperature coefficient of resistance of the platinum wire, and ΔT is the temperature change of the coil. Since platinum has a relatively high temperature coefficient, the temperature increase resulting from the oxidation reaction causes a significant change in the resistance of the measuring element. In typical sensors, a methane concentration of 1% by volume (CCH_4 = 1%) causes the temperature of the catalytically active (measuring) element to rise by 20-30°C. This ensures a high sensitivity for the developed methane sensor. The oxidation reaction of combustible gases on heterogeneous catalysts can occur in both the kinetic and diffusion regions. The rate of methane oxidation in the kinetic region is typically expressed as a function of the volume-molar concentrations of methane and oxygen

$$W=k_{ef}(CCH_4CO_2) \quad (2.4)$$

where w is the reaction rate, mol/s; k is the reaction rate constant, s^{-1}; Fe is the active surface area of the catalyst, m^2. The value of k does not depend on the concentration of methane in the air and increases with increasing temperature.

In the kinetic region, the rate of the oxidation reaction is influenced by several factors, including the type and temperature of the catalyst, as well as the concentrations of the reacting components. Methane oxidation involves the simultaneous adsorption of both oxygen and methane on the catalyst's surface, and the reaction rate depends not only on the methane concentration but also on the oxygen concentration in the atmosphere. This complicates obtaining a signal that is directly proportional to methane concentration. As the catalyst's temperature rises, the rate of the chemical reaction increases significantly, and a zero concentration of the limiting component (methane) and some deficit of the excess component in the gas mixture occur on the catalyst’s active surface. In this case, the reaction rate and the heat generated are controlled by the diffusion rate of the limiting component, methane, under normal operating conditions of gas analyzers.

When methane concentrations range from 0 to 5% by volume, the thermophysical properties of the methane-air mixture are similar to those of clean air. However, at higher concentrations of CH_4, these properties may differ substantially. In certain situations, such as sudden natural gas leaks, gas mixtures with high methane concentrations can form in closed environmental systems. These mixtures also contain significant amounts of methane's higher homologues, carbon monoxide, and other combustible gases. In such cases, existing sensors may fail, making it difficult to respond appropriately to the incident. It should also be noted that at methane concentrations exceeding 9%, the limiting component that determines the reaction rate becomes the oxidizer—atmospheric oxygen [111; p.32, 112; p.31].

The lower explosive limit (LEL) for methane is typically considered to be 5%, and the upper explosive limit (UEL) is 16% [113; p.109]. The maximum explosion strength corresponds to a stoichiometric methane concentration of 9.5%. Thus, the primary application of this method is the detection of pre-explosive methane concentrations, usually in the range of 0 to 5% by volume of CH_4. This highlights the importance of research focused on enhancing the reliability of fire and explosion

hazard monitoring in gas mixtures, particularly through the development of selective sensors for combustible components.

The author [103; p.242, 104; p.165-169] proposed a method to ensure the selectivity of thermocatalytic detection by using thermosensitive elements in the sensor, which incorporate catalysts with varying (non-identical) activity levels toward the components of the gas mixture. In this approach, the output signal of the sensor's measuring sensitive element is proportional to the total concentration of the substances in the mixture (x_1, x_2, and x_3), while the output signal of the comparative sensitive element reflects the concentration of substances (x_1 and x_2), excluding the component being measured (x3). The difference between the signals of the first and second elements is directly proportional to the concentration of the target component (x3) in the mixture.

To develop a catalyst for gas-sensitive elements of a selective thermocatalytic sensor that enables the selective detection of methane in the presence of carbon monoxide and hydrogen, oxidation patterns for combustible substances were studied across various metal oxide catalysts (Ga, In, Ag, Cr, Mn, Fe, Co, Ni, Cu, and Zn). The results revealed that the optimal catalyst for the measuring sensitive element in the thermocatalytic methane sensor is 0.75 In_2O_3-0.25 Ag_2O. It is recommended to use 0.25 Fe_3O_4-0.75 Ni_2O_3 as the catalyst for the comparative element. This combination ensures high selectivity for the oxidation of CO and H_2 in the presence of methane. By applying the selectivity assurance technique [102; pp.44-49] with these catalysts, a thermocatalytic sensor was developed, ensuring selective detection of methane in the presence of carbon monoxide and hydrogen. (Fig. 25).

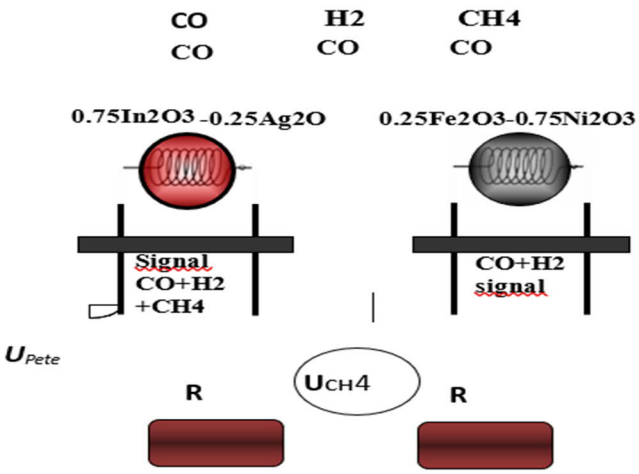

Fig. 2.5. Selective thermocatalytic methane sensor

The output signal from the sensor's measuring sensitive element (catalyst: 0.75 In_2O_3-0.25Ag_2O) is directly proportional to the total concentration of combustible gases, including hydrogen, carbon monoxide, and hydrocarbons. Meanwhile, the output signal from the reference sensitive element corresponds to the concentration of the gas mixture that includes hydrogen and carbon monoxide, but excludes the selectively detectable component, methane. The difference between the signals from the two elements is proportional to the concentration of methane in the gas mixture.

2.4. Investigation of the characteristics of the selective thermocatalytic sensor for methane and natural gas detection

2.4.1. Examination of the analytical performance of developed sensors

Considering the specific problem being addressed, sensors were designed for the selective detection of methane and natural gas, even in the presence of carbon monoxide and hydrogen (Fig. 2.6). The testing of these developed sensors involved several specialized experiments. These experiments aimed to determine the optimal supply voltage, readiness time, dynamic behavior, calibration characteristics, and other performance parameters of the sensor, as well as to assess its selectivity and operational stability. The tests were conducted on sensor samples that were part of portable automatic analyzers and methane/natural gas detectors. The experiments were carried out using metrologically certified equipment.

Fig.2.6. Photograph of a sample of a thermocatalytic methane (natural gas) sensor1- body, 2- protective cap, 3- porous titanium mesh, 4- metal posts.

The relationship between the sensor signal and the supply voltage was examined under standard conditions (temperature of 20±2 ºC, relative humidity of 40-60%, and pressure of 720±30 mm Hg) using natural gas (0.5% vol.) in air as the sample. The results obtained for determining the optimal supply voltage for natural gas sensors are shown in Table 2.9 (Appendix 8). From the data in Table 2.9, it is evident that the highest sensor signal for methane occurs at a supply voltage of 2.6 V. Both increasing and decreasing the supply voltage result in a reduced sensor signal for methane. Therefore, all subsequent experiments for methane detection in the gas mixture were conducted with a supply voltage of 2.6 V.

Similar experiments were carried out to determine the optimal supply voltage using a standard natural gas mixture in air. The findings of these tests are provided in Table 2.10. According to the data in Table 2.10, the maximum signal value for the catalytic thermosensor with the catalysts 0.75 In_2O_3-0.25Ag_2O and 0.25Fe_3O_4-0.75Ni_2O_3 for detecting natural gas is observed when the sensor supply voltage is in the range of 2.8-3.0 V.

A comparison of the sensor signal values presented in Tables 2.9 and 2.10 shows that the optimal supply voltage for the highest TCS signal in the case of natural gas (2.8-3.0 V) is higher than the value for methane (2.6 V) under identical test conditions.

Table 2.10**.**

Dependence of the analytical signal of the sensor on the supply voltage value when determining natural gas (n=5, P=0.95)*

№	Sensor supply voltage, V	Sensor signal, mV		
		$\bar{x}\pm\Delta X$	S	$Sr\cdot10^2$
1	2.0	13.8±0.2	0.03	0.4
2	2.5	20.6±0.1	0.09	1,2
3	2.8	27.0±0.8	0.15	1.7
4	3.0	28.1±0.4	0.11	1.4
5	3.1	27.5±0.8	0.15	1.7
6	3.5	25.9±0.4	0.11	1.4

*Journal "Ecological systems and devices" 2015. No. 9. P. 11-14.

At optimal supply values, the methane signal is 1.14 times greater than the signal of this sensor for natural gas. As is known, the temperature value on the catalyst surface of the sensor's sensitive element is provided by a corresponding change in the sensor's supply voltage. The results of studying the dependence of the sensitive element temperature on the supply voltage in the latter's range from 1 to 5.0 V are presented in Table 2.11.

Table 2.11.

Dependence of the temperature of the temperature-sensitive element on the supply voltage of the sensor (n=5, p=0.95)*

№	Supply voltage, V	Temperature of the GCE, °C		
		$\bar{x}\pm\Delta X$	S	Sr·102
1	1.0	150±2.0	1.7	1.14
2	2.0	250±3.0	2.5	1.05
3	3.0	350±5.0	4.1	1.15
4	4.0	500±5.5	4.6	0.92
5	5.0	650±5.8	4.9	0.75

*Scientific Bulletin of SamDU.2018.No.1.p.137.

The data presented in Table 2.11 indicates that, within the tested voltage range, the temperature of the sensitive element in the sensor has a directly proportional relationship with the applied supply voltage.

To determine the optimal readiness time, the sensor was connected to the KSP-4 self-recording potentiometer, and purified air was passed through the system. The output signal was then recorded. Simultaneously, the useful analytical signal was monitored using a digital voltmeter. These measurements enabled the identification

of the sensor’s optimal readiness time, which is the duration from the start of the self-recording process until the signal reaches the error threshold, and was found to be between 8 and 10 minutes.

The evaluation of the device's dynamic characteristics included studying the sensor's time response, such as the transient process times, which are crucial parameters alongside the calibration characteristic. The experiments were conducted under standard conditions using a mixture containing 0.25% natural gas. Prior to initiating the sensor test, the background signal was established by passing purified air through three TCSs connected in series for 10 minutes, with signals recorded using a KSP-4 and a V7-35 digital voltmeter. The change in the natural gas concentration at the sensor input was monitored with a chart recorder. The results of these tests are provided in Table 2.12.

Table 2.12.

Dynamic characteristics of a thermocatalytic methane sensor (n=5, P=0.95)

TKS	**$t_{0,1}$-response start time, s**	**$t_{0.65}$-constant time, s**	**$t_{0.9}$ - time to establish the reading, s**	**t_n - total measurement time, s**
TKS-1	4	9	12	17
TKS-2	3	8	13	18
TKS-3	4	8	13	17

The tests were conducted multiple times (at least five), and the results indicated that the developed sensor has a response time ($t_{0.1}$) of 3-4 seconds, a time constant ($t_{0.63}$) not exceeding 9 seconds, and a reading stabilization time ($t_{0.9}$) of 13 seconds. It was observed that the overall analytical signal output time (t_n) of the natural gas sensor is relatively short, ranging from 17 to 18 seconds. This further supports the potential for using the developed sensors in real-time monitoring of natural gas concentrations in gas-air mixtures.

The sensor's calibration characteristics were determined using standard verification gas mixtures of methane and air. The experiments were carried out under normal testing conditions by feeding the verification gas mixtures into the sensor. The concentration range of methane used in these tests was 0.1-5.0% vol., and each test was repeated five times. The sensor’s signal was recorded with a digital voltmeter once a stable output signal was reached (after at least 5 minutes of feeding the mixture). The results, which show the relationship between the sensor's signal and methane concentration, are presented in Table 2.13 (Appendix 9).

The analysis revealed that the sensor's signal response over the tested methane concentration range (0.1-5.0% vol.) in air follows a linear trend. Similar experiments using a standard natural gas mixture in air were also conducted, and the results are presented in Table 2.14 (Appendix 10).

The data from Tables 2.13 and 2.14 show that the sensor's signal response to both methane and natural gas concentrations follows the same linear pattern. This consistency supports the feasibility of using the sensor to monitor explosive concentrations of natural gas in various environments, including domestic and industrial settings, as well as in vehicle cabins.

To investigate how the presence of unmeasured components in the gas mixture affects the sensor’s output signal, a gas mixture with a known methane concentration was passed through the sensor, and the signal was recorded. The mixture was then replaced with another under study, and the signal was recorded again. The effects of hydrogen and carbon monoxide—components often found in industrial emissions and mine air—were specifically examined.

Two types of sensors were used during the experiments. The TKS-1 sensor contains catalysts on both the measuring and reference elements: a γ-Al_2O_3 ball impregnated with $0.75In_2O_3$-$0.25Ag_2O$ for the measuring element, and a γ-Al_2O_3 ball impregnated with $0.25Fe_3O_4$-$0.75Ni_2O_3$ for the reference element. The TKS-2 sensor, on the other hand, only has a catalyst on the measuring element: a γ-Al_2O_3 ball impregnated with $0.75In_2O_3$-$0.25Ag_2O$, and the reference element is just a γ-Al_2O_3 ball.

The experiments were carried out under the following conditions: gas mixture temperature of 25ºC, humidity at 64%, and gas flow rate of 10 l/h. The results, showing the impact of unmeasured components on the sensor's output signal, are presented in Table 2.15.

From the comparative experiment results, it was found that the sensor with the compensating element catalyst (TKS-1) shows little sensitivity to hydrogen and carbon monoxide within the tested concentration range. For methane, the signal is 36.8 times stronger than for hydrogen and 159.3 times stronger than for carbon monoxide. In contrast, the TKS-2 sensor, which lacks the compensating element catalyst, is highly sensitive to both hydrogen and carbon monoxide. The signal for 1% hydrogen in the TKS-2 sensor is 103.9 mV, while the signal for 1% carbon monoxide is 29.1 mV, and for 1% methane, it is 97.0 mV under the same conditions.

Table 2.15.

Signal of a catalytic thermosensor with and without a catalyst of the compensating element (catalyst of the measuring element: $0.75In_2O_3$-$0.25Ag_2O$; catalyst of the compensating element: $0.25Fe_3O_4$-$0.75Ni_2O_3$) (n=5, P=0.95)

№	Content of the component in the mixture, % about.	Sensor signal, mV			
		TKS-1 (with KChE catalyst)		TKS-2 (without KCE catalyst)	
		x ± Δx	Sr *102	x ± Δx	Sr *102
1	1.0 H_2	2.6±0.1	3.1	103.9±0.6	0.6
2	1.0 CO	0.6±0.1	1.3	29.1±0.2	0.6
3	1.0 CH_4	95.6±0.3	0.3	97.0±0.7	0.2
4	1.0CH_4+1.0 H_2	97.1±0.4	0.3	195.3±0.4	0.9
5	1.0CH_4+1.0 CO	96.9±0.3	0.2	115.4±1.3	1,1
6	1.0CH_4+1.0H_2+1.0CO	98.1±0.7	0.6	227.9±3.1	0.6

Atmospheric air in environments like boiler rooms, car garages, and mines can be considered a mixture of combustible gases, including CO, hydrocarbons, and H_2. In such cases, the thermal effect produced by the oxidation reactions of these components, along with the sensor's output signal, should represent the sum of the thermal effect and the contributions from each individual component. Based on the

data from Table 1.2, the thermal effect from the oxidation of these combustible gases (per 1% volume) on the working element of the catalytic thermosensor is as follows: for methane, $Q_{CH4} = 174.44 \times 10^2$ K × C_{CH4}; for hydrogen, $Q_{H2} = 189.42 \times 10^2$ K × C_{H2}; and for carbon monoxide, $Q_{CO} = 49.24 \times 10^2$ K × C_{CO}. This indicates that the specific thermal effect from hydrogen oxidation on the sensor's working element is 1.08 times greater than that from methane, while the specific heat released by carbon monoxide is only 0.28 of the heat released by methane.

Thus, when the working and reference thermoelements are installed separately and a gas mixture containing 1.03% volume hydrogen is fed only to the working thermoelement, the output signal of the methane-calibrated sensor should be 1.12% volume, which aligns with the observed results (see Table 2.15). Similar results are noted when other mixtures are introduced (e.g., 1.0 CH_4 + 1.0 H_2; 1.0 CH_4 + 1.0 CO; and 1.0 CH_4 + 1.0 H_2 + 1.0 CO) only to the working thermoelement of the sensor. Therefore, the TKS-2 (without the KChE catalyst) can be considered a versatile sensor. When used to monitor the composition of atmospheric air in environments like boiler rooms or car garages, the sensor provides an output that reflects the combined contribution of all the combustible gases present in the mixture.

As shown in Figure 2.7 (Appendix 11) and Table 2.16, the thermocatalytic sensor with a compensating element catalyst, unlike the TKS-1, demonstrates a high degree of selectivity.

Table 2.16.

Results of determining the selectivity of the natural gas sensor (n=5, P=0.95)*

№	Composition of gas mixture, %vol.	Found natural gas, vol%		
		$\bar{x}\pm\Delta X$	S	$Sr*10^2$
1	Nature gas (0.50)+air (rest)	0.48±0.06	0.05	1,2
2	Natural gas (0.50)+CO(1.00)+air(ext)	0.52±0.03	0.03	1.6
3	Natural gas (0.50)+H2(1.00)+air(ext)	0.51±0.03	0.04	1.7

*Journal “Ecological systems and devices” 2015. No. 9. P. 13.

This sensor ensures selectivity of methane and natural gas determination in the presence of hydrogen and carbon monoxide from the atmospheric air of closed ecological systems. The data in Table 8 show that the developed sensors ensure selectivity of natural gas determination in the presence of combustible air impurities, carbon monoxide and hydrogen. The error of the sensors due to unmeasured components, gas mixtures does not exceed 2.0%.

One of the main indicators of any sensor is the stability of its signal over time. The stability of the methane sensor over time was tested under normal test conditions during 1000 hours of continuous operation, passing the analyzed mixture of natural gas (1.00% vol.) and air. Sensor signals over a regulated time interval. The sensor signal over a regulated time interval is maintained stably.

The results of determining the stability of the operation of the thermocatalytic sensor for methane are presented in Table 2.17 (Appendix 12). The change in the value of the output signal during the regulated time interval was estimated according to GOST 13320-81 by the maximum deviation of the sensor signal:

$$\Delta t_q = (U_{max} - U_{min}) * 100/U_{is} \quad (2.5),$$

Where tq - limit of permissible change in the output signal over a specified time interval; Umax and Umin - maximum signal deviations; Umin - instrument scale (KSP - 4 from 0 to 50 mV).

The calculation results show that the value Δtq for the regulated time interval is equal to 2.5%, which fully satisfies the requirements for gas analyzers according to GOST 13321-81 (Table 2.17). Thus, a highly sensitive sensor has been developed that allows selectively determining methane and natural gas from a mixture of combustible substances. The developed sensor is used to measure pre-explosive concentrations of natural gas in atmospheric air.

Table 2.17.

Results obtained in determining the maximum deviation of the methane sensor (n=5, P=0.95)

№	Sensor	U, mV	U, mV	Δtg	Tolerance according to GOST
1	TKS-1	34.0	31.5	1.5	10
2	TKS-2	35.3	33.2	2.1	10
3	TKS-3	32.9	30.5	2.4	10

The sensor can be used for measurements and alarm signaling when the specified level of natural gas concentration in the atmosphere of explosive zones, production facilities of pumping stations; oil depots; petrol stations; oil producing, gas producing and processing facilities; gas facilities; boiler rooms; all other facilities where constant monitoring of the concentration of accumulating natural gas is required. The sensor is a stationary electrical device with convection supply of the controlled environment. The change in the value of the output signal over a regulated time interval was assessed in accordance with GOST 13381 and the maximum deviations of the sensor signal:

$$D_{tg} = (Up_{max} - Up_{min})\ 100/U_{is,} \quad (2.6.)$$

where D_{tg} is the limit of permissible change in the output signal over a specified time interval; Up_{max}, and Up_{min} are the maximum and minimum signal deviations; U_{is} is the instrument scale (KSP-4 0-50 mV). The calculations performed showed that the D_{tg} value over a specified time interval is equal to 1.2%.

2.4.2. Study of metrological parameters of developed sensors

Metrological characteristics and indicators of metrological assurance are traditionally the object of research and optimization in the development of measuring instruments, including the creation and improvement of sensors for monitoring methane.

For analytical instruments, as a rule, the interval characteristic of error is standardized in the form of the limit of the basic absolute (Δ_i), relative ($\delta_i=\Delta_i/C_t$) or reduced ($\gamma_i=\Delta i/C_k-C_n$) errors.

The basic absolute error (Δi) of the device at the test points was calculated using the formula:

$$\Delta_i = S_p - S_t \text{ (2.7)},$$

where Cp is the instrument readings when feeding the i-th PGS, the volume fraction of methane, %; St is the volume fraction of methane in the standard mixture, %.

The basic relative error (δi) of the sensor was calculated using the formula:

$$\delta_i = S_p - S_t / St \text{ (2.8)}.$$

The basic reduced error (γi) was determined using the formula presented as the difference between the sensor readings and the true concentration values related to the measurement range:

$$\gamma_i = (S_p - S_t) / (S_k - S_n) \text{ (2.9)},$$

where C_k - C_n are the initial and final limits of measurement of concentrations of the determined components of gaseous media, %.

Variations (V) of the instrument readings were determined by the formula:

$$B = A_{max} - A_{min} \text{ (2.10)},$$

where A_{max} (A_{min}) is the reading (the component content determined by the output signal) when approaching the test point from the side of higher or lower contents.

