Development of a selective carbon monoxide sensor

E Abdurakhmanov\textsuperscript{1,4}, Kh G Sidikova\textsuperscript{2}, Z B Muradova\textsuperscript{1} and Z E Abdurakhmanova\textsuperscript{3}

\textsuperscript{1}Samarkand State University, Samarkand, Uzbekistan
\textsuperscript{2}Jizzakh State Pedagogical Institute, Jizzakh, Uzbekistan
\textsuperscript{3}Samarkand State Medical Institute, Samarkand, Uzbekistan

\textsuperscript{4}E-mail: ergash50@yandex.ru

Abstract. In this work, the regularities of the oxidation of combustible substances (\(\text{H}_2\), \(\text{CO}\), \(\text{CH}_4\), and gasoline vapors) in the presence of metal oxides are revealed and catalysts for the sensitive elements of selective carbon monoxide sensors are selected on their basis. The possibility of creating a highly selective sensor using measuring and compensating heat-sensitive elements containing catalysts of different activity to the components of gas mixtures has been experimentally confirmed. The main characteristics of the developed selective carbon monoxide sensors are evaluated. The use of such sensors reduces the error of analysis, increases the instrument readings' stability and service life, and improves reproducibility and selectivity in the continuous automatic determination of gas components in the measurement area.

1. Introduction
One of the most dangerous pollutants in the atmosphere is carbon monoxide, which is present in the emissions of both powerful industrial sources of pollution (factories, thermal power plants) and small sources (furnace heating pipes), as well as distributed sources, which are different types of transport [1]; therefore, to ensure the safety of work at many facilities, constant analytical control over the content of CO is required. The problem of carbon monoxide burning measurement is multidimensional: it belongs to the complex of problems of optimal control of combustion processes and is included in the complex of environmental control problems [2]. In the analytical practice of monitoring the content of combustible gases, semiconductor and thermocatalytic methods and sensors are widely used [3-5].

The purpose of this work is improving the selectivity of measuring the volume concentration of carbon monoxide in a mixture of combustible gases by using a selective semiconductor method for determining the concentration of carbon monoxide.

2. Experimental methods
The principle of operation of the thermocatalytic sensor is based on measuring the concentration of the determining component of the gas mixture by the amount of heat released during the chemical reaction of catalytic oxidation. Structurally, a thermocatalytic sensor is a pair of sensing elements and a pair of resistors included in the bridge circuit. The main disadvantage of this method is low sensitivity and selectivity for the determined component [4].

In contrast to the thermocatalytic method, the semiconductor method and the sensor are characterized by high sensitivity. The principle of operation of metal oxide semiconductor sensors is based on changes in the conductivity of the gas-sensitive layer during chemical sorption on the surface of the
semiconductor of donor gases (various combustible gases, including methane, propane, gasoline vapor, CO, ammonia, hydrogen sulfide, etc.) or acceptors (ozone, nitrogen oxides, chlorine, fluorine). Reversible chemisorption of these impurities leads to a reversible change in the concentration of current carriers in the semiconductor, resulting in a change in the conductivity of the sensitive layer. The detection threshold of semiconductor sensors depends on the detected gas and is equal to ~ 1 ppm for CO. The upper threshold at which it is advisable to use semiconductor sensors is approximately 0.5 NCPR.

In [5], a method for ensuring the selectivity of TCS was developed, which is based on the use of sensitive elements containing catalysts with a different activity to the components of the gas mixture. In connection with the above, the primary task of the research devoted to the development of a selective semiconductor sensor of combustible gases is the development of selective catalytic systems.

To develop a selective sensor for the automatic continuous determination of carbon monoxide, the regularities of the oxidation of combustible substances on various catalysts were studied.

Metal oxides have a sufficiently high catalytic activity concerning the oxidation of combustible gases (CO, H2, CH4, etc.) [6]. During the experiments, the catalytic characteristics of several individual oxides and their mixtures were studied. The development of a catalyst for a selective semiconductor carbon monoxide sensor was carried out on a flow-type installation with a stationary catalyst layer. To control the oxidation process, a gas chromatograph with an ionization flame detector was used.

The catalysts were prepared by impregnating the carrier with solutions of individual salts (nitrates, carbonates, or oxalates), followed by drying (for 3 hours at 120 °C) and calcination at the decomposition temperature of the salts in the air current (for 3 hours). The selection of the catalyst and the optimal conditions for the oxidation of combustible substances was carried out at a temperature of 100-350 °C, the feed rate of the gas-air mixture was 10 l/h, the content of the combustible component in the mixture (% vol.): H2-2.20; CO-2.45; gasoline vapor - 2.00; CH4-2.50. Experiments on the selection of selective catalysts for a semiconductor carbon monoxide sensor were carried out in the presence of metal oxides (ZnO, TiO2, SnO2, CdO, Al2O3, ZrO2, etc.), which, according to [6, 7], are the most active catalysts of the oxidation process. In the results of the study of the activity and selectivity of individual metal oxides in the oxidation of combustible substances (CO, H2, CH4, and gasoline vapors), it was found that hydrogen oxidation is observed on all the studied catalysts at a temperature of 100 °C. It should be noted that the highest selectivity in the oxidation of hydrogen in the presence of carbon monoxide and hydrocarbons is observed on catalysts based on ZnO and ZrO2. At 100 °C in the presence of ZnO, the degree of oxidation of hydrogen and carbon monoxide by air oxygen is 53.5 and 9.0%, respectively. The hydrocarbons on this catalyst are practically not oxidized at 100 °C.