The influence of the gas environment parameters on the additional sensor error (%) for each point was determined by the formula:

$$\gamma_{add} = \gamma_t + \gamma_{nor} \text{ (2.11)},$$

Whereγ_t- the error obtained at the i-th temperature value;

γ_{nor} - error of the gas analyzer under normal temperature conditions (20±2 °C).

The total additional error, characterizing the set of error values under the influence of various factors, was determined by the formula:

$$\gamma_s = \sqrt{(\gamma_1^2 + \gamma_2^2 + \gamma_3^2 + \gamma_4^2 + \gamma_5^2 + \gamma_6^2 + ...)} \text{ (2.12)},$$

The values of the additional errors, denoted as γ_1², γ_2², etc., represent the errors observed when varying influencing factors. These results are considered acceptable if the errors do not exceed the limits specified by GOST 52033-2003. In the experiments, at least five thermocatalytic sensors were tested, with the

experimental conditions and number of tests in accordance with GOST 13320-81. The ambient temperature ranged from 20±5°C, the relative humidity of the gas environment was between 40-60%, and the pressure was set to 710±40 mm Hg. Certified gas mixtures, with known concentrations, were introduced into the device at a flow rate of 20±2 l/h for verification.

As per GOST 13320-81, the following key metrological parameters are required for the methane sensor: a) measurement range, b) basic error, c) variation in the output signal (readings), d) changes in the output signal over a specified time period, and e) the influence of additional error caused by changes in the influencing quantity under operational conditions.

The sensor's metrological parameters were checked under both normal and operational conditions. Five TKS-CH_4 thermocatalytic sensors with a measurement range of 0-5.0% vol. were tested. All tests, conditions, methods, and the number of repetitions adhered to the standards set by GOST 13320-81. The composition and parameters of the verification gas mixtures (GS) were in accordance with the nominal values listed in Table 2.19 (Appendix 13).

The measurement range and basic error were verified by feeding the GS into the sensor input in the sequence of No. 1-3-5-5-1-5, where the GS number corresponds to the measured component's concentration (%): No. 1 = 10±5; No. 2 = 50±5; No. 3 = 95±5. All calculations were performed according to GOST 13320-81. The sensor's basic absolute error at the test points was determined using formula (2.7). All experiments were repeated at least five times. The results of the measurement range and basic error checks for the gas analyzer with measurement limits of 0-5.0% vol. are presented in Table 2.18.

Table 2.18

Results of determining the error of the thermocatalytic methane sensor TKS-CH_4.

Methane content in the mix-ture, % vol.	TCS- CH_4 0-5.0% vol.		
	Found CH4% vol.	Main.abs. burial(Δ)	Basics priv. buried(γ)
0.51	0.52	0.01	0.2
2.55	2.51	0.04	0.8
4.74	4.81	0.07	1.4
2.55	2.58	0.03	0.6
0.51	0.52	0.01	0.2
4.74	4.82	0.08	1.6

As follows from the data provided, in the studied range, the basic reduced error of the sensor with a range of 0-5.0% vol., amounted to 0.2 - 1.6%, respectively (Table 2.20).

The determination of the variation of the TCS-CH_4 readings was carried out under normal conditions by passing through the GS gas analyzer a methane concentration of, vol.%: 1- 1.55; 2-2.67; 3-3.54; 4-4.81. The variations of the gas analyzer readings were determined using formula (2.10). The results of determining the variation of the gas analyzer readings are given in Table 2.21.

Table 2.21

Results of determination of methane sensor variation.

№	Methane con-tent in the mixture, % vol.	Found methane, % vol.		Basic absolute error (Δ)	Main reduced error (γ)	Signal variation, %
		A_{max}	A_{min}			
1	1.55	1.59	1.52	0.04	0.8	0.07
2	2.67	2.71	2.62	0.05	1.0	0.09
3	3.54	3.60	3.51	0.06	1,2	0.09
4	4.81	4.85	4.78	0.04	0.8	0.07

The experimental data (Table 2.21) indicate that the variation in the gas analyzer readings does not exceed 0.5 of the basic reduced error across all measurement ranges.

The additional error of the TCS-CH_4 sensor, resulting from changes in ambient temperature, was examined within the temperature range of -10 to +50ºC, with increments of 10ºC. The experiments were conducted at an atmospheric pressure of 71±40 mm Hg, using a gas mixture containing methane concentrations of 0.5%, 2.5%, and 5.0% by volume. The sequence for setting the temperature in the chamber began at 20ºC (the optimal temperature for determining the basic error), followed by -10ºC, 0ºC, +10ºC, +30ºC, +40ºC, and +50ºC.

To evaluate the additional temperature error, the following procedure was followed: the sensor was placed in a thermostat where standard test conditions were already established. After an hour of stabilization, the main error was checked. The temperature in the chamber was then adjusted to -10ºC, and the sensor was kept at this temperature for one hour, while being in the "switched-on" state. Afterward, calibration gas mixture No. 3 was introduced into the sensor. A copper tube coil was used to equalize the temperature of the gas mixture and the thermostat. The gas was fed into the sensor at a flow rate of 20±0.1 l/h. Only after ensuring proper stabilization of the sensor was the gas mixture analysis commenced. These tests were repeated at least five times. The results of the study on the sensor's response to varying gas environment temperatures are shown in Table 2.22 (Appendix 14).

The effect of the gas environment temperature on the additional sensor error (%) for each data point was calculated using formula (2.11). The results of determining the additional error due to changes in the ambient temperature (0 - 50ºC) are presented in Table 2.23. These results show that within the temperature range of -10 to +50ºC, the error does not exceed 4%, remaining lower than the device's basic error, as specified by GOST 13320-81.

Table 2.23.

Results of establishing additional sensor error in the temperature range from -10 to +40 ºC (n=5, P=0.95).

№	Temperature of gases of the mixture, °C	The found value is the additional error			Additional error according to GOST
		C_{CH_4}=0.5 %	C_{CH_4}=2.5 %	C_{CH_4}=5.0 %	
1	-10	0.4	3.0	2.0	5.0
2	0	0.2	2.0	2.0	5.0
3	+10	0.7	1.0	0.7	5.0
4	+15	0.5	0.4	0.5	5.0
5	+20	0.6	0.3	2.0	5.0
6	+25	0.5	0.4	2.4	5.0
7	+30	0.5	0.3	0.4	5.0
8	+35	0.9	0.4	2.0	5.0
9	+40	0.2	0.3	0.7	5.0

The data presented indicates that the sensor's output signal remains stable, enabling continuous monitoring of methane concentrations even in sub-zero temperature ranges.

The experiments were carried out in the following steps: after performing an external inspection, the sensor was integrated into the circuit and adjusted to standard testing conditions. Once the sensor stabilized, the baseline error was measured under these conditions. The pressure within the system was set using fine adjustment valves, and the flow rate was monitored with a rotameter. The results of the experiments, which assessed the influence of pressure changes within the range of 600-800 mm Hg on the sensor's sensitivity, are summarized in Table 2.24 (Appendix 15).

As indicated by the data, the sensor's signal remained stable across the range of pressure fluctuations (600 and 800 mm Hg). The error values of the analyzer due to changes in the humidity content of the gas mixture were determined by comparing the signals of both humidified and non-humidified gas mixtures under normal conditions. To investigate the effect of humidity, the tests were conducted as follows: the device was placed in a humidity chamber, where standard test conditions were established. After initial stabilization, the change in the sensor's output signal for a 2.0% vol. CH_4 gas sample was measured. An hour later, the error

was assessed by feeding a humidified 2.0% vol. CH_4 gas mixture (with 95% humidity) into the gas analyzer. Some of the results from the tests on the CH_4 sensor's resistance to moisture are shown in Table 2.25. The results demonstrate that the average change in the output signal did not exceed 2.3 mV.

A sensor stability test for concentration overloads was also conducted using a methane concentration of 7.50% vol. in the mixture. The control mixture contained 4.85% vol. methane, and the output signal of the TCS-CH_4 sensor was compared before and after exposure to the overload mixture. The exposure time to the overload mixture was 20 minutes.

Table 2.25.

Results for establishing the dependence of the methane sensor signal (TCS-CH_4) on the change in the moisture content of the analyzed gas mixture (methane content in the mixture 2.00%; n=5, P=0.95)

№	Sensor signal (x ± Δx), mV		Output signal change (Δ)
	Dry gas mixture	Humidified gas mixture	
1	126.4	123.8	2.6
2	127.7	124.8	3.1
3	126.3	124.9	1.4
	Avg. 126.8	Average 124.5	Avg.2.3

The time of restoration of normal operation of the sensor was determined by its output signal in the zone of the main error. Experiments showed that the developed methane sensor in the studied concentration range withstands concentration overloads (Table 2.26).

As can be seen from the data in Table 2.26, the value of the basic reduced error of TKS-CH_4 under the influence of overload concentration does not exceed 2.24%. The total additional error, characterizing the set of error values from the influence of various factors, was determined by formula (2.12). According to GOST 13320-81, the maximum permissible values of the total additional error should not exceed twice the limit of the permissible basic error.

Table 2.26.

Results of checking the signal stability to concentration overloads (methane measurement range 0-5.0% vol., C_{CH_4}=4.85% vol., n=5, P=0.95)

№	TCS signal, mV		Basic absolute error, (Δ), mV	Basic reduced error, (γ),%
	Before overload impact	After exposure to overload		
1	312	305	7	2.24
2	310	307	3	0.97
3	311	308	3	0.96
4	312	306	6	1.92
5	314	308	6	1.91

The total additional error of the TCS-CH_4 catalytic sensor was 2.1%. Research indicates that the thermocatalytic methane sensor TKS-CH_4, developed in this study, fully meets the requirements outlined by GOST for this category of devices, both in terms of metrological performance and other characteristics.

Methane is one of the most hazardous components in the atmosphere of enclosed ecological systems. It is not only toxic and flammable to humans but also creates an explosive mixture when combined with air. Therefore, it is crucial to monitor methane concentrations in the air. The primary cause of explosions and fires in both residential and industrial settings is the leakage or emission of methane. Existing technical solutions, such as alarms and fire detectors, do not provide sufficiently accurate and timely monitoring of the concentrations of toxic and explosive components in the air, especially methane. As a result, there is a significant need for research focused on improving the detection and control of methane levels in the air.

2.4.3. Results of comparative studies of developed methane (natural gas) sensors.

In comparative tests between the proposed sensors and those outlined in patent 5769, three certified binary gas mixtures with combustible components were used: CH_4 (1.00 vol.%), H_2 (1.00 vol.%), and CO (1.00 vol.%). All thermocatalytic sensors

analyzed in the study are suitable for use in gas analysis systems, particularly for the selective detection of methane and natural gas.

The key difference between these sensors lies in their gas sensitivity coefficients, which are defined as the ratio of the sensor's response to gas concentration (Figure 2.8.A, Appendix 16). For the thermocatalytic sensor used in this study, the gas sensitivity coefficient is 96 mV, while for the sensor in the patent (featuring a catalyst composition of $8.0Al_2O_3+91.5Co_3O_4+0.5Pt$ for the measuring element and $6.8Al_2O_3+93.2Co_3O_4$ for the comparative element), it is 87 mV/%. The sensor developed in this research, using catalysts for both the measuring and compensating elements ($Al_2O_3(0.75In_2O_3-0.25Ag_2O)$ and $Al_2O_3(0.25Fe_3O_4-0.75Ni_2O_3)$), exhibits a higher sensitivity of 96.3 mV/%. Consequently, the newly developed thermocatalytic sensor is more responsive to methane compared to the sensor described in patent No. 5769.

The comparison of selectivity between the developed sensor and the known sensors, including those previously developed in the Gas Analysis Laboratory at Samara State University, in determining methane in the presence of hydrogen and carbon monoxide, is illustrated in Figure 2.8.B (Appendix 16). The comparative results show that the sensor developed in this study offers the most promising performance. Its selectivity is 1.54 times greater than that of the sensor with the catalyst composition $8.0Al_2O_3+91.5Co_3O_4+0.5Pt$ and $6.8Al_2O_3+93.2Co_3O_4$.

Experiments with sensors TKS-1 and TKS-2 revealed that the methane output signal of TKS-1 is 1.15 times greater than the signal for hydrogen at the same concentration, while for carbon monoxide, it is 0.37 times the signal for methane. For TKS-2, the methane output signal is 1.04 times greater than the signal for hydrogen, and 0.37 times for carbon monoxide. Thus, the selectivity of TKS-1 for methane in the presence of hydrogen and carbon monoxide is 1.2 times greater than that of TKS-2. Additional experimental studies showed that the settling time for TKS-1 readings is faster than that of serial sensors, typically by about three to five seconds, which is likely attributed to the higher catalytic activity of the TKS-1 catalyst. The output signal of sensors with a catalyst only on the measuring element,

unlike those with catalysts on both the measuring and compensating elements, is the sum of the responses to all combustible components in the gas mixture.

Further experiments to assess the selectivity of the developed sensor involved parallel analysis of various premade mixtures containing hydrogen, carbon monoxide, and methane. The tests utilized sensors developed in the Gas Analysis Laboratory at SamDU, using catalysts described in [115, pp. 135-140, 116, pp. 44-47] (sensor-1), and sensors produced in the Scientific and Technical Center of Measuring Gas-Sensitive Sensors (NTC IGD) [1, p. 134, 2, p. 274] (sensor-2). The experiments used standard mixtures of methane, carbon monoxide, and hydrogen in air, with component concentrations set at 1%. Some of the obtained results are summarized in Table 2.27.

Table 2.27.

Results of comparative assessments obtained when determining the selectivity of thermocatalytic sensors (n=5; P=0.95).

№	Controlled parameter	Sensor signal, mV	
		Sensor-1	Sensor-2
1	The content of CH_4 in the air is 1% vol.	97.0	13.0
2	The content of CO in the air is 1% vol.	0.6	5.7
3	The content of H_2 in the air is 1% vol.	2.1	14.6
4	Selectivity coefficient: by CO by H_2	 46.2 161.7	 0.9 2,3

As follows from the presented data, the proposed thermocatalytic sensor is much superior in selectivity to the mass-produced sensor. During the experiments, the comparative characteristics of the developed selective thermocatalytic sensors for the period 1990-2019 in the gas analysis laboratory of Samara State University were also studied. The experiments used sensors with catalysts: 75% In_2O_3 + 25% AgO and 25% Fe_3O_4 + 75% Ni_2O_3 [116; pp. 44-47] (sensor 1), Pt-CoO-MnO_2/Al_2O_3 and Pt-NiO/Al_2O_3 [117; pp. 5-12] (sensor 2), Co_3O_4 + 1 % Pt and Co_3O_4 + MoO_3 [114; pp. 1-5] (sensor 3).

As follows from the data in the table, the developed thermocatalytic sensor -1, manufactured using sol-gel technology based on the catalyst: 75% In_2O_3 + 25% AgO and 25% Fe_3O_4 + 75% Ni_2O_3, is more sensitive than previously developed analogs (sensor 2 and sensor 3).

At the same time, the use of the developed two-chamber sensors allows for a significant increase in the reliability of monitoring the explosiveness of gas mixtures and preventing accidents caused by the failure of gas protection equipment.

Chapter 3. DEVELOPMENT AND STUDY OF PARAMETERS OF A HOUSEHOLD METHANE (NATURAL GAS) ALARM DEVICE

3.1. Design and operating principle of a stationary household methane alarm

Safety has always been a key factor in determining the quality of human life, and the desire for safety has been one of the central goals of human activities. Methane is a particularly hazardous component of the air in both residential and industrial environments, as it forms an explosive mixture with air. Therefore, monitoring methane concentrations is crucial, especially since gas leaks are the primary cause of explosions and fires. However, current alarms and fire detectors do not offer the necessary accuracy and speed in monitoring the concentrations of explosive gases, especially methane. Given this, research focused on enhancing methane detection in the air is highly relevant.

The primary requirements for methane monitoring devices include compact size, low power consumption, and high reliability. Currently, various alarms are used

to ensure fire and explosion safety in domestic and industrial settings, with these devices functioning based on detecting smoke, high temperatures, open flames, and other indicators. One drawback of these systems is that they typically "wait" for dangerous fire conditions to reach the detector. This delay is why it is essential to detect hazardous situations early by monitoring the chemical composition of the air and providing timely warnings to personnel.

To address these issues, we have developed a gas alarm system that eliminates these limitations by using a selective thermocatalytic sensor. This system not only enhances methane detection but also allows monitoring of other gases, such as natural gas, propane, and butane in both household and workplace environments. Prototypes of this device have been built, tested in laboratory conditions, and are now being prepared for real-world testing.

The development of the methane alarm was based on research involving thermocatalytic sensors with various catalysts. The alarm is designed for continuous, automatic monitoring of methane concentrations, triggering both sound and light signals once the set concentration limits are exceeded. A block diagram of a stationary household methane alarm is presented in Fig. 3.1 (Appendix 17).

The device is intended for use in industrial and domestic settings and includes:
A microprocessor unit for converting and processing data;
A thermocatalytic methane sensor;
Control elements, a digital display, and sound indicators;
A power supply.

The front panel of the methane alarm is shown in Fig. 3.2 (Appendix 18), and the external appearance of the alarm is depicted in Fig. 3.3 (Appendix 19). The alarm’s front panel features control elements and a digital display. The design allows for easy adjustment of zero readings and sensitivity without opening the device. Calibration gas mixtures are used to test and adjust the alarm. The sensitive components of the alarm are protected to prevent the direct exposure of liquids and dust to the sensor.

Adjustments for zero readings, sensitivity, and alarm thresholds are carried out using calibration gas mixtures. The device ensures that the methane concentration data provided is clear and consistent, in accordance with GOST 24032 standards.

3.2. Study of metrological parameters of stationary household methane alarm.

The stationary household methane alarm is designed for continuous automatic monitoring of the content of methane and natural gas in the air of closed industrial and public utility premises and issuing an alarm about exceeding the established values of the volume fraction of combustible gases.

The results of the dependence of the signal from the alarm on the concentration at the given values of the latter are given in Table 3.1.

Table 3.1

Dependence of the alarm signal on the concentration of methane in the mixture (measurement range 0-5.0% vol. n=5, P=0.95)

№	Methane concentration in the mixture % vol..	The set value of the CH_4 concentration in the device, % vol.	Concentration at which the alarm is triggered, (x±Δx), % vol.	Signaling errors	
				basic absolute,	the main given
1	0.50	0.50	0.53	0.03	0.6
2	1.00	1.00	0.95	0.05	1.0
3	2.00	2.00	2.08	0.08	1.6
4	2.50	2.50	2.45	0.05	1.0

The limit of the basic reduced error in measuring the volume fraction of methane in the air at the given concentration values: 0.5%; 1.0; 1.5; 2.0 and 2.5% is no more than 10%.

Warm-up time is no more than 10 minutes. The alarm response time at each set point (with a sudden change in methane content from 0 to 2.5) is no more than 20 s. The average time between failures of the alarms is at least 5000 h (determined by the sensor operating life), and the average service life is at least 3 years.

The measurement of the volume fraction of methane in the range from 0 to 5% is carried out by a thermocatalytic methane sensor with catalytic coatings of different compositions.

The additional error of the TCS-CH_4, caused by changes in the ambient temperature, was checked in the temperature range of 0 - 60 ºC. The experiments were carried out at an atmospheric pressure of 680□40 mm Hg using a gas mixture containing methane, % vol.: 0.50 and 2.50. The sequence of establishing the temperature in the chamber is +20 0C (normal temperature, established when determining the basic error) 0; +30; +50ºC.

The number of parallel experiments at each temperature is not less than five times. The results of the study of the influence of ambient temperature on the operation of the methane alarm are given in Table 3.2.

Table 3.2.

Results of the study of the influence of temperature on the efficiency of the alarm (n=5, P=0.95).

№	Temp-ra surrounding Wednesday	Signal, mV				Additional error	
		C_{CH_4}=0.50% vol.		C_{CH_4}=2.50% vol.			
		x ± Δx	Main absolute immersion	x ± Δx	Basic absolute immersion	C_{CH_4}=0.5% vol.	C_{CH_4}=2.5% vol.
1	+20	0.48±0.02	0.02	2.55±0.08	0.05	-	-
3	0	0.53±0.01	0.03	2.60±0.07	0.10	0.01	0.05
4	+30	0.47±0.01	0.03	2.41±0.09	0.09	0.01	0.04
5	+60	0.54±0.02	0.04	2.56±0.06	0.06	0.02	0.01

The effect of the gas environment temperature on the additional error of the sensor (%) for each point was determined using formula (2.11). The results of determining the additional error of the alarm caused by changes in the ambient temperature (0 – 60 ºC) are presented in Table 3.2, from which it follows that in the temperature range of 0 - 60 ºC it does not exceed 4% and is less than the basic error of the device itself. The effect of atmospheric pressure on the additional error of the

alarm was carried out in the range of 600-800 mm Hg using the example of analyzing a gas mixture with a methane content of 1.00 and 2.50 vol. The experiments were carried out in the following sequence: after an external inspection of the gas analyzer, it was included in the circuit and brought to normal test conditions (ambient temperature 20 ± 2.0 ºC; pressure 740 ± 30 mm Hg). After initial stabilization, the basic error under normal test conditions was determined. The further sequence of establishing the pressure in the chamber, mm Hg: 600; 700 and 800. The results of experiments to determine the influence of pressure in the range of 600-800 mm Hg on the additional error of the device are given in Table 3.3.

Table 3.3.

Table 8. Additional error of the alarm from changes in ambient pressure (temperature 20 ºC, n=5, P=0.95)

№	Ambient pressure Wednesday	Signal, mV				Additional error	
		C_{CH_4}=1.00% vol.		C_{CH_4}=2.50% vol.			
		x ± Δx	Main absolute immersion	x ± Δx	Main absolute immersion	C_{CH_4}=1.0 % about.	C_{CH_4}=2.5 % about.
1	760 10	1.04±0.02	0.04	2.53±0.05	0.03	-	-
2	600 10	1.05±0.03	0.05	2.56±0.04	0.06	0.01	0.03
3	700 10	1.07±0.02	0.07	2.55±0.08	0.05	0.03	0.02
4	800 10	1.03±0.04	0.03	2.56±0.05	0.06	0.01	0.03

As follows from the data provided, in the studied range of pressure changes (600 and 800 mm Hg), the operation of the alarm remains stable. The values of the additional error of the analyzer due to the change in ambient pressure, determined by formula 2.11, are no more than 0.03%.

In the experiments, the error of the alarm due to changes in the moisture content of the gas environment was determined as the difference in the signals of the humidified and non-humidified mixture of the analyzed gas at a temperature of 20±2 ºC, the methane content in the mixture of 0.5 and 2.5% vol. Tests to study the effect of humidity were carried out in a humidity chamber, in which normal test conditions were established. After the initial stabilization, the change in the value of the output signal of the alarm for a gas mixture with a methane content of 0.5 and 2.5% vol.

After an hour, the error was determined by feeding a mixture with a methane content of 0.5 and 2.5% vol. CH_4 humidified to 95% to the input of the alarm. The results of establishing the additional error of the CH_4 alarm due to the humidity of the gas environment are presented in Table 3.4. From the data in Table 3.4 it is evident that the value of the additional error due to the humidity of the gas environment does not exceed 10% and is much less than that established by GOST.

Table 3.4.

Results of establishing additional error of methane detector from change in moisture content of analyzed gas mixture (temperature 20±2 0C; n=5, P=0.95)

№	Methane content in the mixture, % vol.	Sensor signal, mV				Additional error
		Dry gas mixture		Moistened mixture		
		x ± Δx	Basic absolute error	x ± Δx	Basic absolute error	
1	1.00	1.06±0.02	0.06	1.04±0.03	0.04	0.02
2	2.50	2.57±0.05	0.07	2.59±0.04	0.09	0.02

The total additional error of the alarm, reflecting the influence of temperature, pressure, and humidity on its performance, was determined using formula (2.12). According to GOST 13320-81, the maximum permissible value for the total additional error should not exceed twice the limit of the permissible basic error. The catalytic thermo-alarm's total additional error was found to be 2.1%. The conducted studies confirmed that the thermocatalytic methane alarm developed by our team fully meets the GOST standards for this category of devices.

For practical use of the methane alarm in residential and industrial settings, a long-term aging test under methane exposure was carried out. Various methane concentrations (from 0 to 0.5% by volume) were used in these tests. The sensor operated at a temperature of 40 ºC. Higher methane concentrations were employed to assess any potential irreversible changes in the alarm's performance under such conditions. Additionally, the aging tests were conducted under different ambient

temperatures (ranging from 20 to 40 ºC) and varying gas mixture humidity levels (from 70 to 98%). Over the course of a year-long experiment, the sensor resistance increased by 2-4%, while sensitivity decreased by 1-3%. These minor variations in sensor parameters introduce a negligible error in the measurement, which still complies with production standards. The environmental conditions had little impact on the aging of the sensor. The device is capable of detecting natural gas leaks and accumulations across a wide range of methane concentrations.

The alarm features a control signal to connect an electromagnetic valve and can operate as part of an information network. The sensor is housed inside the device and is protected by a dust-proof mesh. The alarm performs the following functions: Continuous automatic monitoring of methane content in the air, triggering both light and sound alarms when the threshold methane concentration is exceeded, and controlling the electromagnetic valve.

Unlike existing gas monitoring devices, this alarm utilizes a microcontroller in the universal module of the explosive gas alarm, significantly reducing energy consumption, decreasing the number of components, and improving resolution. Additionally, the device has a compact design, is highly reliable (due to the use of highly integrated components), and is easy to set up and maintain. It is also compatible with any thermocatalytic sensors (for CO, H2, gasoline vapor, etc.), making it suitable for analyzing gas environments with various compositions.

The analyzers are operated using two buttons: the working button (KR) and the verification button (KP). The KR button is used to activate the analyzer, while the KP button is for setup and calibration. In the operational mode, the methane concentration is measured, and both sound and color indicators are used to signal the required thresholds. In the calibration mode, zero readings are adjusted, alarm threshold values are calibrated, and the display shows the indicator’s limit. The analyzers are powered by an intrinsically safe power supply unit containing compact batteries. Prototypes of the developed analyzer have successfully passed laboratory tests.

Application area of the alarm:- The developed household alarm is designed to detect leaks and continuous automatic monitoring of accumulations of flammable gases (natural gas, propane-butane mixture) in closed ecological systems (kitchens, residential buildings, cottages, garages, car interiors, basements, utility wells) and boiler rooms of various capacities operating on liquefied or natural gas;

- The alarm can also be used in various industries, production and administrative premises, underground structures, gasified vehicles and fuel storage facilities, to monitor gas contamination and ensure fire and explosion safety when using natural gas.

Response thresholds: first threshold - 20 mg/m^3 second threshold - 100 mg/m3

Chapter 4. DEVELOPMENT AND STUDY, METROLOGICAL CHARACTERISTICS OF A SEMICONDUCTOR METHANE SENSOR

4.1. Synthesis of gas-sensitive nanocomposite metal oxide films for semiconductor sensors of natural gas and methane

The growing interest in methane sensors can be attributed to their broad application in various fields such as ecology, chemical industries, petrochemicals, and safety engineering. Metal oxides are increasingly being used as sensitive elements in semiconductor sensors. For methane sensors, metal oxides such as zinc, iron, nickel, cobalt, indium, and silver are often recommended as the semiconductor material [108; pp. 164-187]. Depending on the specific requirements, different methods are employed to produce gas-sensitive films that offer stable and reproducible characteristics, with sol-gel technology being one of the most commonly used techniques.

The sol-gel method for producing gas-sensitive films is particularly promising for fabricating materials used in sensitive elements of semiconductor gas sensors. When combined with subsequent heat treatment of the reaction products, this method is widely employed to create oxide composite materials. The sol-gel process most commonly relies on controlled hydrolysis of alkoxide compounds, where the alkoxide-based method involves hydrolytic polycondensation of precursors

followed by drying. In the initial phase of hydrolysis, hydroxy derivatives of organosilicon compounds are formed, with hydroxyl groups directly bonded to silicon. These compounds then undergo polycondensation, creating a polymeric network composed of silicon and oxygen atoms.

When producing modified or mixed oxide materials for the sensitive elements of gas sensors, the sol-gel method is more advantageous than traditional film deposition and sintering techniques. Unlike these traditional methods, sol-gel technology allows for a more flexible control over the structural-phase states of oxide systems by adjusting synthesis conditions, component ratios, and heat treatment processes. This method is easy to implement, does not require expensive or complex equipment, operates at low temperatures, ensures stoichiometry of compounds, and allows for precise control over the introduction of impurities. Moreover, it enables the control of the material’s thickness, composition, and microstructure.

To obtain a selective gas-sensitive layer through the sol-gel method, strict adherence to process sequence and conditions is essential. It is crucial to develop controlled and reproducible processes for producing a given nanostructure and ensuring the appropriate properties for the gas-sensitive layer. Despite the advantages of the sol-gel approach, there is a lack of systematic studies in the scientific and technical literature regarding the optimization of sol-gel synthesis for gas-sensitive films used in semiconductor methane sensors. Thus, conducting research and developing guidelines for the synthesis of nanocomposite films based on this method is a promising direction for producing advanced materials for methane sensors.

To develop a method for creating gas-sensitive films with specified properties and sensor elements based on composite materials, the following sequence should be followed: synthesis conditions → morpho-structure → material properties → sensor output parameters. Achieving this pattern requires a comprehensive investigation of the composite materials' properties, which should include studies on

the formation kinetics, morphology of films, and their electrical properties using modern analytical equipment.

Key parameters for determining the transition of a sol-based film-forming solution into a gel include viscosity, electrical conductivity, and the stability of the initial solution. Therefore, the kinetics of structural formation in sols are often studied by measuring the viscosity and electrical conductivity of the initial solutions. In this study, we used capillary viscometry to assess the solution's stability. As per GOST 33-2000 (ISO3104-94), the viscosity determination method involves measuring the flow time in seconds of a specific volume of liquid under gravity at a constant temperature using a calibrated glass viscometer. For all viscometers, the flow time of a given liquid volume is directly proportional to its kinematic viscosity (ν).

Additional monitoring of hydrolysis and condensation processes was carried out periodically by determining the alcohol and water content in the reaction mixture. The water content was determined via titration with Fischer reagent, while the alcohol content was analyzed by gas chromatography.

Alkoxide solutions in organic solvents, water, and acid, referred to as hydrolysates, develop film-like properties over time, ranging from several hours to months, depending on the solution's composition. To produce nanocomposites, inorganic additives (e.g., metal salts) are introduced into the primary components. The inclusion of such additives enables the creation of sensitive and selective nanocomposites. These composites are formed by embedding metal oxides into the silicate matrix. Altering process conditions, such as temperature, pH, component ratio, and concentration, provides effective regulation of phase composition, particle size, and shape.

The most important parameters in synthesis include the concentration of initial substances, temperature, pH, and the method of mixing the components. Consequently, in our experiments, we examined the influence of composition, component ratios, and temperature on the viscosity, density, electrical conductivity,

and stability of the film-forming solution, as well as on the sensitivity and selectivity of the semiconductor films.

In the experiments, the primary focus was on the stages involved in preparing the solution: forming a stable sol, transforming the sol into a gel-like state, and producing oxide films with gas-sensitivity properties. Based on experimental data, which examined the effects of various factors such as composition, ratios, temperature, time, and homogenization intensity on the sol-gel process, a method for controlling the processes of producing sensitive films for gas-sensing applications was developed.

The optimization of the sol-gel synthesis of gas-sensitive films is typically conducted through empirical methods, utilizing experimental design techniques within a multifactorial space. The key to success lies in selecting the initial values of critical experimental factors and determining the appropriate variation steps. The molar ratios of the initial components were varied within the following ranges: $Si(OC_2H_5)4:H_2O:ROH:HX = (1-4):(1-40):(1-45):(0.01-0.3)$, where ROH refers to simple alcohols, and HX represents an acid. Aliphatic alcohols, such as ethanol, propanol-2, and isobutanol, were used as organic solvents because of their good solubility for TEOS and most metal salts used as dopants.

In experiments investigating the effect of solvent type on the sol maturation kinetics, the ratio of TEOS to alcohol was varied from 1:1 to 1:45. The change in this ratio was achieved by adding the required amount of alcohol to the initial solution. The results demonstrated that as the solvent content in the hydrolysate increased, the viscosity of the solution decreased for all the tested systems. The viscosity of the hydrolysate, within the range of TEOS: alcohol ratios from 1:1 to 1:45, fluctuated as follows: for ethanol, from 3.10 to 1.85 cPa; for propanol-2, from 3.20 to 1.90 cPa; and for isobutane, from 3.30 to 1.95 cPa. For all alcohols studied, the viscosity change in the solution correlated with the molecular weight of the alcohol. Notably, a significant viscosity change occurred when the alcohol/TEOS ratio was up to 30, after which the viscosity changed less noticeably with further increases in the ratio.

As the ratio of TEOS to ethanol in the solution increased from 1:1 to 1:45, the density (ρ) of the solution decreased from 0.9783 to 0.8350, a reduction of 1.172 times. The most

substantial decrease in density occurred for the ethanol/TEOS range up to 30 mol. For isopropanol and isobutane solutions, the density decreased by 1.129 and 1.169 times, respectively, when the alcohol/TEOS ratio increased from 1 to 45.

The stability of the solution also varied depending on the composition and amount of solvent (ethanol) present in the hydrolysate. For all tested solvents (isopropanol and isobutane), a similar trend was observed: increasing the solvent content up to a certain point enhanced the stability of the solution and slowed down the gelation process. However, beyond a certain alcohol content, the stability period of the solution decreased. In ethanol solutions, the stability period ranged from 4 to 18.5 days, depending on the TEOS: ethanol ratio. The highest stability (18.5 days) was observed at a TEOS: ethanol ratio of 30-35, while further increasing the ratio to 1:45 resulted in a slight reduction in stability (down to 17.5 days). For isopropanol solutions, the stability varied from 5 to 20.5 days, and for isobutane solutions, it ranged from 6 to 21.5 days. The maximum stability for propanol and butanol solutions occurred at TEOS: alcohol ratios of 1:35 and 1:40, respectively.

The highest stability and viscosity for the ethanol solution were observed at a TEOS: ethanol ratio of 1:30. At this ratio, the viscosity remained stable for up to 450 hours, making it suitable for manufacturing a gas-sensitive element for a semiconductor sensor. The composition of the solvent significantly influences the solution's stability. As the molecular weight of the alcohol increases (from ethanol to butanol), the gelation transition time increases from 18.5 to 21.5 days. Under similar conditions, a higher molecular weight alcohol results in greater solution stability. Additionally, adjusting the water content in the solution allows for the regulation of gelation time from 5 to 18.5 days, which controls the dispersion of the sol and the depth of TEOS polymerization. The optimal ratio for water to TEOS is 20, ensuring sufficient solution stability and homogeneity when a dopant is included.

The introduction of metal oxide dopants such as Zn, Fe, Co, Ni, In, Ag, and others into a silicate matrix enables the production of highly sensitive and selective nanocomposites for use in chemical sensors detecting combustible gases. Thin-film layers based on these metal oxides show promising characteristics but have been less explored in previous studies. The research focused on investigating the processes

involved in the formation of structure in TEOS-based sols when doped with a ZnO-based additive.

In the experiments, double-distilled TEOS and pure ethyl alcohol were used, with zinc chloride (ZnCl2) serving as the source of the modifying metal oxide. The preparation of the sols for the creation of gas-sensitive thin films was carried out in three stages. In the first stage, the exchange interaction between tetraethoxysilane (TEOS) and ethanol (referred to as Solution 1) was performed at room temperature for 30 minutes. Specifically, a mixture of TEOS and ethyl alcohol was prepared in a test tube in a predefined ratio. For the sol solution, the ratio of ethanol to TEOS was set at 30, where 88.5 ml of 96% ethanol (equivalent to 85.0 ml of absolute ethanol) was combined with 10.0 ml of freshly distilled TEOS. The mixture was vigorously stirred for 30 minutes at 20°C.

In experiments aimed at studying the impact of the dopant on the sensitivity and selectivity of the resulting nanocomposite, the molar ratio of SiO2 to ZnO in the sol was varied between 1:0.1 and 1:2.0. It was observed that the dynamic viscosity of dopant-containing solutions (3.8 cPa) was higher than that of the solution without the dopant (2.1 cPa). Additionally, the stability period of the solutions with the dopant was shorter compared to those without. Specifically, when ZnO was added to the solution with the composition TEOS:H2O:C2H5OH:HCl = 1:20:30:0.05 (and a SiO2/ZnO ratio of 2), there was an increase in viscosity along with a decrease in the stability period. The kinetic relationship between viscosity changes and the experiment duration for dopant-containing solutions is illustrated in Figure 4.1.

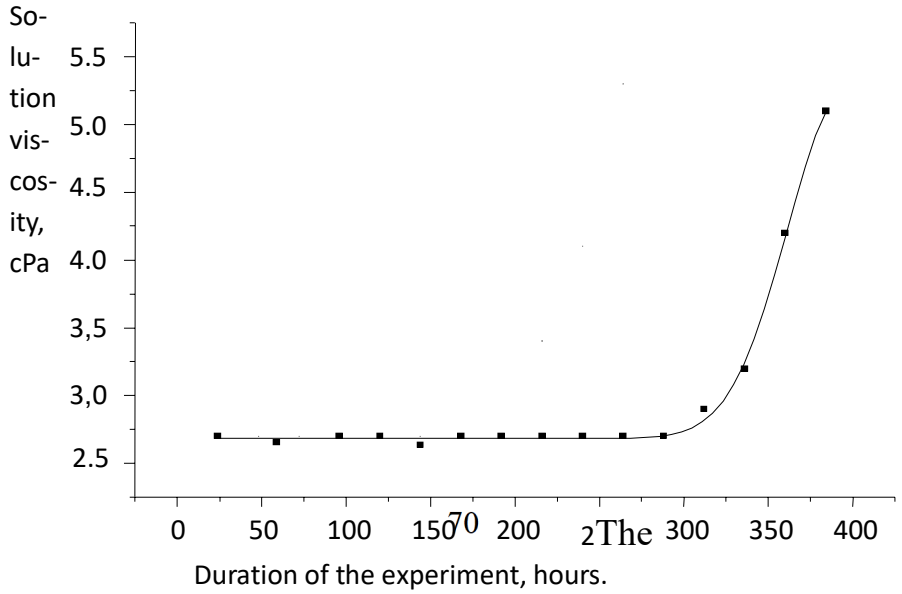

Fig.4. 1. Dependence of the viscosity of $ZnCl_2$-containing solutions on the duration of the experiment

As follows from the data presented in Fig. 4.1, the dopant-containing solution is characterized by a certain period of stable values of the solution viscosity, ensuring the formation of a homogeneous gas-sensitive film. The results of experiments to determine the effect of the amount of dopant on the properties of the solution were carried out in the range of SlO2: ZnO ratios from 1.0:0.1 to 1.0:2.0. The results of the experiments are presented in Table 4.2.

Table 4.2.

Effect of dopant amount on solution properties

№	SiO_2:ZnO	Knitting, spa	Stability, days
1	1.0:0.1	2.4	15.5
2	1.0:0.4	2.6	14.5

The data indicates that in the investigated Tetraethyl orthosilicate (TEOS) solutions with added dopants, the gelation rate of the sol varies widely depending on the composition and quantity of the dopant. Experimental results show that the viscosity of sols with a dopant is higher compared to the corresponding sols without any dopant. In all the systems studied, increasing the metal oxide content in the solution led to a rise in viscosity. Furthermore, the stability of the doped systems is inversely proportional to the amount of metal oxide present, meaning that as the dopant concentration increases, the stability of the solution decreases.

In solutions with SiO2:MexOy ratios ranging from 1.0:0.1 to 1.0:2.0 (in moles), the solution's stability decreases by a factor of 2.6 when using ZnCl2 as the dopant. This suggests that a higher dopant content results in a shorter lifespan for the solution. Films were produced from the zinc-containing solutions by applying them to glass substrates. The film was applied by pouring the solution onto the substrate and then centrifuging at 2000 rpm. The resulting films adhered firmly to the glass surface. When the zinc oxide content exceeded 10%, the films began to develop a

more pronounced crystalline structure. After annealing the films at 450°C, those made from this specific sol composition showed the highest degree of crystallinity. Increasing the annealing time from 30 minutes to 60 minutes also led to an increase in pore size, although the overall porosity of the film decreased.

This suggests that the presence of an inorganic modifying additive in the sol helps form pores in the resulting silicate films. In this case, the dopant acts similarly to a loosening agent in the inorganic polymer structure, as seen in glass-making processes. Our research further revealed that when applying gas-sensitive coatings derived from TEOS solutions containing inorganic zinc compounds, it is crucial to maintain the environmental temperature at least between 20-25°C and ensure the relative humidity remains between 55-60%.

Therefore, the study demonstrates that using sol-gel technology enables the creation of gas-sensitive films based on metal oxides. These films exhibit sensitivity to flammable and toxic gases, including methane. The semiconductor sensor elements developed from these films can be utilized in air quality monitoring systems, particularly for hazardous zones in industrial settings.

4.2. Design and operating principle of a semiconductor sensor for methane and natural gas

Utilizing a semiconductor layer composed of zinc oxide and cobalt oxide—where the CoO concentration does not exceed 10%—has proven effective for methane detection applications [118,119]. The methane sensors developed in this research feature a spiral structure built on a platinum microwire coated with glass, which is subsequently covered with a gas-sensitive film consisting of zinc and cobalt oxides. The platinum core, housed within a glass tube, acts as the heating element, a critical component since the surface chemical reactions associated with gas detection are temperature-dependent.

The gas-sensitive material and catalytic layer are deposited onto the sensor electrode using a sol-gel technique. The sensor operates by detecting changes in the electrical characteristics of the semiconductor layer, which vary according to the

composition of the surrounding gas atmosphere. The resistance—or, equivalently, the conductivity—of the sensor shifts in response to different methane concentrations.

During the investigation, various performance metrics of the sensors were examined, including sensitivity, response time, and recovery time across a range of temperatures. Measurements primarily focused on the resistance (Rs) of the sensing material applied to an insulating substrate. In the presence of a reducing gas such as methane, the resistance of the layer drops considerably compared to its baseline in clean air. The response behavior generally follows an exponential model described by the equation:

Here, C represents the concentration of methane in the gas mix, and K and α are constants characterizing the sensor response.

To better understand the semiconducting behavior, it's useful to analyze a plot of the logarithm of conductivity against the inverse of temperature (1/T) over a broad thermal range. Sensor sensitivity is often represented by a dimensionless parameter S, also referred to as the "sensor response" in various scientific sources. This is defined as:

$$\mathbf{S = R_{air} / R_{gas} = \sigma_{gas} / \sigma_{air}} \qquad \textit{(Equation 4.2)}$$

where R_{air} and σ_{air} are the resistance and conductivity in clean air, and R_{gas} and σ_{gas} are the values under methane exposure.

An alternative formulation for sensitivity is:

$$\mathbf{S = (\sigma_{gas} - \sigma_0) / \sigma_0} \qquad \textit{(Equation 4.3)}$$

In this expression, σ_0 is the conductivity in air without the presence of gas, while σ_gas is the conductivity under methane exposure.

The research ultimately led to the creation of a methane sensor that demonstrates both high selectivity and strong sensitivity. It is suitable for environmental monitoring and industrial process control, and can be integrated into gas analyzers and methane leak detection alarms.