As follows from the obtained data, the degree of conversion of hydrocarbons (CH4 and gasoline) is much lower than that of hydrogen and carbon monoxide on all the studied catalysts in the studied temperature range.

The conducted studies show that catalysts based on individual metal oxides do not provide selectivity for the thermocatalytic determination of carbon monoxide in the presence of hydrogen, which is often found together with CO in various natural and technological objects. The catalytic activity and selectivity of individual oxides in many catalytic processes can be changed to varying degrees by the addition of other oxides to them, forming new chemical compounds or solid solutions with them. With an increase in temperature in the range from 100 to 350 °C, a sharp increase in the degree of conversion of combustible substances on individual metal oxides is observed. The results of the experiments show the following sequence of activity of the studied metal oxides in the process of carbon monoxide oxidation: ZnO(100%)>TiO2(100%)>SnO2(96%)>CdO(91%)>Al2O3(67%)>ZrO2 (46%). As follows from these data, the highest activity in the process of CO oxidation is characterized by the oxides of the metals zinc and titanium, in the presence of which a 100% degree of conversion of carbon monoxide is provided.

In the experiments, the characteristics of a mixture of the most active and selective metal oxides obtained in different ratios were studied. The following series of activity of a mixture of oxides in the
processes of CO oxidation was found: Zn+Ti>Ti+Sn>Zn+Sn>Cd+Ti>Cd+Zn>Al+Ti>Al+Sn>Cd+Al>Cd+Zr>Al+Zr>Sn+Zr>Ti+Zr>Zn+Zr.

As follows from the studied catalytic systems for the oxidation of carbon monoxide, the most selective is the catalyst based on the oxides of Cd, Ti, Zr, etc. In the presence of these catalysts at 200 °C, the highest selectivity of carbon monoxide oxidation is provided in the presence of hydrogen, methane, and gasoline vapors. Under identical conditions on the studied catalysts, the following selectivity series is observed in the process of CO oxidation: Cd+Ti>Ti+Zr>Ti+Sn>Cd+Zn>Zn+Al.

Thus, the most active and selective mixtures of metal oxides in the processes of carbon monoxide oxidation in the presence of methane, gasoline vapors, and hydrogen were selected in the results of the experiments.

Using selected catalysts and optimized conditions for the analysis of gas systems, a semiconductor sensor was manufactured to selectively determine carbon monoxide content in a mixture of toxic, fire- and explosive gases.

The selectivity of the developed sensor for carbon monoxide was determined in the presence of hydrogen, gasoline vapor, and methane, which are present with carbon monoxide in the composition of the flue, exhaust, and process gases of internal combustion engines. The results of determining the selectivity of the sensor based on Cd ITI oxides in the determination of carbon monoxide are shown in table 1.

### Table 1. Results of the determination of the selectivity of the sensor based on Cd and Ti oxides in the determination of carbon monoxide (n = 5; P = 0.95).

| Gas mixture introduced, vol.%       | Carbon monoxide content, vol.% |
|-------------------------------------|---------------------------------|
|                                    | \(x \pm \Delta x\) | S | Sr*10^2 |
| CO(0.60)+air(rem.)                  | 0.61±0.01               | 0.01 | 0.5 |
| CO(0.60)+H2(2.00)+ air(rem.)        | 0.64±0.03               | 0.02 | 1.4 |
| CO(0.60)+CH4(2.00)+ air(rem.)       | 0.64±0.02               | 0.02 | 1.0 |
| CO(0.60)+diesel fuel, (2.00)+ air(rem.) | 0.62±0.04           | 0.03 | 1.9 |
| CO(0.60)+patrol, (1.00)+ air(rem.)  | 0.63±0.03               | 0.02 | 1.5 |

As follows from the data given in table 1, the developed sensor allows selectively detecting carbon monoxide in multicomponent gas-air mixtures, where hydrogen and hydrocarbon vapors (gasoline, diesel fuel) are also contained simultaneously with carbon monoxide. Such mixtures include gaseous emissions from heating systems, exhaust gases from internal combustion engines, atmospheric air from gas filling stations, etc.