Technical specifications of the developed semiconductor methane sensor include:

1. The range of measured concentrations of CH_4 mg/m3 is 1-1000.

2. Power consumption (average) mV 50-70

4. Current consumed by the heater mA 60-110

5. Warm-up time min. 3

7. The limit of the basic permissible error is no more than 10 ppm

8. Heater resistance at 20 ºC 8 – 15 Ohm

9. Resistance of the sensitive layer, MOhm 1 – 4

9.Weight g, not more than 1

10. Overall dimensions 5x8mm

4.3. Influence of various factors on the metrological parameters of a semiconductor methane sensor

4.3.1. Effect of temperature on the sensitivity of a semiconductor methane sensor

Methane has its own temperature dependences of the rates of adsorption, reaction, and desorption on the surface of the semiconductor layer. The change in resistance of the gas-sensitive layer of the methane sensor at a given temperature change rate must be unique for each composition of the gas-sensitive material. In methane sensors, the change in temperature of the gas-sensitive semiconductor layer is ensured by a corresponding change in the heater voltage [120].

The results of determining the dependence of the power consumed by the heater on the operating temperature of the PPS-CH_4 sensor are shown in Fig. 4.2.

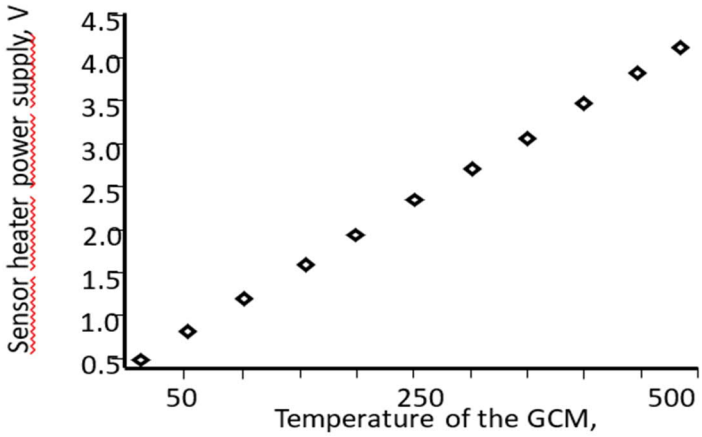

Fig.4.2. Dependence of the temperature of the GCM on the supply voltage of the PPS-SN4 heater

According to the data presented in Fig. 4.2, the power consumption of the PPS-CH4 sensor shows a linear relationship with the operating temperature across the studied range. The sensor's construction ensures a minimal temperature gradient between the heating element and the gas-sensitive layer, which supports precise temperature control during operation.

The ideal temperature for heating the gas-sensitive layer is determined based on the point where the sensor demonstrates peak sensitivity to methane. This parameter was evaluated using a dynamic method within the 200–500 °C range, with temperature increments of 50 °C. The procedure for testing the temperature-dependent sensitivity included the following steps:

1.The test chamber was set to a specific temperature, and measurements began once thermal equilibrium was reached.

2.A steady flow of ambient air was introduced, and the resistance of the nanostructured sensor film was recorded at this temperature.

3.Methane was then introduced by switching the airflow to a calibrated gas mixture. After allowing the sensor's resistance to stabilize, the measurement was recorded.

4.To initiate recovery, the methane flow was stopped, air flow resumed, and the time required for the sensor resistance to return to within ±10% of its initial value was measured.

Results from these tests, summarized in Table 4.3 (Appendix 22), show that resistance (and thus conductivity) of the sensors based on ZnO and CoO does not vary uniformly with temperature. As the heater temperature increases up to around 370–380 °C, resistance decreases for all compositions of the gas-sensitive material. Beyond this point, however, the resistance begins to rise again.

Further analysis, shown in Fig. 4.3 (Appendix 23), confirms that the highest sensitivity to methane occurs at 375 °C for sensors composed of SiO_2/ZnO films with cobalt oxide additives. Sensitivity drops when the sensor operates outside this

temperature range. At lower temperatures, incomplete desorption of reaction products limits regeneration of the active sites for methane and oxygen. At higher temperatures, reduced adsorption efficiency of both oxygen and methane impairs sensor response. Furthermore, excessive heating introduces large thermal gradients that can lead to material degradation and eventual sensor failure [121; pp. 54–56].

The study also found that increasing the CoO content in SiO_2/ZnO-based sensors enhances the signal strength at the optimal temperature. The best performance was achieved with a 10% CoO composition, where the sensor delivered the strongest response to a given methane concentration. Experiments confirmed that maintaining a heater voltage of 2.1 V reliably ensures the sensor surface reaches the optimal temperature of 375 °C, which was subsequently used in all further testing.

Variations in conductivity behavior with temperature across different gas-sensitive compositions are attributed to differences in gas adsorption characteristics and the mechanisms of surface interactions. These differences offer opportunities for selective methane detection in environments containing multiple gases.

In summary, the experimental findings demonstrate that the optimal operating temperature for achieving maximum methane sensitivity in sensors based on zinc and cobalt oxide films is 375 °C. At this temperature, sensitivity improves with increasing CoO content, with the best performance observed in SiO_2/ZnO-10%CoO compositions. A consistent heater voltage of 2.1 V is sufficient to maintain this temperature across the gas-sensitive layer.

4.3.2. Response time and recovery time of a semiconductor sensor for detecting methane and natural gas

The response and recovery times of gas sensors provide insights into their dynamic behavior and are determined through experimental methods. The response time refers to the period needed for the sensor to reach 90% of its final signal value after exposure to a sudden change in gas concentration. This is often labeled as τ_{09} or τ_response. Conversely, the recovery time, denoted as τ_{01} or τ_recovery, is the time taken for the sensor to return to 10% of its initial baseline value after the gas is removed and clean air is introduced.

In this study, the methane detection speed of the sensor was thoroughly analyzed at a working temperature of 375°C. The sensor's response time is influenced by several factors: physical and chemical reactions on the adsorption layer, gas diffusion through the sensitive film, and the rate at which the surrounding gas environment changes. To enhance response speed, the influence of the latter two factors should be minimized.

In practical applications such as environmental monitoring and industrial emissions control, where gas concentrations are typically measured at intervals of 10 seconds or more, sensors with time constants ranging from several seconds to minutes are generally sufficient.

Experimental testing of methane sensors using metal oxides at 375 °C revealed the following: sensors based on SiO_2-ZnO-CoO composites demonstrated quick reaction times of 15–18 seconds and recovery times between 23–27 seconds. A notable exception was the SiO_2-ZnO sensor lacking cobalt oxide, which showed a slower response of approximately 28–30 seconds and a recovery duration exceeding one minute due to the absence of a catalytic enhancement layer.

Table 4.4.

Response time and recovery time of the methane sensor (experiment temperature 375 °C, methane concentration in the mixture 500 mg/m^3)*.

№	Composition of gas-sensitive material	Sensor response time (τтк or τ09), sec	Sensor recovery time (τвос or τ01), sec
1	SiO_2-ZnO	30	66
2	SiO_2-ZnO-1.0%CoO	18	27
3	SiO_2-ZnO-5.0%CoO	17	25
4	SiO_2-ZnO-10%CoO	15	23

The methane sensitivity of sensors operating on the principle of conductivity variation in the gas-sensitive material (HFM) was evaluated using response curves obtained at a constant temperature of 375 °C when the sensor was exposed to a known concentration of the gas.

Figure 4.4 illustrates the time-dependent resistance change observed for the SiO_2-ZnO-10%CoO sample upon exposure to methane. The behavior of the resistance over time, as depicted in the figure, aligns with theoretical models describing the response mechanism of gas-sensitive layers to reducing gases. Specifically, the response includes a phase where resistance decreases during gas exposure and a recovery phase when the gas is no longer present.

Experimental findings indicate that the minimum response time for sensors based on SiO_2-ZnO-CoO composites ranges from 15 to 18 seconds, while the recovery period varies between 23 and 27 seconds across all examined compositions of this type.

These results confirm the feasibility of using zinc-cobalt oxide-based gas-sensitive composite materials (GCMS) for rapid methane detection. This capability makes the developed sensors suitable for fire risk monitoring in enclosed ecological environments. Additionally, when the concentration of the test gas begins to drop, the time constant and duration of the transient response slightly increase.

4.3.3. Sensitivity of a semiconductor sensor to the effects of methane

The gas sensitivity property in semiconductor materials is demonstrated through changes in resistance (R) or electrical conductivity (σ) when the material is exposed to a gas with a known concentration. These changes in resistance or conductivity result from a series of successive surface physicochemical processes.

The adsorption processes occurring on the surface are linked to alterations in the electronic state of the surface and the near-surface atomic layers, which in turn affects the surface conductivity of the gas-sensitive material.

The methane sensitivity of the silicon oxide film, produced through the hydrolysis of Tetraethyl orthosilicate (TEOS), increases when zinc oxide is incorporated into its structure. The most sensitive methane sensors are achieved by using mixed oxides of silicon, zinc, and cobalt. Typically, one of the oxides, zinc oxide (ZnO), forms the majority of the composition, while cobalt oxide (CoO), added in small amounts or applied to the surface of the zinc oxide, enhances the gas-sensitive properties of the film and the overall performance of the sensor.

To create a composite gas-sensitive material, doping was performed during the sol-gel solution maturation stage by adding cobalt chloride at concentrations ranging from 1 to 10 wt. % CoO. Cobalt oxide is known for its high catalytic activity in methane oxidation. After the films were applied to the substrate, heat treatment was conducted in an oxygen atmosphere. The results of the sensitivity tests for films based on ZnO doped with CoO in methane detection are presented in Table 4.5.

Ttable 4.5

Results of the study of the sensitivity of films based on SiO2/ZnO-CoO in determining methane (n=5, P=0.95)*.

№	Composition of the GCM	Methane content in the mixture, mg/m³	Sensor signal, 1/R kOhm-1		
			x+Δx	S	Sr
1	SiO_2/ZnO	1000	397±2	1.61	0.41
2	SiO_2/ZnO+1%CoO	1000	605±3	2.41	0.40
3	SiO_2/ZnO+5%CoO	1000	1441±5	4.02	0.28
4	SiO_2/ZnO+10%CoO	1000	2273±7	5.63	0.25

9.*Eshkobilova M.E., Abdurakhmanov I.E. Nasimov A.M. Some metrological characteristics of a semiconductor methane sensor./Scientific Bulletin of SSU. 2018. No. 1. P.

The experimental data indicates that incorporating 1 to 10% CoO into the HFM enhances its methane sensitivity. Specifically, adding 1% CoO to the SiO2/ZnO-based HFM increases the methane sensor's sensitivity by a factor of 1.5 (Table 4.5). As the CoO concentration in the HFM rises to 5% and 10%, the sensor's sensitivity to methane increases by 3.6 and 5.7 times, respectively. The most sensitive methane sensors are achieved when using a combination of zinc and cobalt oxides, particularly with a CoO content of 10% in the HFM.

In conclusion, the sensitivity of the silicon oxide film to methane improves with the incorporation of zinc and cobalt oxides into its structure. The highest sensitivity to methane is observed when mixed silicon, zinc, and cobalt oxides are used, with the CoO content in the GCM reaching 10%.

4.3.4. Calibration characteristic of a semiconductor sensor for determining methane

The sensor's response to various methane concentrations was investigated using the measurement setup shown in Fig. 4.5 (Appendix 25). To assess the gas sensitivity at the optimal temperature (375°C), the sensor’s resistance was measured both in air and in the presence of methane at different concentrations. The resistance was measured using a two-probe method, and the methane concentration was controlled using a diluent generator, which mixed a standard gas mixture with the analyte gas.

Figure 4.6 (Appendix 26) displays the resistance (Rs) of a SiO2/ZnO-based sensor in relation to methane concentration. The experiments were conducted at a sensor temperature of 375°C. The results show a decrease in sensor resistance by 280 kOhm (from 3530 to 3250 kOhm) as methane concentrations rise to 500 ppm. Further increases in methane concentration to 1500 ppm result in an additional resistance drop of 260 kOhm (from 3250 to 2990 kOhm).

However, in practice, this type of calibration curve is not entirely convenient for fundamental research or sensor and gas analyzer testing. This is because it does not fully capture the range of parameter changes of the gas analyzer. A more useful representation of the sensor’s behavior is in normalized or logarithmic coordinates. The calibration characteristic, based on the ratio of resistance values (Rair/Rgas), offers advantages such as facilitating comparisons between different sensors under similar conditions. This method also allows for easy tracking of performance changes in a single sensor under varying operating conditions.

Using conductivity as a measured parameter, rather than resistance, has the advantage of providing a clearer visualization of the calibration curve. This approach is particularly helpful in designing the signal processing circuits for gas analyzers. Additionally, the sensor’s electrical characteristics are influenced by the physical structure of its sensitive layer and the modes of its formation.

Experiments across a broad range of methane concentrations also examined the impact of doping impurity content (CoO) in the gas-sensing material (GCM). For comparison, an undoped SiO2/ZnO film was also tested. The results revealed that

sensors based on SiO2/ZnO-CoO films exhibited high sensitivity to methane. Figure 4.7 (Appendix 27) illustrates the relationship between the sensor signal and methane concentration at 375°C. From the graph, it is clear that in the methane concentration range from 50 to 1000 mg/m³, the dependence of σgas/σair on methane concentration is linear. This linear relationship enabled the development of a simple methane concentration meter design.

In summary, experiments covering a wide range of methane concentrations demonstrated that the sensor signal's dependence on doping impurity (CoO) content in the GCM results in high methane sensitivity. In the concentration range of 50 to 1000 mg/m³, the relationship between σgas/σair and methane concentration is linear.

4.3.5. Checking the service life and stability of signal valuesPPS-CH_4

To evaluate the service life and potential for real-world application of the methane sensor in industrial settings, an aging test was conducted by exposing the sensor to methane for extended periods. The test involved exposing the sensor to gas-air mixtures with methane concentrations of 0.01% and 0.20% by volume. Additionally, the sensor was subjected to varying ambient temperatures (ranging from 20 to 50°C) and air humidity levels (from 60% to 98%).

An artificial climate chamber was used to control the humidity and temperature during the tests, maintaining humidity levels between 60% and 100% at temperatures ranging from +20°C to +60°C. The sensor was exposed to methane gas for 16 hours each day over a two-month period. Following these prolonged exposures, the sensor's resistance increased by 2.1%, while its sensitivity decreased by 2.2% (see Table 4.6, Appendix 28). These changes in sensor parameters resulted in a minimal measurement error, which still met the production requirements, indicating that environmental conditions had little impact on the sensor's aging process.

Signal stability is a critical factor in the continuous operation of gas-sensitive sensors. The longevity of a sensor's continuous operation is closely tied to the stability of its output signal. To assess this, the sensor's output was monitored continuously for 2000 hours. The signal was recorded on a chart tape of a recording

device over the specified time period. When analyzing the results, transient emissions of the output signal lasting no longer than 10 seconds were excluded. Similar experiments were also conducted to assess the stability of a hydrogen sulfide sensor under normal conditions (740 ± 20 mm Hg), using a gas sample containing methane at concentrations of 0.01% and 0.2% by volume.

The results from the 2000-hour continuous operation test, presented in Table 4.7 (Appendix 29), indicate that the output signal of the PPS-CH4 sensor remained stable and consistent throughout the test period.

The calculations carried out show that the value tg for the regulated time is 3.9%(table 4.8).

Table 4.8

Results obtained when determining the maximum discrepancy methane sensor

Sensor	**Umax,, mV**	**Umin, mV**	**tg**	**Admission according to GOST**
CCH_4=0.01% by volume	1,525	1,465	0,060	5.0
CCH_4=0.2 vol.%	5,709	5,497	0.212	5.0

Thus, the developed semiconductor sensors are characterized by high signal stability.

4.3.6. Selectivity of a semiconductor sensor for determining methane

The effectiveness of gas analyzers based on semiconductor sensors for monitoring the composition of the gas-air environment largely depends on their selectivity. Selectivity is both a key requirement for these devices and one of the most challenging technological issues, as various reducing gases can cause similar changes in sensor parameters.

In environments where methane levels need to be monitored, gases such as hydrogen and carbon monoxide are also commonly present. During experiments, the

selectivity of the developed sensors for methane was evaluated in the presence of hydrogen and carbon monoxide, which, along with methane, are the primary components of exhaust gases from internal combustion engines, gaseous emissions from heating systems, and industrial and manufacturing processes. These gases are also commonly found in the atmosphere in areas like mines, quarries, gas stations, and other sites. To study the impact of undetected components in the gas mixture on the sensor's output signal, a gas sample with a known methane concentration was passed through the sensor, and the resistance signal was recorded. Then, a mixture of an unmeasured component along with methane was introduced, and the signal was measured again.

In gas analysis, several methods are used to improve selectivity, such as controlling the operating temperature, using selective filters, and applying catalysts and promoters. Temperature control enhances selectivity because different gases have distinct adsorption-desorption energy ratios. Doping is another technique that shifts the operating temperature by altering the values of potential adsorption barriers.

To ensure the selectivity of methane detection in the presence of hydrogen and carbon monoxide, the impact of temperature and doping on the gas-sensitive layer, composed of SiO2-ZnO with cobalt oxide, was investigated. This research focused on understanding the sensor properties and electrical conductivity of SiO2-ZnO+CoO semiconductor films. Cross-sensitivity studies are essential to assess this capability. Among the possible gas impurities, cross-sensitivity was specifically examined for methane, hydrogen, and carbon monoxide.

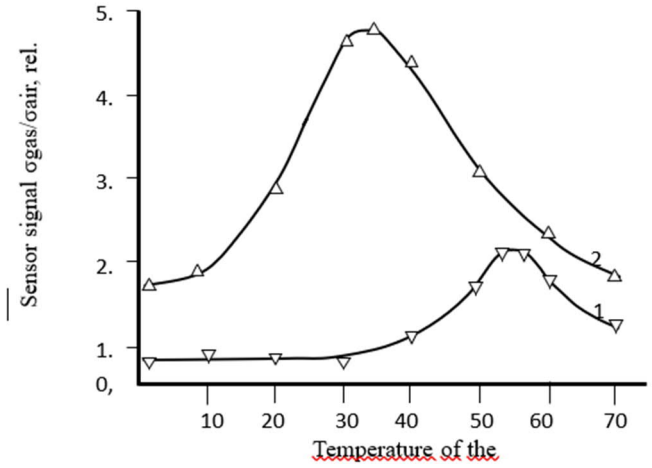

Fig. 4.8. Temperature dependences of the semiconductor sensor signal on the composition of the gas-sensitive material: 1- SiO_2/ZnO+1%CoO ; 2- SiO_2/ZnO+10%CoO

The optimal temperature for achieving high selectivity in the sensor was determined based on its maximum sensitivity to the target gas. The relationship between the surface conductivity (resistance) or sensitivity of the sensors and temperature is not linear. The variation in conductivity-temperature relationships is attributed to the differing adsorption capacities of gases and the distinct mechanisms by which they interact with the surface of the gas-sensitive material. This phenomenon can be utilized for selective detection, such as distinguishing CH4 from H2 and CO. The sensor tests were conducted with five repetitions for each gas mixture.

Through experimental investigations of the temperature dependence of the conductivity of ZnO+CoO in the presence of methane, hydrogen, and carbon monoxide, it was found that the optimal operating temperature for the PPS-CH4 sensor, ensuring maximum sensitivity to methane, is 350 ºC for SiO2/ZnO+10% CoO and 450 ºC for SiO2/ZnO+1% CoO (Fig. 4.8).

Among the materials tested, SiO2-ZnO+10% CoO demonstrated the highest selectivity for methane when exposed to hydrogen and carbon monoxide. The temperature dependence of the sensor signal for the SiO2-ZnO+10% CoO nanocomposite in the presence of CH4, H2, and CO is shown in Fig. 4.9.

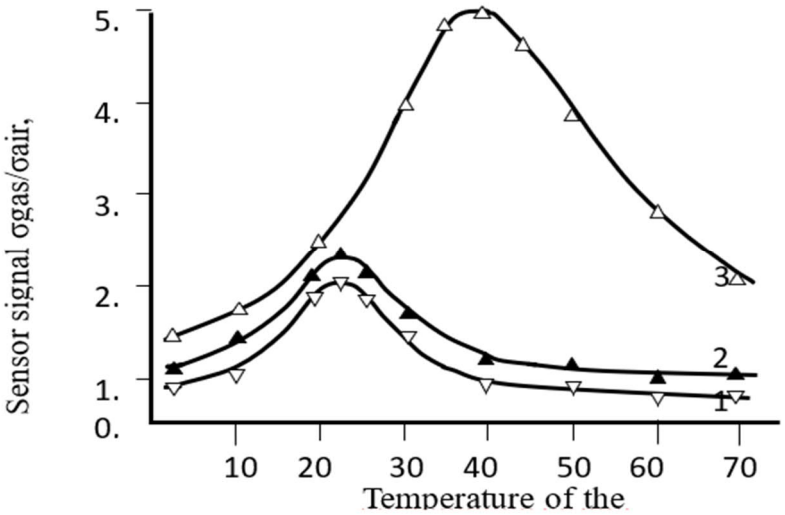

Fig. 4.9. Temperature dependence of the signal from a semiconductor sensor based on ZnO + 10% CoO in the presence of CH4, H2, and CO

From the conducted studies, it can be concluded that the developed sensor is highly suitable for continuous, automatic monitoring of carbon monoxide levels across a broad concentration range in vehicle exhaust gases. The sensor can function in continuous mode as part of an automatic exhaust gas analyzer system.

Unlike traditional gas sensor mechanisms that rely on surface processes, the sensor in this case experiences changes in conductivity due to the chemical reaction between catalytically active cobalt oxide and methane. This interaction enhances the sensor's selectivity and sensitivity to CH4, especially in the SiO2/ZnO+CoO configuration.

The key metrological properties of the developed semiconductor sensor (PPS-CH4) for methane detection have been evaluated. These sensors can detect flammable gases across a wide concentration range and offer superior metrological and operational performance. In terms of expressivity, reproducibility, and detection limits, the PPS-CH_4 sensor performs similarly to existing analogs, and in some aspects (such as weight, size, power consumption, speed, and selectivity), it outperforms widely used hydrocarbon analyzers.

The benefits of semiconductor-based sensors and analyzers, which are based on this technology, include their ease of use, long service life, and rapid measurement capabilities. These advantages make them ideal for automating

industrial processes, quickly gathering and storing analytical data for the creation of subsequent databases.

The PPS-CH_4 sensor is designed to convert methane concentration levels in the air into an electrical (resistive) signal. The recommended areas for applying the developed semiconductor methane sensors include thermal power engineering, the oil and gas industry, and housing and utility services (HCS). This facilitates early methane detection, enhances fire safety in industrial settings, reduces operational risks, enables the creation of automated gas safety systems, and supports the development of microclimate systems.

Chapter 5. GAS ANALYZER FOR METHANE MONITORING BASED ON THERMOCATALYTIC AND SEMICONDUCTOR SENSORS (TPG-CH_4)

5.1. Design and operating principle of TPG-CH_4

The development of gas detection devices for personal use to ensure safety and address issues in safety engineering and environmental protection is becoming increasingly important. Traditional devices, such as various types of spectrometers and chromatographs, are often costly, require lengthy analysis times, and demand skilled personnel for maintenance. As a result, there is a growing interest in creating gas sensors and devices that are both affordable and easy to operate. Significant progress has been made using TKS and PPS technologies. Building upon the selective TKS and PPS described in Chapters 3 and 4 of this work, a two-channel automatic methane gas analyzer called "TPG-CH4" was developed. This portable device is designed to measure methane concentration in gas samples. The measurement range for the first channel (PPS) is 0–1000 mg/m^3, and for the second channel (TKS) is 0–4.0% by volume. The maximum permissible time for obtaining readings on both channels is no more than 15 seconds. The warm-up time for channel

1 is no longer than 10 minutes, while for channel 2, it is no more than 7 minutes.

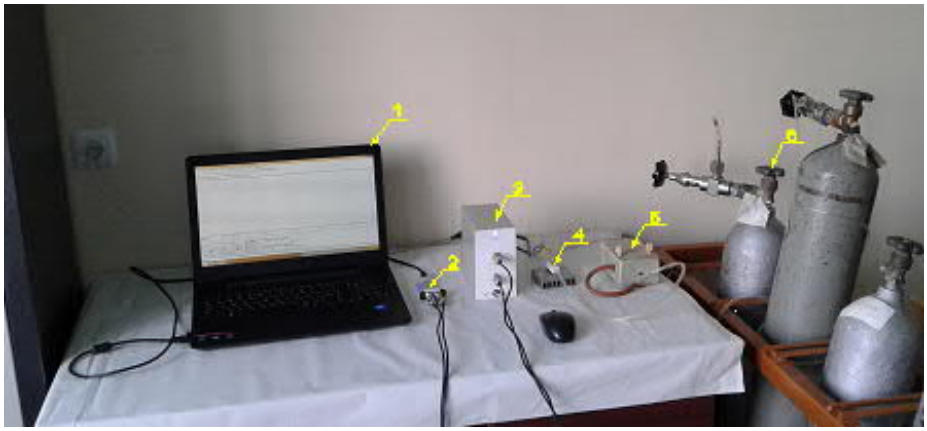

Fig.5..1 External appearance of a two-channel methane gas analyzer

The study of the effect of gas on the gas analyzer signal was carried out using a laboratory setup that included the following main components (Fig. 5.2): 1) a cylinder with a calibrated gas mixture; 2) a reducer; 3) a float rotameter; 4) a clean air generator; 5) a diluent generator; 6) a power source.

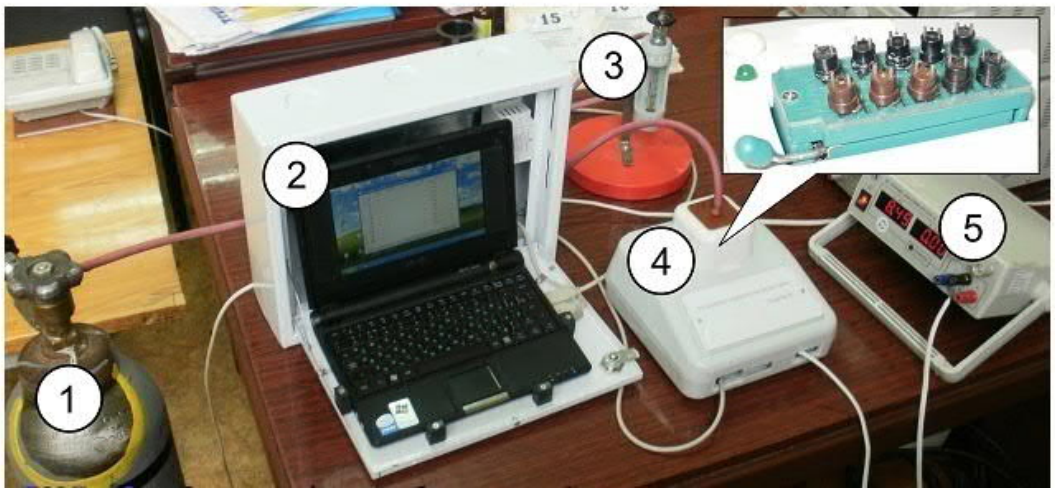

Fig. 2. Photograph of the laboratory setup for studying the PG-CH_4 gas analyzer. 1) cylinder with calibrated gas mixture; 2) reducer; 3) float rotameter; 4) clean air generator; 5) diluent generator; 6) power source.

The "TPG-CH4" gas analyzer (Fig. 5.1) consists of a primary converter (1), a signal amplifier (secondary converter) (2), an analog-to-digital converter (3), and a

personal computer (4). Sensor signal measurement is provided by a multi-channel voltage measuring device, which is controlled by a personal computer. The same computer is also responsible for collecting and processing the sensor signals. A rotameter is employed to ensure a constant flow of test gases to the sensors. In the experiment, standard methane-in-air gas mixtures, a clean air generator, and a diluent generator were used to prepare the gas mixtures.

5.2. influence of various factors on the metrological characteristics of the methane gas analyzer "PTG-CH_4"

During the experimental phase, the operational concentration ranges of the target gas were established, along with evaluations of the primary measurement error, output signal variation, and potential additional errors due to environmental factors such as temperature, pressure, and humidity. The PTG-CH_4 gas analyzers were tested within methane concentration intervals of 0–1000 mg/m³ and 0–5.0% by volume, both under controlled laboratory settings and simulated operational conditions.

In laboratory settings, parameters were maintained as follows: test gas temperature at 20 ± 5 °C, atmospheric pressure at 760 ± 30 mm Hg, relative humidity between 40–60%, and power supply at 220 ± 10 V AC. Under simulated field conditions, the test gas temperature ranged from +5 to +50 °C, pressure varied between 600–800 mm Hg, relative humidity extended from 25% to 95%, and the sensor could be inclined at angles up to 30°.

To assess the analyzer’s measurement range and basic error at concentrations of 0–1000 mg/m³ and 0–5.0%, calibration gases were introduced to the analyzer in a specific sequence (1-3-5-3-1-5), where each number corresponds to a reference gas mixture with defined component concentrations and ranges (%): No. 1 = 10%, No. 3 = 50%, No. 5 = 95%.

The primary absolute error at each calibration point was calculated using the formula:

$$\mathbf{C = Ai – A_0} \quad \text{(Equation 5.1)}$$

where **Ai** represents the measured concentration indicated by the analyzer at a given test point, and **A_0** is the actual concentration specified in the reference gas certificate.

To quantify the relative error, the following expression was used:

$$C = (Ai - A_0) / (Ck - Cn) \quad \text{(Equation 5.2)}$$

where **Ck** and **Cn** denote the upper and lower bounds of the analyzer's measurement range for the gas component, in mg/m³ or %.

Tables 5.1 and 5.2 provide data on how the PTG-CH_4 analyzer's signal output correlates with methane concentration within its specified measurement ranges.

Table 5.1

Dependence of the signal of the PTG-CH_4 gas analyzer with a semiconductor sensor on the concentration of methane in the range of CH_4 0-1000 mg/m³

CH_4 content in the mixture, mg/m3	Found CH_4 (x± x), mg/m³	S	Sr*102
10	11±0.3	0.24	2,2
50	48±0.9	0.72	1.5
250	245±1.5	1.21	0.5
500	510±2.0	1.61	0.3
750	740±2.8	2.25	0.3
980	973±4.8	3.86	0.4

Table 5.2

Results of checking the measurement range of the PTG-CH_4 gas analyzer with a thermocatalytic sensor (measurement range 0-5.0% vol.) (n=5,P=0.95.)

CH_4 introduced, % vol.	Found CH_4, (x± x), % vol.	S	Sr*102
0.10	0.97±0.02	0.02	1.7
0.50	0.45±0.06	0.05	1,1
1.50	1.54±0.09	0.07	2.7
2.50	2.56±0.16	0.13	2.5
3.50	3.41±0.15	0.12	2.5
4.50	4.43±0.19	0.15	2.4
4.90	4.95±0.21	0.17	2.4

The data presented indicate that, within the tested concentration ranges, the gas analyzer's output signal shows a linear relationship with carbon monoxide concentration. Based on the values in Tables 5.1 and 5.2, the calculated basic absolute error for gas analyzers operating within the ranges of 0–1000 mg/m³ and 0–5.0% by volume was determined to be 17.0 mg/m³ and 0.9%, respectively. To assess signal repeatability, the PTG-CH_4 analyzer was tested by introducing gas mixtures with methane concentrations of 0.55%, 2.45%, and 4.86% through the device three times.

The analyzer is deemed to meet performance criteria if, at each concentration level, the following condition is satisfied: $\mathbf{B < B_9}$, where $\mathbf{B_9}$ represents the permissible signal variation threshold.

As shown in Table 5.3, the observed variation in the gas analyzer's readings remains within 50% of the allowable basic error across all measurement intervals, which is consistent with the limits established by GOST 13320-81. In fact, the recorded variations do not exceed 0.5 of the absolute value of the permissible basic error, indicating high signal consistency.

Table 5.3

Results of determining the signal variation of the PTG-CH_4 gas analyzer (n=5, P=0.95)

Methane content in the mixture, % vol.	**Methane found(x± x), % vol.**		**Basic abs. pogresh ity**	**Variation, %**
	A_{max}	A_{min}		

0.55	0.45±0.02	0.46±0.02	0.05	0.01
2.45	2.51±0.03	2.49±0.04	0.06	0.02
4.86	4.91±0.04	4.89±0.03	0.05	0.02

To evaluate the influence of ambient temperature variations on the PTG-CH_4 analyzer's performance, tests were conducted across a temperature range of 10 °C to 50 °C. A gas sample containing 2.85% methane was used during these trials. The temperature in the test chamber was adjusted sequentially, starting from the baseline of +20 °C—identified as the optimal point for assessing the primary error—followed by settings at 10 °C, 35 °C, and 50 °C. At each temperature level, the analyzer was allowed to stabilize for one hour before the test gas was introduced and readings were recorded. Each temperature condition was tested at least three times to ensure consistency.

As shown in Table 5.4, the additional error associated with temperature shifts did not exceed 0.02% and remained significantly below the device's inherent basic error in all instances.

Table 5.4.

Results of thermocatalytic determination of methane at different temperatures with the PTG-CH_4 gas analyzer (CCH_4=2.50% vol., n=5, P=0.95)

Temperature, 0C	**CH_4 introduced, vol. %**	**Found CH4 (x± x) , vol. %**	**Sr*102**	**Error at the experimental temperature,**	**Additional error,**
20	2.85	2.83±0.06	1.6	0.02	-
10	2.85	2.81±0.07	2.1	0.04	0.02
35	2.85	2.82±0.01	0.5	0.03	0.01
50	2.85	2.88±0.01	0.5	0.03	0.01

To investigate the impact of humidity on the device's performance, a series of experiments were conducted using the following procedure: the gas analyzer was first placed inside a controlled humidity chamber, where standard testing conditions were initially established. Once the system stabilized, the baseline error of the analyzer was measured using a gas sample (GS) containing 2.55% carbon monoxide by volume.

After one hour, the same gas sample was passed through a series of three interconnected Tishchenko bottles filled with distilled water, which humidified the gas up to 95% before entering the analyzer. The error under high-humidity conditions was then recorded.

Following this phase, the gas analyzer was turned off, and standard ambient conditions were restored. After a two-hour stabilization period, the device was powered back on, and its baseline error was rechecked under normal conditions.

A similar method was applied to test the GA-O2 analyzer's humidity resistance using GS No. 2. The device's response to highly humidified gas was compared against its performance under standard conditions. Selected results from this set of experiments are shown in Table 5.5.

Table 5.5

Results for establishing the dependence of the PTG-CH4 analyzer signal on the change in the moisture content of the analyzed gas mixture (methane content in the mixture 2.45% vol., n=5, P=0.95)

Gas analysis number-Torah	Methane found, vol.%.		
	Dry gas mixture	Humidified gas mixture	Changed output-signal
1	2.47	2.48	0.01
2	2.45	2.47	0.02
3	2.48	2.47	0.01

Based on the data shown in the table, it can be concluded that the analyzer's additional error within the evaluated humidity range is 0.8%, which falls within the acceptable limits set by GOST 13320-81.

Signal stability testing of the analyzer was performed under varying pressure conditions ranging from 600 to 900 mm Hg. These tests were conducted at a constant temperature of 25 °C and a relative humidity of 60%. A reference gas mixture containing 500 mg/m³ of methane was used during the trials.

Table 5.6 presents the outcomes of these experiments assessing the effect of pressure variation on the analyzer's accuracy. According to the results, the greatest observed additional error occurred at the lowest tested pressure of 600 mm Hg and amounted to 1% (equivalent to 5 mg/m³).

Table 5.6.

Results of determining the concentration of methane at different pressures (n=5; P=0.95).

Pressure, mm Hg	CH_4 content in the mixture, mg/m³	Found CH4 (x± x), mg/m³	Sr*10 2	Error in experimental pressure,	Additional error,
760 ±10	500	512±5.8	2,3	12	
600±10	500	517±7.6	1.6	17	5
800±10	500	490±8.6	1.6	10	2
900±10	500	486±6.5	1,2	14	4

In accordance with GOST 13320-81, any additional error caused by pressure variations in gas analyzers of this category must not exceed the allowable basic error. Furthermore, this standard specifies that the total permissible additional error—accounting for fluctuations in temperature, humidity, and pressure—should not be more than double the limit of the basic error. In all tests, the combined influence of these environmental factors on the analyzer's performance was consistently within ±1.5%.

The results of the experiments confirm that the PTG-CH_4 automatic gas analyzer we developed meets the established GOST standards for devices of its class, particularly with respect to metrological characteristics. To evaluate its measurement accuracy, a series of tests were carried out using reference gas mixtures with varying methane concentrations. Selected findings from these tests are presented in Tables 5.6 and 5.7. As demonstrated by the results, the proposed thermocatalytic sensor and analyzer significantly outperform conventional thermoconductometric and electrochemical systems in both accuracy and repeatability of methane detection in gas environments.

Table 5.6

The results obtained when determining the methane content using the developed (thermocatalytic) and thermoconductometric sensor (n=5 P=0.95).

Contents CH_4 in the mixture, % about.	Methane found, % vol.					
	PTG-CH_4 (1-channel) with TCS			Thermoconductometric (TP-1120)		
	x±x	S	Sr*102	x±x	S	Sr*102
0.45	0.47±0.03	1.05	2,2	0.40±0.03	0.88	1.9
1.66	1.60±0.06	2.09	2.0	1.68±0.12	1.45	1.3
2.84	2.86±0.04	1.93	0.8	2.76±0.13	2.65	1.0
3.55	3.52±0.03	2.65	0.5	3.49±0.03	3.46	0.7
4.95	4.98±0.12	3.38	0.5	4.88±0.12	3.38	0.5

Table 5.7

The results of comparative assessments obtained in determining methane content by semiconductor and gas chromatographic methods (n=5 P=0.95).

Contents CH_4 in the mixture, % about.	Methane found, % vol.					
	Developed analyzer with PPS-CH_4 (2-channel)			Gas chromatograph "crystal-500"		
	x±Δx	S	Sr*102	x±Δx	S	Sr*102
50	47±1.3	1.05	2,2	47±1.1	0.88	1.9
100	106±2.6	2.09	2.0	108±1.8	1.45	1.3
250	256±2.4	1.93	0.8	257±3.3	2.65	1.0
500	512±3.3	2.65	0.5	489±4.3	3.46	0.7
750	738±4.2	3.38	0.5	735±4.2	3.38	0.5
1000	991±5.2	4.18	0.4	995±5.5	4.42	0.4

As a result of the study conducted, a novel approach has been introduced to enhance the selectivity of methane detection through thermocatalytic methods. This approach involves integrating both semiconductor and thermocatalytic sensing elements into a unified system, utilizing catalysts that exhibit minimal activity toward other components present in the analyzed gas mixture. The measurements of absolute and relative errors, along with signal variability, remained within acceptable thresholds defined for standard conditions in accordance with GOST 13320-81

CONCLUSION

A novel thermocatalytic approach has been designed for quantifying methane (CH_4) in atmospheric air and various process gases, even when coexisting with significant concentrations of CO, H_2, N_2, H_2O, and CO_2. Through detailed analysis of oxidation behaviors in flammable substances, an effective, durable, and selective catalyst was identified. This catalyst comprises $0.75In_2O_3–0.25Ag_2O$ and $0.25Fe_3O_4–0.75Ni_2O_3$ and is used in both the detection and reference components of the thermocatalytic methane sensor. The implementation of this catalytic system enabled the production of specialized sensors capable of rapidly detecting methane in closed environmental systems without interference from other gases in the tested concentration ranges.

A dedicated selective technique has been developed, combining thermocatalytic and semiconductor technologies, to determine methane levels in the air of enclosed ecosystems. Comprehensive evaluation of the measurement devices and analyzers created under this method confirmed their ability to detect a wide spectrum of methane concentrations with superior accuracy and operational performance.

Key findings from the research include:

Advanced thermocatalytic techniques with enhanced metrological performance have been established. These were used to develop methane sensors aimed at identifying gas leaks and accumulations in residential and industrial environments, with measurement errors maintained below 15%.

Detailed studies on the oxidation behavior of hydrogen, carbon monoxide, and methane led to identifying $0.75In_2O_3–0.25Ag_2O$ as the most effective catalyst for the primary sensing component. For the reference element, $0.25Fe_3O_4–0.75Ni_2O_3$ proved optimal. The feasibility of using temperature-responsive catalytic elements with differing activities for gas mixture components was confirmed experimentally, highlighting their high selectivity.

The thermocatalytic sensors (TCS) underwent metrological evaluation, identifying optimal operational parameters such as a 3.0 V power supply, a transient response time of 9–10 seconds, and an operational lifespan of up to 1500 hours. These sensors demonstrated high sensitivity and selectivity, making them suitable for rapid detection of pre-explosive methane concentrations in homes and vehicles.

Methane gas alarms based on thermocatalytic principles have been developed for application in mixed gas environments. These devices enhance safety by continuously monitoring natural gas levels to prevent explosions and fires in enclosed ecosystems. Their performance metrics meet or exceed the standards outlined in the applicable GOST specifications.

A manufacturing process was established for gas-sensitive thin films composed of ZnO and CoO using the sol-gel method. Semiconductor-based methane sensors (PPS-CH_4) were fabricated using these films, featuring a sensitive layer, an inert

substrate, and a heating element. These sensors exhibited fast response times, improved accuracy, enhanced stability, and extended operational life. Their high sensitivity and selectivity enable consistent, automated methane monitoring.

A dual-channel gas analyzer integrating both thermocatalytic and semiconductor sensors was created. This device can accurately measure methane concentrations across broad ranges, delivering improved measurement reliability and compliance with relevant GOST standards.

APPLICATION

Appendix 1.

Table 2.1.

Composition and parameters of the PGS for testing TKS-CH_4 with a measurement range from 0.1 to 5.0% vol.

Number of verification gas mixture	Content corresponding to points for the measurement range, %	CH_4 content in sand and gravel mixture (% vol.) - the rest is air
1	2 ± 0.2	0.11 ± 0.01
2	10 ± 0.5	0.65 ± 0.02

3	25 ± 0.5	1.45 ± 0.02
4	50 ± 0.5	2.80 ± 0.02
5	95 ± 0.5	4.85 ± 0.02
6	overload	7.50 ± 0.04

Appendix 2

Table 2.2.

Composition and parameters of the PGS for testing TKS-CH_4 with a measurement range from 0.1 to 50 mg/m3

Number of verification gas mixture	Content corresponding to points for the measurement range, %	CH_4 content in sand and gravel mixture (mg/m^3) - the rest is air
1	5.5 ± 0.5	2.5 ± 0.1
2	10 ± 0.5	5.9 ± 0.1
3	25 ± 0.5	13.0 ± 0.1
4	50 ± 0.5	25.7 ± 0.1
5	95 ± 0.5	48.3 ± 0.1
6	overload	112.0 ± 0.1

Appendix 3

Table 2.3

Results of dilution of methane gas-air mixture using the GR-03 generator.

(Methane content in the mixture 0.25% vol. or 2232 mg/m^3)

№	Dilution factor (K) for diluent gas – air	Valve number	Concentration of methane in the mixture	
			% about.	mg/m^3
1	2735	0.1	91.4*10–4	0.81
2	1530	0.2	1.63*10–4	1.45
3	1386	1	1.80*10–4	1.61

4	1025	0.3	2.44*10–4	2.17
5	771	2.1	3.24*10–4	2.89
6	520	3	4.80*10–4	4.29
7	503	0.4	4.97*10–4	4.43
8	498	1.2	5.02*10–4	4.48
9	379	1.3	6.59*10–4	5.89
10	312	2.3	8.01*10–4	7.15
11	256	4	9.76*10–4	8.72
12	216	1.4	11.5*10–4	10.3
13	193	2.4	13.0*10–4	11.5
14	171	5	14.6*10–4	13.0
15	129	3.5	19.3*10–4	17.3
16	103	4.5	24.2*10–4	21.6
17	86.8	6	23.3*10–4	25.7
18	74.6	3.6	33.5*10–4	29.9
19	60.5	7	41.3*10–4	36.9
20	49.2	4.7	50.8*10–4	45.3
21	43.1	8	57.7*10–4	51.4
22	34.9	5.8	71.6*10–4	63.9
23	30.9	9	80.3*10–4	72.2
24	26.4	5.9	94.7*10–4	84.5
25	23.2	6.9	107 *10–4	96.2
26	19.9	10	125*10–4	112
27	18.5	8.9	135*10–4	120
28	14.1	8.1	177*10–4	158

Appendix 4

Table 2.4

Results of establishing the compositions and parameters of gas mixtures of natural gas in the air in the concentration range of 0-200 mg/m3 and 0-4.0% vol.

№	Content corresponding to points for the measurement range, %	Natural gas content in the mixture (residual air)	Error in certification of GS, %
natural gas content in GS, mg/m^3			
1	10±5	23.9	0.5
2	30±5	59.1	0.5
3	50±5	95.6	0.5
4	70±5	143.0	0.5
5	95±5	180,0	0.5
6	150±5	305.0	0.5
natural gas content in GS, % vol.			
1	10±5	0.21	0.01
2	30±5	1.16	0.02
3	50±5	2.05	0.02
4	70±5	2.75	0.02
5	95±5	3.84	0.02
6	150±5	5.90	0.02

Appendix 5

Table 2.5.

Results of gas chromatographic determination of the composition of natural gas

№	Name	Mole %	Volume .%	Mass.%
1	Carbon dioxide	1,643	1,638	4,204
2	Nitrogen	0.4335	0.4343	0,7060
3	Ethane	2,881	2,865	5,038
4	Propane	0.4852	0.4782	1,244
5	N-butane	0.08945	0,08681	0.3028
6	i-pentane	0.02444	0.02335	0.1025

7	N-pentane	0.01957	0,01853	0,08209
8	2,2-dimethylbutane	0,008304	0,007782	0.04161
9	N-hexane	0,008756	0,008065	0.04387
10	methane	94.33	94.37	87.99

*International scientific journal "Symbol of Science" 2015.№ 3.P.8.

Appendix 6

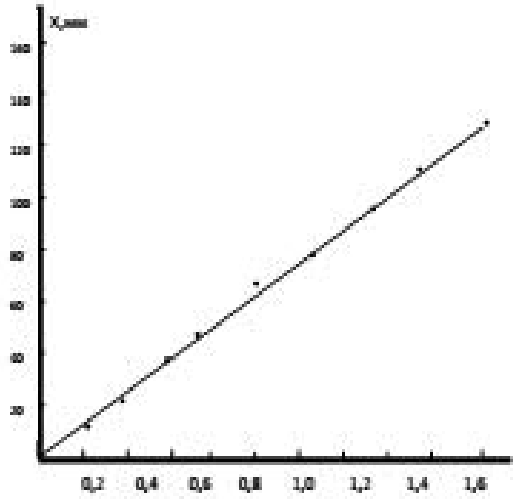

Figure 2.1. Graph of the dependence of the height of the chromatographic peak (X, mm) on the concentration of natural gas in the mixture. (*International scientific journal "Symbol of Science" 2015.№ 3.P.8.)

Appendix 7

Table 2.6

Results of the study of the activity of metal oxides in the catalytic oxidation of H_2, CO and methane with atmospheric oxygen (content in the mixture: CH_2-2.5% vol., CCO-2.4% vol., CCH_4- 2.5% vol.)*

№	Composition of the catalyst	Experimental temperature, °C					
		100	150	200	250	300	350
Degree of hydrogen oxidation (x±Δx), %							
1	Ga_2O_3	10.5±0.1	17.9±0.2	35.7±0.3	60.9±0.3	84±1.5	100.0±1.0
2	In_2O_3	36.8±0.4	76.7±0.6	96.1±0.5	100.3±1.5	100.0±1.5	100.0±1.5

3	Ag_2O	40.5±0.3	82.6±0.3	100.0±0.6	100.0±1.0	100.0±2.0	100.0±1.0
4	Cr_2O_3	13.7±0.2	17.9±0.6	28.4±0.2	42±1.0	55.7±1.0	73.5±1.5
5	MnO_2	46.2±0.1	62.5±0.2	83±0.4	98.7±0.5	100.0±1.0	100.0±1.0
6	Fe_3O_4	25.2±0.2	73.5±0.5	93.5±0.4	100.0±1.0	100.0±1.5	100.0±2.0
7	Co_2O_3	21.5±0.3	62.5±1.0	90.3±1.5	100.0±1.5	100.0±1.0	100.0±1.0
8	Ni_2O_3	33.6±0.1	73±0.1	90.8±0.8	98.7±0.3	100.0±1.5	100.0±2.0
9	CuO	16.8±0.1	32.6±0.2	47.8±0.8	64.1±0.5	78.8±0.2	91.4±1.5
10	ZnO	26.3±0.3	33.1±0.3	44.1±0.5	62.5±0.5	89.3±2.0	100.0±2.0
Degree of oxidation of carbon monoxide (x±Δx), %							
11	Ga_2O_3	7.8±0.2	14.7±0.1	31.5±0.5	41±0.3	73±1.5	100.0±1.0
12	In_2O_3	45.2±0.1	70.5±0.1	97.2±0.3	100.0±0.3	98.7±0.5	100.0±1.0
13	Ag_2O	33.6±1.0	78.4±0.4	100.0±0.5	100.0±2.0	100.0±1.0	100.0±1.5
14	Cr_2O_3	38.9±0.3	72.5±0.1	93.5±0.3	100.0±1.0	100.0±1.0	100.0±1.5
15	MnO_2	43.6±0.1	68.3±0.3	96.1±0.5	100.0±1.0	100.0±2.0	100.0±1.0
16	Fe_3O_4	98.9±0.5	67.8±0.4	90.3±0.3	100.0±1.0	100.0±1.0	100.0±1.0
17	Co_2O_3	13.7±0.3	31.5±0.1	50.4±0.5	69.3±0.3	97.1±0.8	100.0±1.0
18	Ni_2O_3	40.5±0.4	79.5±0.2	95.1±0.3	100.0±0.5	100.0±0.5	100.0±1.0
19	CuO	23.6±0.3	40.3±1.5	68.2±0.3	86.6±0.3	100.0±1.0	100.0±1.5
20	ZnO	4.2±0.4	26.8±0.1	41.0±0.4	67.2±0.5	90.3±1.5	91.5±1.0
Methane oxidation state (x±Δx), %							
21	Ga_2O_3	11.5±0.1	24.5±0.2	55.5±0.7	67.6±0.8	95.4±0.9	100.0±0.5
22	In_2O_3	36.8±0.5	70.4±0.5	90.2±0.7	94.1±0.9	100.0±1.5	100.0±1.0
23	Ag_2O	41.4±0.5	83.0±0.7	100.0±0.9	100.0±0.6	100.0±1.5	100.0±1.3
24	Cr_2O_3	2.8±0.1	5.2±0.1	9.3±0.2	21.1±0.4	27.1±0.3	50.8±0.5
25	MnO_2	4.7±0.1	14.3±0.1	20.9±0.2	27.8±0.3	35.5±0.3	48.1±0.3
26	Fe_3O_4	-	-	5.2±0.1	9.6±0.1	13.7±0.2	26.2±02
27	Co_2O_3	11.0±0.2	26.2±0.2	41.9±0.2	59.1±0.4	83.2±1.0	98.5±1.1
28	Ni_2O_3	-	-	3.5±0.1	8.5±0.2	12.7±0.1	20.4±0.6
29	CuO	28.7±0.2	51.1±0.2	63.5±0.1	92.2±0.6	100.0±0.9	100.0±1.6
30	ZnO	6.2±0.1	17.1±0.1	27.2±0.2	40.3±0.3	46.0±0.3	58.0±0.5

*International scientific journal "Symbol of Science" 2015. No. 3. P. 9-10.

Appendix 8.

Table 2.9.

Dependence of the analytical signal of the sensor on the supply voltage value when determining methane (n=5, P=0.95, methane 1.5% vol.)

№	Sensor supply voltage, mV	Sensor signal, mV		
		x ± Δx	S	Sr 102
1	1.0	6.2±0.1	0.08	1.3
2	1,2	8.1±0.1	0.08	1.0
3	1.4	14.0±0.2	0.16	1,1
4	1.6	19.1±0.1	0.08	0.4
5	1.8	30.0±0.3	0.24	0.8
6	2.0	48.5±0.5	0.41	0.8
7	2,2	60.0±0.9	0.72	1,2
8	2.4	77.4±1.3	1.05	1.4
9	2.6	96.1±1.7	1.37	1.4
10	2.8	91.2±1.0	0.81	0.9
11	3.0	87.5±1.0	0.8	0.9
12	3.5	83.4±1.3	1.05	1.3
13	4.0	79.5±1.2	0.97	1,2
14	4.5	76.0±1.5	1.21	1.6

Appendix 9

Table 2.13.

Dependence of the signal of the thermocatalytic sensor on the concentration of methane in the gas mixture (n=5, P=0.95)

№	Concentration of methane in gas mixture. % vol.	Sensor signal, mV		
		x ± Δx	S	Sr 102
1	0,1	6.2±0.1	0.08	1.3

2	0.5	32.1±0.1	0.08	0.3
3	1.0	63.0±0.3	0.24	0.4
4	1.5	74.5±0.5	0.4	0.5
5	2.0	127.0±0.9	0.72	0.6
6	2.5	160.4±2.0	1.61	1.0
7	3.0	186.1±1.7	1.37	0.7
8	3.5	217.5±2.6	2.09	1.0
9	4.0	256.4±3.2	2.58	1.0
10	4.5	291.0±3.1	2.49	0.9
11	5.0	323.3±2.8	2.25	0.7

Appendix 10

Table 2.14.

Results of establishing the dependence of the signal of a thermocatalytic sensor on the concentration of natural gas in a gas mixture (n=5, P=0.95)

Content of natural gas in the mixture, % vol.	Sensor signal ($\bar{x}\pm\Delta x$), mV	S	Sr*10 2
0.10	5,50±0,30	0.16	2.9
0.22	9,71±0,28	0.23	2.4
0.45	19,62±0,45	0.36	1.9
0.63	27,51±0,64	0.51	1.9
1.04	51,30±0,50	083	1.7
1.35	66,64±1,30	1.05	1.6
1.96	90,70±1,32	1.05	1,2
2.00	108,80±0,50	1.01	1.1
2.84	158,27±1,84	1.45	1.3
3.10	181,11±2,13	1.69	1.4

Appendix 11

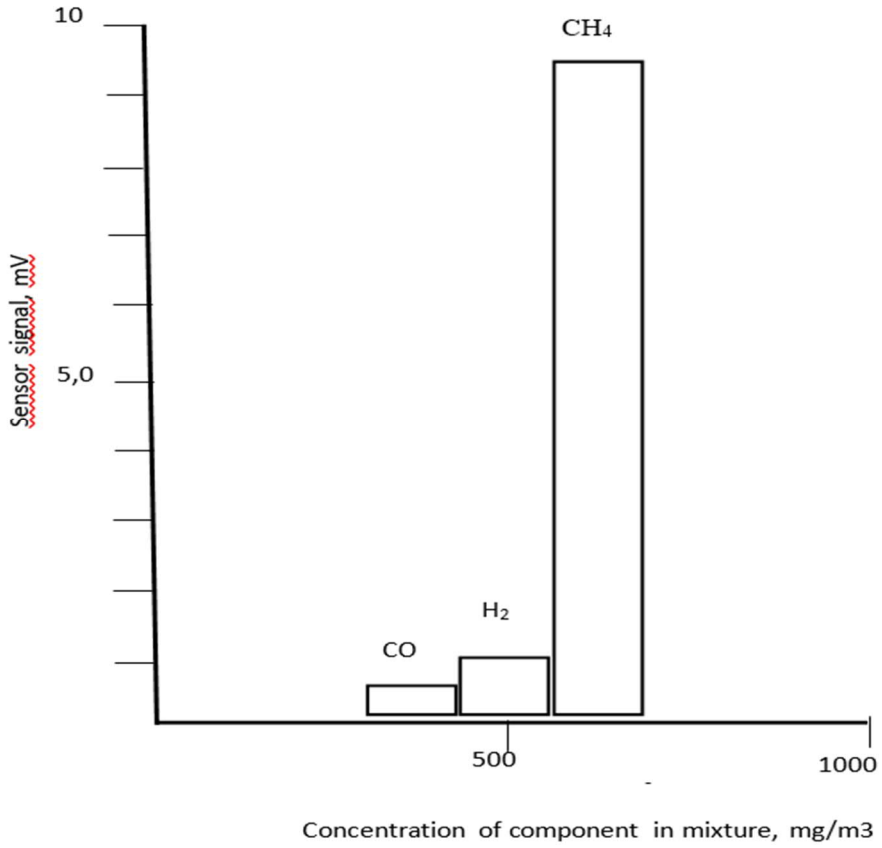

Fig.2.7. Selectivity of a thermocatalytic sensor in determining methane in the presence of hydrogen and carbon monoxide. (Scientific Bulletin of SSU 2018. No. 1. P. 139)

Appendix 12

Table 2.17.

Results of the study of the sensor operating life when determining methane (n=5, P=0.95)

№	Time, hour	Sensor signal, mV					
		TKS-1		TKS-2		TKS-3	
		x ± Δx	Sr 102	x ± Δx	Sr 102	x ± Δx	Sr 102
1	1	32.5±0.2	0.5	34.4±0.4	0.9	31.1±0.3	0.8

2	12	31.5±0.2	0.5	33.4±0.3	0.7	31.6±0.3	0.8
3	24	33.0±0.4	1.0	34.8±0.3	0.7	30.4±0.2	0.5
4	48	32.3±0.3	0.7	34.1±0.2	0.5	32.0±0.1	0.3
5	120	33.0±0.3	0.7	33.2±0.2	0.5	31.9±0.3	0.8
6	240	31.9±0.1	0.3	32.7±03	7.4	30.6±0.4	1,1
7	360	32.7±0.4	1.0	34.1±0.3	0.7	32.5±0.4	1.0
8	480	33.1±0.3	0.7	34.6±0.5	1,2	32.9±0.3	0.7
9	600	34.0±0.2	0.5	35.3±0.3	0.7	31.0±0.3	0.8
10	720	32.7±0.2	0.5	33.5±02	0.5	30.5±0.2	0.5
11	840	32.1±0.4	1.0	34.0±0.4	0.9	31.8±0.2	0.5
12	960	31.4±0.4	1.0	34.0±0.2	0.5	31.2±0.3	0.8
13	980	31.6±0.3	0.8	34.8±0.3	0.7	31.6±0.4	1.0
14	1000	32.9±0.3	0.7	34.1±0.3	0.7	30.9±0.1	0.3

Appendix 13

Table 2.19.

Results of establishing the compositions and parameters of gas mixtures for testing TCS-CH_4 with a measurement range of 0-5.0% vol.

№	Content corresponding to points for the measurement range, %	Methane content in GS (remaining air)	Error in certification of GS, %
1	10±5	0.51	0.01
2	25±5	1.26	0.02
3	50±5	2.55	0.02
4	75±5	3.75	0.02
5	95±5	4.74	0.02
6	150±5	7.50	0.02

Appendix 14

Table 2.22

Results of the study of the dependence of the sensor signal on the temperature of the gas environment. (n=5, P=0.95)

№	Temperature of gas mixture	Sensor signal, mV					
		C_{CH_4}=0.5% vol.		C_{CH_4}=2.5% vol.		C_{CH_4}=5.0% vol.	
		x ± Δx	Sr 102	x ± Δx	Sr 102	x ± Δx	Sr 102
1	+20	32.0±0.6	1.5	162.5±1.8	0.9	324.5±2.3	0.6
2	-10	32.4±0.3	0.7	159.5±2.0	1.0	320.5±2.1	0.5
3	0	32.2±0.9	2,2	160.5±1.7	0.9	322.5±3.1	0.8
4	+10	32.7±0.4	1.0	161.5±0.9	0.4	323.8±2.8	0.7
5	+15	32.5±0.7	1.7	162.1±1.1	0.5	324.6±2.3	0.6
6	+20	32.6±0.7	1.7	162.8±1.8	0.9	325.5±3.5	0.9
7	+25	32.5±0.2	0.5	161.9±1.7	0.8	325.1±2.8	0.7
8	+30	32.5±0.8	2.0	162.8±2.2	1,1	324.9 ±3.3	0.8
9	+35	32.9±0.8	2.0	163.1±2.3	1,1	324.5±3.1	0.8
10	+40	32.2±0.4	1.0	161.8±1.0	0.5	325.2±2.1	0.5

Appendix 15

Table 2.24.

Results of the study of the dependence of the sensor signal on the pressure of the gas environment. (n=5, P=0.95)

№	Temperature of gas mixture	Sensor signal, mV					
		C_{CH_4}=0.2% vol.		C_{CH_4}=1.0% vol.		C_{CH_4}=2.0% vol.	
		x ± Δx	Sr 102	x ± Δx	Sr 102	x ± Δx	Sr 102
1	760±10	12.8±0.2	1.3	62.5±0.8	1.0	124.5±2.1	1.4

2	600±10	13.1±0.3	1.8	59.5±1.0	1.4	120.5±2.5	1.7
3	610±10	12.7±0.2	1.3	60.5±0.8	1,1	123.5±2.1	1.4
4	640±10	12.9±0.4	2.5	61.5±0.9	1,2	123.8±2.2	1.4
5	680±10	12.5±0.1	0.6	62.1±1.2	1.6	124.6±1.3	0.8
6	700±10	13.2±0.1	0.6	63.7±1.2	1.5	125.5±1.5	1.0
7	720±10	12.6±0.2	1.3	62.9±0.7	0.9	125.1±1.5	1.3
8	740±10	13.3±0.3	1.8	62.7±1.2	1.5	124.9 ±1.2	0.8
9	780±10	12.9±0.3	1.9	63.1±1.1	1.4	124.5±1.1	0.7
10	800±10	13.2±0.4	2.4	62.8±1.0	1.3	125.2±2.0	1.3

Appendix 16

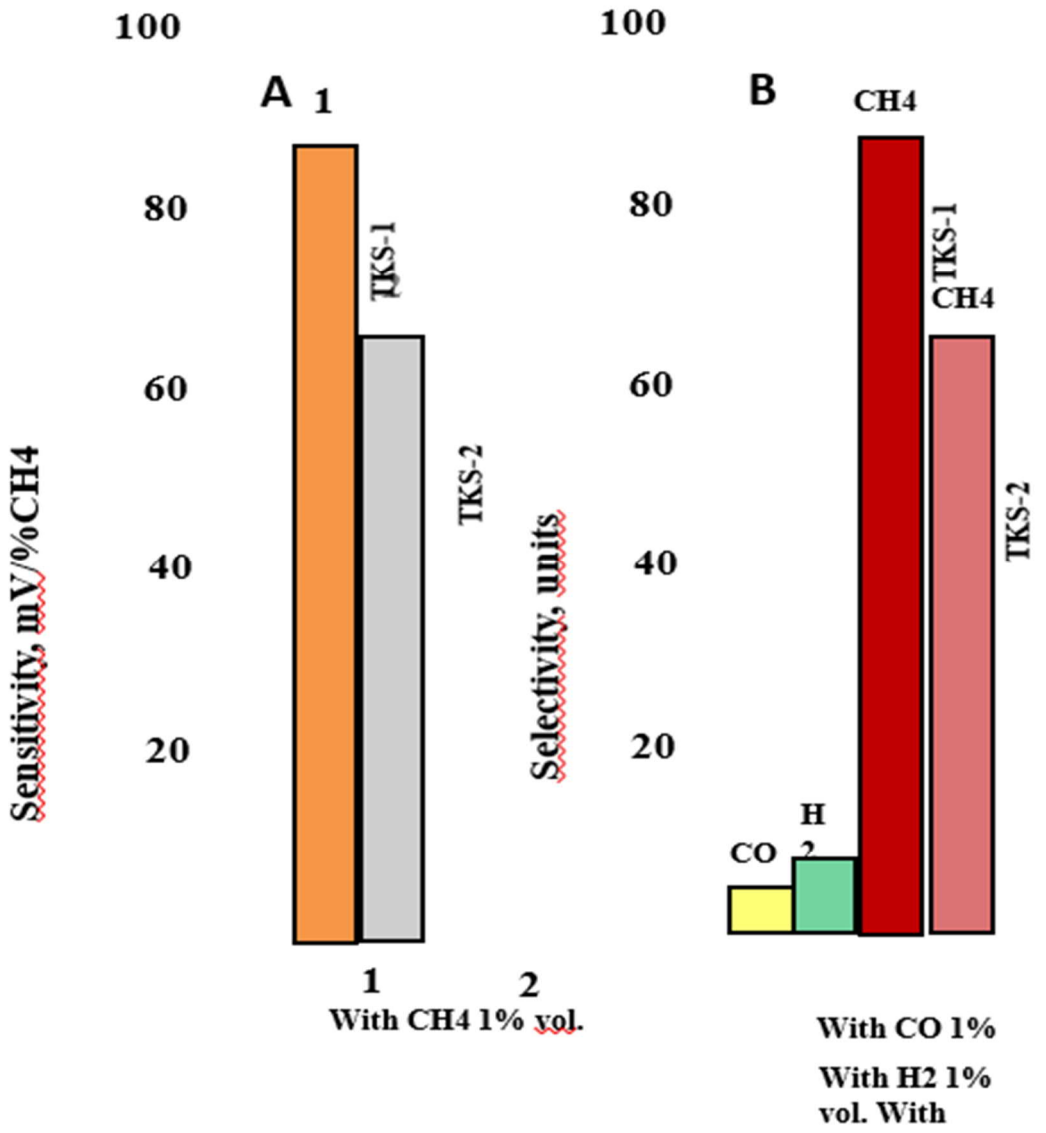

Fig.2.8. Results of comparison of the sensitivity (A) and selectivity (B) valuesthermocatalytic sensors. TKS-1. Developed input operation sensor. TKS-2. Sensor given in patent 5769. (Abdurakhmanov E., Norkulov U.M., Khoshimov T.Zh. Development of thermocatalytic sensor. Patent of the Uzbek Republic No. 5769.25.03.1999.)

Appendix 18

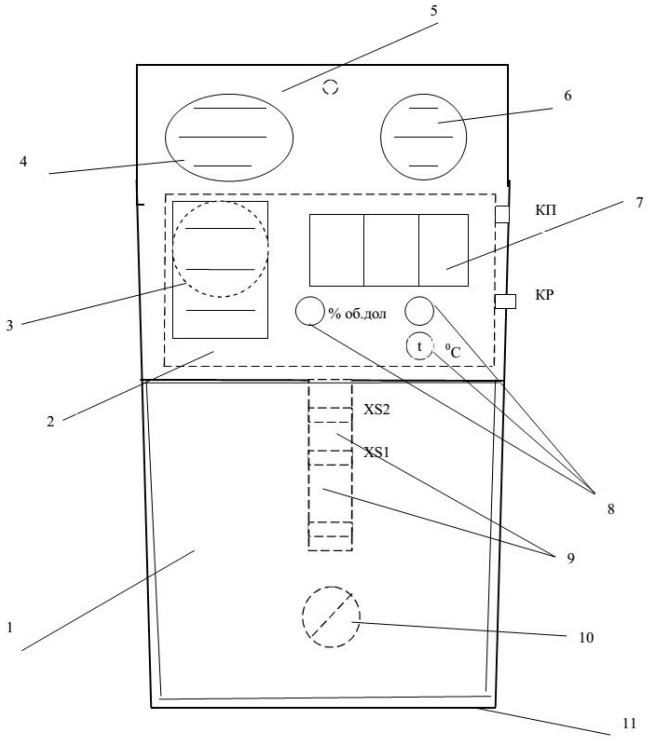

Fig. 3.2. Diagram of the front panel of the methane detector "Signal":1-removable battery power supply; 2-measuring and indicating unit; 3-thermocatalytic methane sensor; 6-sound emitter; 7-light indicator of the indicated parameter; 8-digital indicator; 9-contacts for connecting the power supply; 10-special screw for fastening the power supply; 11-alarm housing.

Appendix 19

Fig.3.3 External appearance of the stationary methane alarm "Signal"

Appendix 20

Table 3.5.

Technical characteristics of the "Signal" alarm

№	Name of the characteristic	Controlled parameters
1	Measurement range, % vol.	0-5.00
2	Price of the smallest digit of digital indication	0.01
3	Functional dependence of current on concentration	linear
4	Conversion coefficient, not less than:	25mV/% vol.
5	Permissible reduction in the conversion factor compared to the original, no more than, % per month	2
6	Response time to the presence of flammable gases, s, no more than	2
7	Output signal establishment time t0.9, no more than, sec	10
8	Recovery time after maximum concentrations, min, no more than	1
9	Limit of permissible basic reduced error	10
10	Limit of permissible basic absolute error	±0.2
11	Limit of permissible basic absolute error of alarm response based on analyzer readings	±0.2
12	Terms of Use:ambient temperature, oC	from minus 10 to + 50
13	Relative air humidity at 25°C, %, no more than	90
14	Supply voltage in the bridge circuit U, V.	1.8
15	Current consumption, no more than,	mA 100
16	Sensor weight, no more than, g.	4
17	Weight of the alarm (with AA batteries) kg, no more	0.3
18	Overall dimensions, mm, not more than	48x210x25
The SGG consists of an electronic unit and a sensor. The device is powered by alternating current 220±40V or direct current 12±2V (AA battery).		
Method of sampling- diffusion		

Alarm type- stationary.

Appendix 21

Table 4.1.

Results of determining the influence of the composition and amount of solvent on the stability of the mixture: TEOS-H2O-alcohol-HCl.

№	Ratio of solution components, mol				Stability, days
	TEOS	H2O	alcohol	HCl	
Ethanol					
1	1	20	1	0.05	4.0
2	1	20	5	0.05	5.0
3	1	20	10	0.05	6.0
4	1	20	15	0.05	7.0
5	1	20	20	0.05	12.0
6	1	20	25	0.05	15.0
7	1	20	30	0.05	18.5
8	1	20	35	0.05	18.5
9	1	20	40	0.05	18.0
10	1	20	45	0.05	17.5
Iso-propanol					
1	1	20	1	0.05	5.0
2	1	20	5	0.05	7.0
3	1	20	10	0.05	9.0
4	1	20	15	0.05	12.0
5	1	20	20	0.05	16.0
6	1	20	25	0.05	18.5
7	1	20	30	0.05	19.5
8	1	20	35	0.05	20.5
9	1	20	40	0.05	20.5
10	1	20	45	0.05	20.0
Iso-butanol					
1	1	20	1	0.05	6.0
2	1	20	5	0.05	7.5
3	1	20	10	0.05	9.5

4	1	20	15	0.05	13.0
5	1	20	20	0.05	16.5
6	1	20	25	0.05	19.0
7	1	20	30	0.05	20.5
8	1	20	35	0.05	21.0
9	1	20	40	0.05	21.5
10	1	20	45	0.05	21.5

Appendix 22

Table 4.3

Dependence of the resistance of the SiO2/ZnO-CoO-based GC on the sensor temperature (methane concentration in the gas-air mixture 1000 mg/m3).

Composition of the GCM	Rair.	Temperature of the GCM, ^{0}WITH									
		50	100	150	200	250	300	350	400	450	500
SiO_2/ZnO-	3500	3280	3026	2900	2784	2677	2578	2486	2522	2677	2784
SiO_2/ZnO-1%CoO	2920	2646	2316	2184	2010	1890	1755	1663	1654	1755	1930
SiO_2/ZnO-5%CoO	2380	1926	1538	1200	983	828	715	656	694	858	1026
SiO_2/ZnO-10%CoO	1900	1407	1091	813	656	550	456	416	440	542	693

Appendix 23

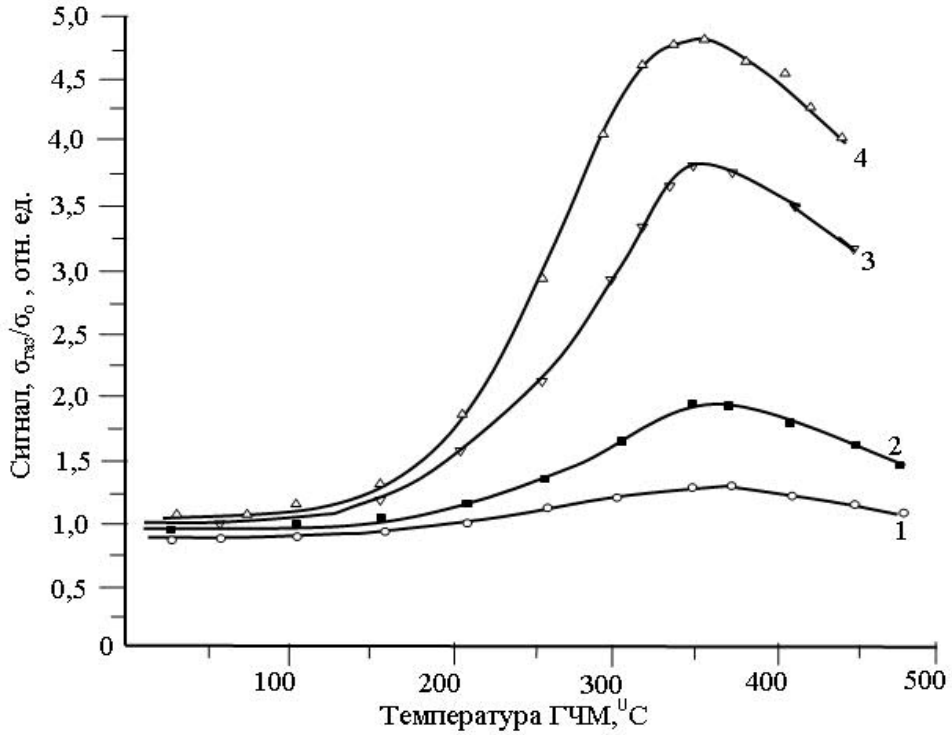

Fig. 4.3. Dependence of the signal (σgas/σo) of the semiconductor sensor on the temperature of the PPS-CH4 heater in the presence of methane (CCH4 - 500 mg/m3, 1- SiO2/ZnO; 2- SiO2/ZnO-1%CoO; 3- SiO2/ZnO-5%CoO; 4- SiO2/ZnO-10%CoO).*

Appendix 24

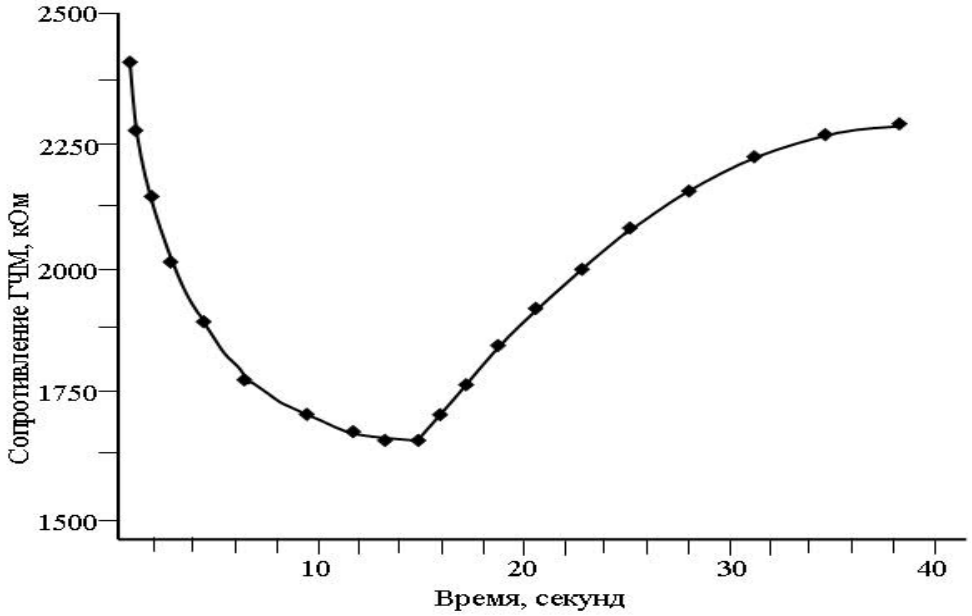

Fig.4.4. Time dependence of the change in resistance of the SiO2/ZnO-10%CoO-based GC sample upon interaction with the detected gas.

Appendix 25

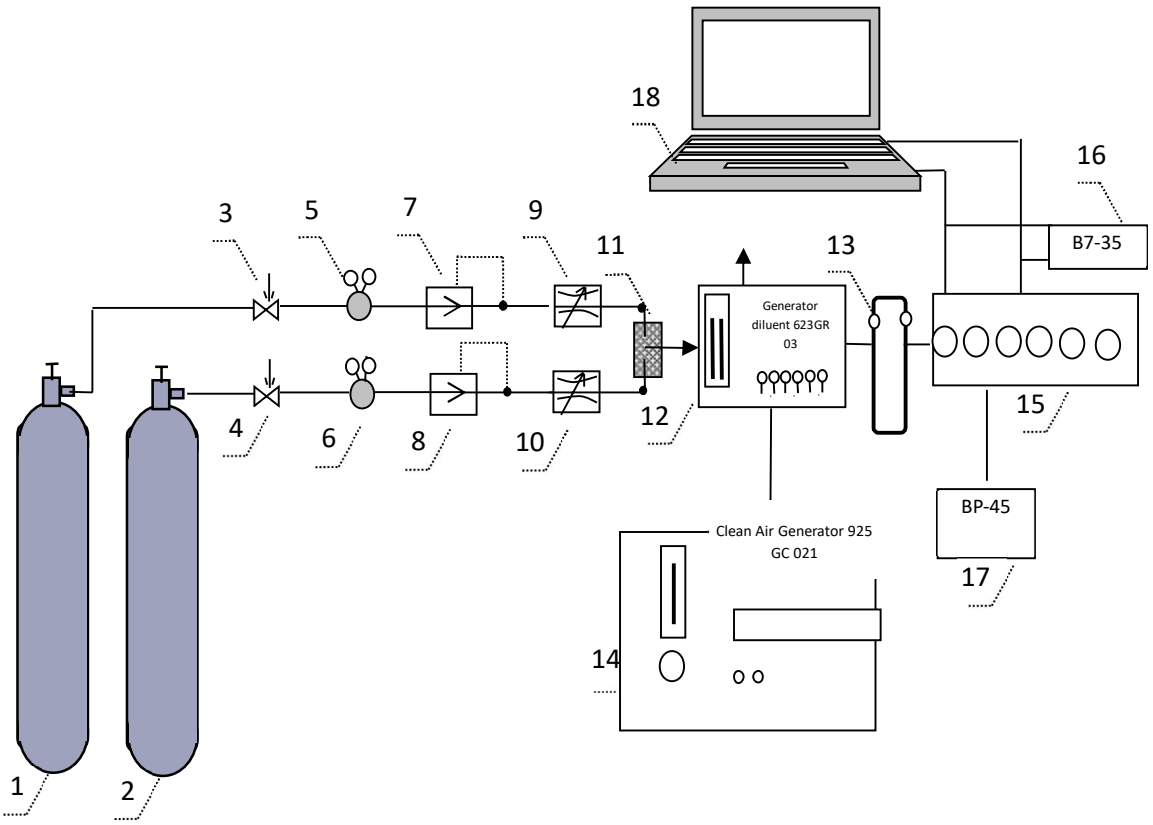

Fig. 4.5. Schematic diagram of the installation for testing a semiconductor sensor: 1 and 2-cylinders with standard gas; 3 and 4-stopcocks; 5 and 6-control pressure gauges; 7 and 8-pressure stabilizers; 9 and 10-adjustable throttles; 11-mixer; 12-generator-diluent, type 623 GR 03; 13-rheometer (or rotameter); 14-clean air generator-925 GC 02; 15-remote control for sensor signal and a set of semiconductor sensors; 16-millivoltmeter; 17-unit of calibrated voltage sources BP-45; 18-computer.

Appendix 26

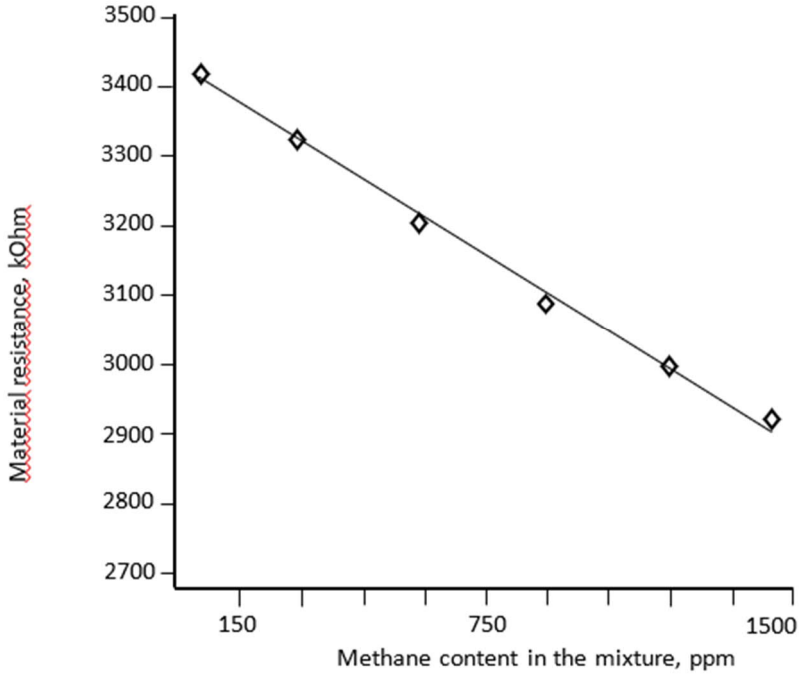

Fig. 4.6. Dependence of the sensor resistance based onSiO2-ZnO from methane content in air.

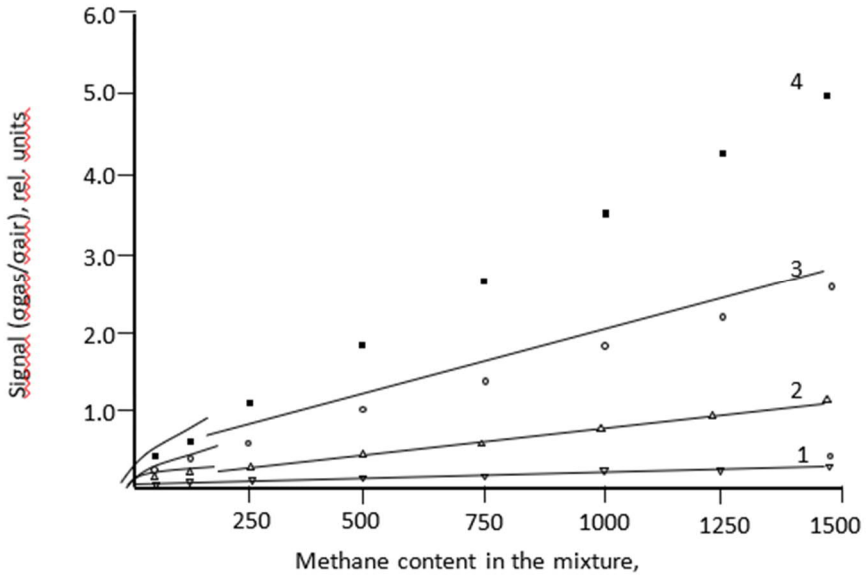

Fig.4.7. Signal dependence (σgas/σair) semiconductor sensor from methane concentration at a temperature of 375 oC. 1-SiO2/ZnO; 2- SiO2/ZnO-1%CoO; 3-SiO2/ZnO-5%CoO; 4- SiO2/ZnO-10%CoO.

LIST OF REFERENCES

1. Golinko V.I., Kotlyarov A.K., Belonozhko V.V. Monitoring the explosion hazard of mine workings. D: Science and Education, 2004. – 207 p.

2. Karpov E.F., Birenberg I.E., Basovsky B.I. Automatic gas protection and control of mine atmosphere. Moscow: Nedra, 1984. – 285 p.

3. Dorozhkin L.M., Rozanov I.A. Chemical gas sensors in environmental diagnostics // Sensor. 2001. No. 2. P. 2-10.

4. Karpov E.F., Klebanov F.S., Petrosyan A.E. Natural hazards in mines. Methods of their control and prevention. Moscow: Nedra, 1981. 471 p.

5.Abdurahmanov E., Ibodullaev U. Sensor for selective monitoring of the toxic and explosive components of air. // Global technical conference.- Pittcon. New Orleans, La USA. 2002. p. 513.

6. Cattrall Robert V. Chemical sensors. M.: Scientific world, 2000. 144 p.

7. Schmidt D., Schwartz A. Optoelectronic sensor systems. Moscow: Mir, 1991. 96 p.

8. Bernath Peter F. Spectra of Atoms and Molecules Second Edition, New York.: Oxford University Press, 2005. 454 pages.

9. Culshaw B., Stewart G., Dong F., Tandy C., Moodie D. Fiber optic techniques for remote spectroscopic methane detection – from concept to system implementation//Sensors and Actuators B: Chemical, Vol. 51, 1998. pp. 25–37.

10. Liu D., Fu S.N., Tang M., Shum P., Liu D.M. Comb filter-based fiber-optic methane sensor system with mitigation of cross gas sensitivity//J. Lightwave Technol, 30, 2012. pp. 3103–3109.

11. Brambilla G., Finazzi V., Richardson D. Ultra-low-loss optical fiber nanotapers // Opt. Express, 12, 2004. pp. 2258–2263.

12. Jin W., Ho H.L., Cao YC, Ju J., Qi LF Gas detection with micro- and nanoengineered optical fibers//Optical Fiber Technology, Volume 19, Issue 6, Part B, December 2013. Pages 741-759.

13. Schmid T. Photoacoustic spectroscopy for process analysis//Anal. Bioanal. Chem, 384, 2006. pp. 1071–1086.

14. Livchak I.F., Voronov Yu.V. Environmental protection. Moscow: Stroyizdat, 1988. 564 p.;

15. Environmental control post for vehicles (PECA)// Devices and systems for monitoring exhaust gases from motor vehicles. CJSC "Ukranalit" - All-Ukrainian Institute of Analytical Instrumentation. Received from the Internet: E-mail:*analyt@ukranalyt.com.ua*, E-mail:*ksm05@ukr.net*.

16. Environmental Chemistry / edited by J. O. M. Bockris. Moscow: Chemistry, 1982. Pp. 197 - 236.;

17. Karpov E.F., Ryazanov A.V. Automation and control of degassing systems. Moscow: Nedra, 1983. 162 p.

18. SMP-NT mine atmosphere parameter monitoring system. – Katowice: EMAG Mining Electrification and Automation Center, 2001. 8 p.

19. Safety rules in coal mines. NPAOP 10.0-1.01-10. - K.: Okho-rona pratsi, 2010. 430 p.

20. Romanchuk A.L., Aleynikova G.M., Privalov N.I. Degassing when extinguishing fires in coal mines. Kyiv: Tekhnika, 1985. 119 p.

21. Golinko V.I., Kotlyarov A.K. Study of heat exchange process in thermoconductometric methane sensors//Methods and means of creating safe and healthy working conditions in coal mines: b. scientific. tr., Issue 18. – Makeyevka-Donbass: MakNII, 2006. Pp. 301-314.

22. Boyko V.O., Frundin V.Yu., Bilonozhko V.V. Thermoconductometric sensor // Pat. 13933A Ukraine, MK G01N27/18. Publ. 04/25/97 Bulletin. No. 2. 8 p.

23. Golinko V.I., Kotlyarov A.K. Theoretical substantiation of the parameters of a thermal conductometric methane sensor with a non-isolated comparative element. // B. scientific. t. NSU. 2006. No. 26. P. 60-67.

24. Combustible gas detector // Patent No. 2475733 France, IPC G01N 27/16. Published 08.01.1982. "Inventions in Russia and Abroad" No. 1, 1982. 9 p.

25. Shcherban A.N., Furman N.I. Methods and means of mine gas control. K.: Naukova Dumka, 1965. 411 p.

26. Margolis Z.I. Oxidation of hydrocarbons on heterogeneous catalysts. Moscow: Chemistry, 1977. 363 p.

27. Medvedev V.N. Mathematical model of formation of output signals of thermocatalytic methane sensors // Methods and means of creating safe and healthy working conditions in coal mines: collection of scientific papers of MakNII. – Makeyevka, 2006, No. 18. P. 121-129.

28. Collection of instructions on safety rules in coal mines. Volume 2. – K.: Dernaglyadokhoronpratsi, 2003. – 416 p.

29. Grinchuk, A.P. Development of gas sensors for monitoring combustible gases / A.P. Grinchuk, I.A. Taratyn, V.V. Khatko // Instruments and methods of measurements. - 2010. - No. 1. - P. 51-55.

30. Features of the design and manufacturing technology of thin-film metal oxide integrated gas sensors / S.I. Rembeza [et al.] // Sensor. - 2004. - No. 1. - P. 20-28.

31. Taratyn, I.A., Khatko V.V. Features of the sensory response of thermocatalytic gas sensors with different types of heaters.//Vestn. Polotsk state University. Series B. Applied sciences. 2011. No. 3. P. 53–57.

32. Kormosh V.V. Semiconductor thick-film sensors based on SnO2–Au for CO detection.// Sviridov readings: collection of articles. – Minsk, 2012. Issue 8. Pp. 51–58.

33. Nancy Savagea, Brian Chwierothb, Arwa Ginwallaa, Bruce R. Pattonb, Sheikh A. Akbarc, Prabir K. Duttaa // Sens. Actuators B. 2001. Vol. 79. P. 17–27.

34.. Molodechkina T.V. Alloyed titanium oxides as a basis for the formation of sensitive elements of gas sensors// Vestn. Polotsk state University. Series B. Applied sciences. 2011. No. 3. P. 81–87.

35. Abdurakhmanov, E.A. Sensor for monitoring pre-explosive concentration of hydrogen in a gas environment // Sensor. 2004. No. 1. P. 37–41.

36. Molodechkin M.O. Thermocatalytic sensor based on titanium oxides for detecting methane.//Bulletin of Polotsk State University. Series B. Industry. Applied Sciences. Mechanical Engineering and Mechanical Engineering 2017. No. 3. P. 68-72.

37.Abdurakhmanov E., Nasimov A.M., Salekhdzhanova R.M.-F. Thermocatalytic analyzer for selective control of hydrogen in a gas environment // Zavodsk. Laboratory. Moscow, 2000. Vol. 66, No. 8. P. 21.

38. Abdurakhmanov E., Khoshimov T.Zh., Nasimov A.M. Analyzer for ecoanalytical monitoring of hydrocarbons by the thermocatalytic method// Ecological systems and devices. Moscow, 2001. No. 11. P. 12-17.

39. Abdurakhmanov E., Khoshimov T.Zh., Thermocatalytic gas analyzer of carbon monoxide. // Patent of the Republic of Uzbekistan. IHDP9800063.1.

40. Abdurahmanov E., Ibodullaev U. Sensor for selective monitoring of the toxic and explosive components of air. // Global technical conference.- Pittcon. New Orleans, La USA 2002. p. 513.

41. Abdurakhmanov E., Ruziev E.A. Selective thermocatalytic sensors in ecoanalytical monitoring of gaseous emissions // Chemical Industry, - St. Petersburg, 2003. Vol. 80. No. 9. P. 19-25.

42. Automatic carbon monoxide gas analyzer type GA-SO // Technical description, passport, operating instructions and verification instructions 61-16096982-97 TO. - Samarkand, 1996. 26 p.

43. Abdurakhmanov E., Nasimov A. M., Sakhibov Sh.D. Carbon monoxide gas analyzer (GA-CO) // Patent R Uz. No. 505.1998.

44. Gas analyzer testo 330-3 // Obtained from the Internet:***www.pribor*.ru/term_ob/132html#. 8s.**

45. Stationary gas analyzers of toxic gases and vapors of flammable liquids (modular complex)//Devices and systems for monitoring exhaust gases of motor vehicles. CJSC "Ukranalit" - All-Ukrainian Institute of Analytical Instrumentation. Received from the Internet: E-mail:*analyt@ukranalyt.com.ua*, E-mail:*ksm05 @ukr.net*.;

46. Gas analyzer FP11.2K [Electronic document] / OOO GazFARMEK. – Access mode:http://gaz-farmek.ru/gazoanalizator yperenosnye/*fp*112k / (date of access 26.01.2015). 6 p.

47. Polyakov Yu.A., Ivanov A.E., Kabanov D.G. Development of sensors and automatic alarm for monitoring pre-explosive methane concentrations.//Internet journal "Technosphere safety technologies" (*http://ipb.mos.ru/ttb*) Issue No. 4 (32) 2010. P.44-49.

48. Persaud K., Dodd G. Analysis of discrimination mechanisms in the mammalian olfactory system using a model nose //Nature. 1982. Vol.299. P.352-355.

49. Ganshin V.M., Fesenko A.V., Chebyshev A.V. From olfactory models to the "electronic nose". New possibilities of parallel analytics // Special equipment. - 1999. - No. 1-2. P.24-28.

50. Sysoev V.V., Zyuryukin Yu.A. Multisensory gas recognition systems of the "electronic nose" type: a brief review of the literature // Bulletin of the Saratov State Technical University. 2007. Issue 1, No. 2 (24). P. 111-119.

51. Sysoev V.V., Kucherenko N.I., Kisin V.V. Textured tin oxide films for gas recognition microsystems//Letters to the "Journal of Technical Physics". 2004. Vol. 30. Issue. 18. Pp. 14-20.

52. Lashkov A.V., Dobrokhotov V.V., Sysoev V.V. Thermocatalytic multisensor chip.// Bulletin of SFedU. Technical sciences Section III. Nanosystem technology. 2016. No. 5. P. 146-149.

53. Karpova E.E., Mironov S.M., Suchkov A.A., Karelin A.P., Karpov E.F. Continuous monitoring of possible natural gas leaks in residential premises// Bulletin of MANEB, Vol.19, No.1, 2014. pp. 113-121.

54. Rose Ge´rard, Zdanevitch Isabelle A new method using a catalytic sensor for the identification and concentration measurement of combustible gases // Sensors and Actuators B: Chemical, Volume 25, Issues 1–3, April 1995. Pages 426-428.

55. Baratov A.N. and others. “Fire hazard of substances and materials and means of extinguishing them, in 2 books,” M.: Khimiya, 1990. 496 p.

*56.*Karpova thermochemical (catalytic) sensors of combustible gases and vapors// Bulletin of MANEB, Vol.19, No.1, 2014 P. 121-131.

57. Saveliev V.A.; Kommisarov A.V. Method for determining

concentrations of flammable gases in an oxygen-containing environment./Pat. RU 2156972, IPC7 G 01 N 27/16. No. 99120034/27.09.2000.

58. Karelin A.P. Methods, principles and devices for multicomponent analysis of combustible gases in the air // Scientific works (Bulletin of MATI), Issue 24 (96). – M.: MATI, 2014. P. 78–88.

59. Karelin A.P. Creation of an explosimeter: a device for determining the explosive concentration of gases using thermocatalytic sensors//XXXVI International Youth Scientific Conference "Gagarin Readings 2010", Vol. 3, 2010. pp. 25-26.

60. Routkevitch, D., Mardilovich, P., Govyadinov, A. et. al. Nanostructured ceramic platform for micromachined devices and device arrays // Patent No. US 2002/0118027 A1, USA, 2002

61. Website of the company "Housesensor" // Semiconductor gas sensors based on tin oxide manufactured by Figaro (Japan). URL: housesensor.ru/images/prodvozduh/1%20FIGARO. Pdf

62. Product catalog of the company “Figaro” (www.figarosensor.com). 2013. 46 p.

63. A.L. Gusev [et al.]. Hydrogen and hydrogen-containing molecule sensors // Alternative energy and ecology. 2005, No. 5 (25). P. 23-31.

64. Gromov V. F. Mechanism of the sensor effect in conductometric sensors based on tin dioxide for detecting reducing gases // Russ. Chem. J. (Journal of the Russ. Chem. Society named after D. I. Mendeleyev). 2008, Vol. LII (No. 5). P. 80-87.

65. Bednaya T.A., Konovalenko S.P., Semenistaya T.V., Petrov V.V., Korolev A.N. Gas-sensitive elements of a nitrogen dioxide and chlorine sensor based on

cobalt-containing polyacrylonitrile//News of higher educational institutions. Electronics. 2012, No. 4 (96). P. 66-71.

66. Bashkirov L.A., Bardi U., Gunko Yu.K. On the use of metal-semiconductor phase transition in metal oxides and their compounds for creating chemical sensors // Actual problems of solid state physics. 2003, pp. 146-162.

67. Zamburg E.G. Development and study of technological bases for the formation of nanostructured ZnO films by pulsed laser deposition for sensitive elements of gas sensors: diss. Cand. of Technical Sciences. Taganrog. 2015.167 p.

68. Petrov, V. V., Korolev, A. N. Modern semiconductor sensors for monitoring gas environments: a textbook for universities. Taganrog: TTI SFedU, 2009. 114 p.

69. Myasnikov I. A. Semiconductor sensors in physical and chemical studies Moscow: Nauka, 1991. 327 p.

70. Petrov V.V. Study of the features of interaction of gas molecules with the surface of oxide gas-sensitive materials//Nano- and microsystem technology. 2007, No. 1. pp. 24-27.

71. Chang JF [et al.]. The effects of thickness and operation temperature on ZnO:Al thin film CO gas sensor // Sensors and Actuators B. 2002, No. 84. P. 258–264.

72. Stamataki M. [et al.]. Annealing effects on the structural, electrical and H2 sensing properties of transparent ZnO thin films, grown by pulsed laser deposition // Thin Solid Films. 2009, No. 518. P. 1326–1331.

73. Al-Hardan NH, Abdullah MJ, Abdul Aziz A.. Sensing mechanism of hydrogen gas sensor based on RF-sputtered ZnO thin films //International journal of hydrogen energy. 2010, No. 35. P. 4428–4434.

74. J. Yi [et al.]. Vertically aligned ZnO nanorods and grapheme hybrid architectures for high-sensitive flexible gas sensors // Sensors and Actuators B: Chemical. 2011, No. 24. P. 6–12.

75. Calestani D., Zha M., Mosca R. Growth of ZnO tatrapods for nanostructure–based gas sensors // Sensors and Actuators B: Chemical. 2010, No. 65. P. 472-478.

76. Wang W., Huang H., Li Z. Zinc oxide nanofiber gas sensor via electrospinning // J. Am. Ceram. Soc. 2008, No. 91. P. 3817–3819.

77. Wang JX [et al.]. Hydrothermally grown oriented ZnO nanorod arrays for gas sensing applications // Nanotechnology. 2006, No. 17. P. 4995–4998.

78. Jackson, R.G. Newest sensors. - M.: Tekhnosfera, 2007. 384 p.

79. SatelDG-1 digital gas detectors // Satel company website. *URL:http://www.satel*. com.pl 2017. P.284-295.

80. A. Vasiliev, I. Olikhov, A. Sokolov. Gas sensors for fire detectors // Electronics. 2005, No. 2. P. 24-27.

81. Figaro website // GENERAL INFORMATION FOR TGS SENSORS. URL: http://www.figaro.co.jp 6 p.

82. Polyakov Yu.A., Chistyakov Yu.D., Buturlin A.I., Ivanov A.E., Chakhunashvili G.B., Kabanov D.G. Development of a gas-sensitive detector for signaling explosive concentrations of methane and a study of its response time.//Report on research and development, State registration number 028.80074737. Moscow: VIPTSh MVD USSR and MIET State Committee for People's Education, 1988. 53 p.

83. Buturlin A.I., Polyakov Yu.A., Ivanov A.E., Kabanov D.G. Early warning device for endogenous fire hazard based on an integral gas-sensitive resistor//Proceedings of the All-Union Scientific and Technical Conference "Improving Methods of Combating Endogenous Fires". Donetsk, VNIIGD, 1987. P. 20-22.

84. M.S. Aleksanyan. Methane sensor based on SnO2/In2O3/TiO2 nanostructure// Bulletin of the National Academy of Sciences of Armenia, Physics, 2010. Vol.45, No.2, pp.116-121

85. Gogish-Klushin S.Yu., Gogish-Klushina O.S., Elchanin A.V., Kharitonov D.Yu. Semiconductor gas analyzers based on SnO2 for measuring threshold

concentrations of methane.//International scientific journal "Alternative Energy and Ecology" No. 11 (103) 2011 P.11-16

86. Figaro: Gas sensors. Moscow: Publishing house "Dodeka-XXI", 2002. (Library of electronic components, issue 30.) 54 p.

87.ATMEL company catalog.http://www.hpinfotech.ro/html/cvavr.htm.2018 6c

88. Kostyuk A., Fadeev E. Programmable BASIC controller // Radio. 2006. No. 10, pp. 11-14.

89. Belov A.V. Self-study Guide for Developers of Devices on AVR Microcontrollers. 2nd edition, revised and enlarged. St. Petersburg: Science and Technology, 2010. Pp. 44-47.

90. Gogish-Klushin S.Yu., Gogish-Klushina O.S., Elchanin A.V., Kharitonov D.Yu. Features of the behavior of film-type semiconductor gas sensors when operating in energy saving mode// Alternative Energy and Ecology – ISJAEE. 2010. No. 7. P. 18–22.

91. Morrison S. Chemical physics of solid surfaces. Moscow: Mir, 1980. P. 488.

92. Buturlin A.I., Polyakov Yu.A., Ivanov A.E., Kabanov D.G. Early warning device for endogenous fire hazard based on an integral gas-sensitive resistor//Proceedings of the All-Union Scientific and Technical Conference "Improving Methods of Combating Endogenous Fires". – Donetsk, VNIIGD, 1987. P. 20-22.

93. Astapenko V.M., Shevlyakov A.N., Polyakov Yu.A., Makarov V.L. Mathematical description of the development of the process of methane leakage into a room and determination of the time of reaching its explosive concentration//Index of deposited manuscripts, 1988, No. 4. P.56-63.

94. Yu. A. Polyakov, A. E. Ivanov, D. G. Kabanov. Development of sensors and automatic alarm for monitoring pre-explosive methane concentrations.//Internet journal "Technosphere Safety Technologies" (*http://ipb.mos.ru/ttb*) Issue No. 4 (32), 2010. P.44-49.

95. Zyatkov I.I., Maksimov A.I., Moshnikov V.A. Sensors based on field-effect transistors. Study guide – St. Petersburg: Publishing house of ETU “LETI”, 2002. 31 p.

96. Corcoran P., Shurmer HV, Gardner JW Integrated tin oxide sensors of low power consumption for use in gas and odour sensing // Sensors and Actuators B: Chemical, 1993, Vol 15, Issues 1-3. Pages 32-37.

97. Jaaniso R. and Tan OK Semiconductor Gas Sensors, In Woodhead Publishing Series in Electronic and Optical Materials, edited by Raivo Jaaniso Ooi Kiang Tan., Cambridge, UK.: Woodhead Publishing. 2011. 552 pages.

98. Jin W., Ho H.L., Cao YC, Ju J., Qi LF Gas detection with micro- and nanoengineered optical fibers // Optical Fiber Technology, Volume 19, Issue 6, Part B, December 2013. Pages 741-759.

99. Choudhary Meenakshi, Kumar Singh Nitish, Mishra VN, Dwivedi R. Selective detection of hydrogen sulfide using copper oxide-doped tin oxide based thick film sensor array // Materials Chemistry and Physics, Volume 142, Issue 1, 15 October 2013. Pages 370-380.

100. Li Xiaopeng, Cho Jung Hwan, Kurup Pradeep, Gu Zhiyong Novel sensor array based on doped tin oxide nanowires for organic vapor detection // Sensors and Actuators B: Chemical, Volume 162, Issue 1, 20 February 2012. Pages 251-258.

101. Vasiliev A.A., Gogish-Klushin S.Yu. New approach to micromachine technology for sensor manufacturing: microelectronic chips with a thin membrane of aluminum oxide. //Sensor, 2002, No. 3, pp. 23-29.

102. Abdurakhmanov, E. A., Ruziev E. A. Selective thermocatalytic sensors in environmental monitoring of gaseous emissions // Chemical Industry. 2003. Vol. 80. No. 9. P. 44-49.

103. Abdurakhmanov E. Creation of selective thermocatalytic sensors and their application in atmospheric air monitoring. // Catalog of abstracts and articles of the international forum "Analytics and Analysts", Voronezh., 2003., v.1, p.242.

104. Abdurakhmanov E. Sensor for selective monitoring of carbon monoxide in air and industrial gaseous emissions. // Magazine Analytics and Control (Russia), 2004, v.8, no. 2, pp.165-169.

105. Abdurakhmanov E., Daminov G., Sultanov M. Selective chemical sensor for monitoring gasoline and diesel fuel vapors from the exhaust gases of internal combustion engines// Chemical Industry. 2007. Vol. 84. No. 6. pp. 317-320.

106. Margolis Z.I. Oxidation of hydrocarbons on heterogeneous catalysts Moscow: Chemistry, 1977. 363 p.

107. Krylov O.V. Catalysis with non-metals. Patterns of catalyst selection// L.: Chemistry, 1987, p. 210

108. Maksimov A.I., Moshnikov V.A., Tairov Yu.M., Shilova O.A. Fundamentals of sol-gel technology of nanocomposites St. Petersburg: Publishing house of St. Petersburg State Electrotechnical University "LETI", 2007. 273 p.

109. Ryazanov, A. V. Sensitive elements based on cast microwire / A. V. Ryazanov, A. N. Dokichev // Sensors and systems. 2007. No. 11. P. 42-45.

110. Karpov E.F., Klebanov F.S., Petrosyan A.E. Natural hazards in mines. Methods of their control and prevention. Moscow: Nedra, 1981. 471 p.

111. Abdurakhmanov E, Tillaev S., Sultanov M. Abdurakhmanov I.E. Berdiev B.U. Thermocatalytic oxygen sensor // Application for invention of the Republic of Uzbekistan. No. IAP 20100122. 03/26/2010. Ichthirolar. Rasmiy akhborotnoma, No. 9. 09/30/2011. P.32.

112. Abdurakhmanov E., Tillayev S. U., Sultanov M. M., Abdurakhmanov I. E. Method for Determining Oxygen Content// Application for Invention of the Republic of Uzbekistan. No. IAP 20100123. 03/26/2010. 7 p. Ichthyolarium. Rasmium akhborotnoma, No. 9. 09/30/2011. P. 31

113. Kaimakova A.A. Explosion safety of mine electrical equipment. Moscow: Nedra, 1994. 207 p.

114. Abdurakhmanov E., Norkulov U.M., Khoshimov T.Zh. Metanni aniqlash uchun teplokatalitik sensing element. Patent. 5769.25.03.1999. 8 p.

115. MEEshqobilova, JNBegimqulov, AMNasimov. Metanni aniqlovchi termokatalitik sensorning ayrim metrologik tavsiflari // Ilmiy axborotnoma. Kimyo. 2018. 135-140 b.

116. Eshkobilov Sh.A., Eshkobilova M.E., Abdurakhmanov E. Catalyst for selective thermocatalytic sensor of natural gasMagazine "Chemical Industry" Russia. 2015. P.

117. Sultanov M.M. Chikindi va tutun gazlar monitoring uchun avtomatlashgan thermocatalik usullarni ishlab chikish/ Kimyo fanlari doctor Monograph and abstract. Tashkent.2019. 64 pp.

118. Eshkabilova M.E., Yunusov F., Abdurakhmanov E. Synthesis of gas-sensitive nanocomposite films for thermocatalytic and semiconductor methane sensors // Journal Composite, 2018. P.

119. Abdurakhmanov I.E., Norkulova N., Kholmirzaev F.F., Eshkobilova M.E., Bekmurodova K, Matmurodov Sh.A. Metanni aniylovchi yarimshtkazgichli sensorning metrologick tavsifi/Oil va gas complexida Burgulash,kazib olish va kaita ishlash zharayonlarining zamonaviy tehnologiyalari. Republic of Ilmiy-Amalii Anzhumani Materiallari. Karshi 2018. B.432-435

120. Kholmirzaev F.F., Eshkobilova M.E., Urakov D.M., Abdurakhmanov E. Influence of temperature on the sensitivity of a semiconductor methane sensor.//Uzbekistan analytical journal. Republic of Kazakhstan – international scientific research institute. Tashkent. 2018. P. 78-81.

121.Eshkobilova M.E., Abdurakhmanov I.E. Nasimov A.M. Some metrological characteristics of a semiconductor methane sensor. / Scientific Bulletin of SSU. 2018. No. 1. P.

TABLE OF CONTENTS