The signal value and selectivity of the semiconductor sensor depend on the supply voltage of the heater, a change in which leads to a non-constant surface temperature of the gas-sensitive layer of the sensor’s sensitive elements. The increase and decrease in the power supply from the optimal one are accompanied by a decrease in the value of the useful analytical signal of the sensor. The effect of the supply voltage on the sensor signal was studied under the following conditions: temperature 20±2 °C, gas pressure 720±10 mm Hg, ambient humidity 60%. The experiments used HS with a CO content of 2.50% vol., the results obtained are presented in table 2.

As follows from the above data, the highest sensor signal (46.7 mV) is observed at a power value equal to 2.1 V, so all subsequent experiments were conducted at this power value.

The dynamic characteristics of the sensors were determined by a sudden change in the concentrations at the sensor input. The experiments were carried out with a continuous recording of the transition process of the diagram tape of the recorder. As it was found, the developed sensors have a response start time \((t_{0.1})\) of 1-2 seconds, a time constant \((t_{0.65})\) of no more than 6 seconds, a reading setting time \((t_{0.9})\) of up to 8 seconds, and a total measurement time \((t_{p})\) of 9-10 seconds.
Table 2. Results of studying the dependence of the analytical signal of a semiconductor carbon monoxide sensor on the supply voltage of the sensor heater (n= 5, P= 0.95).

| CO content in the mixture, % vol. | Voltage, V | Sensor signal, mV x±Δx | S | Sr*10^2 |
|----------------------------------|------------|-------------------------|---|---------|
| 2.50                             | 1.5        | 20.6±0.3 | 0.2 | 2.3    |
| 2.50                             | 1.7        | 33.7±0.5 | 0.3 | 1.2    |
| 2.50                             | 2.0        | 45.1±0.5 | 0.4 | 1.1    |
| 2.50                             | 2.1        | 46.7±0.5 | 0.3 | 0.7    |
| 2.50                             | 2.2        | 42.1±0.5 | 0.3 | 0.9    |
| 2.50                             | 2.4        | 42.1±0.3 | 0.2 | 0.8    |
| 2.50                             | 2.7        | 35.4±0.5 | 0.4 | 1.5    |
| 2.50                             | 3.0        | 32.2±0.7 | 0.3 | 1.6    |

These data show the possibility of rapid determination of carbon monoxide by the developed sensors. The dependence of the sensor signal on the concentration of the detected component in the mixture was studied in the range of carbon monoxide concentration of 0.10-12.53% vol. Each test point for the measurement range was characterized by ten values: five for the forward and five for the reverse cycles of concentration change. The experiments were carried out under normal conditions (T_o.c = 20±2 °C and P_o.c = 720±30 mm Hg). The results of the evaluation of the calibration characteristics of the CO sensor are shown in Table 3.

Table 3. The results of the evaluation of the dependence of the CO sensor signal on the concentration of carbon monoxide in the mixture (n= 5, P= 0.95).

| CO concentrations, % vol | Sensor signal, mV x±Δx | S | Sr*10^2 |
|--------------------------|-------------------------|---|---------|
| 0.10                     | 2.41±0.10               | 0.08 | 5.8    |
| 0.46                     | 11.60±0.21              | 0.17 | 2.5    |
| 1.21                     | 28.08±0.84              | 0.65 | 4.0    |
| 2.50                     | 58.1±0.61               | 0.50 | 1.3    |
| 4.60                     | 112.9±0.56              | 0.45 | 0.7    |
| 5.02                     | 120.5±0.45              | 0.38 | 0.5    |

It is established that in the studied interval, the dependence of the CO sensor signal on the concentration of carbon monoxide is rectilinear.

3. Conclusion
Based on the conducted research, it can be concluded that the developed sensor is quite suitable for continuous automatic monitoring of the carbon monoxide content in a wide range of its concentrations in exhaust, flue, and process gases. The sensor can operate in continuous mode as part of an automatic exhaust gas analyzer.

References
[1] Sidikova Kh G, Abdurakhmanov I E, Mumunova N I, Kholboev O N and Abdurakhmanov E 2020 Development and research of metrological characteristics of selective thermocatalytic methane (natural gas) sensor IOP Conf. Series: Materials Science and Engineering 862 062102 doi: 10.1088/1757-899X/862/6/062102
[2] Sultanov M M, Abdurakhmanov E and Isomiddinov Zh K 2020 Studying the Influence of External Parameters on the Error of the Thermocatalytic Analyzer of Carbon Monoxide
International Journal of Mechanical and Production Engineering Research and Development (IJMPERD) 10(4) 11493-6

[3] Antonenko V, Vasiliev A and Olikhov I 2001 Early detection of a fire. Solid-state gas sensors ELECTRONICS: Science, Technology, Business 4 48-51

[4] Abdurakhmanov E, Sidikova Kh G, Abdurakhmanov I E and Muminova N I 2020 Elaboration and Investigation of Metrological Characteristics of SemiConductor Sensor of Methane International Journal of Advanced Science and Technology 29(7) 2058-65

[5] Eshkobilov Sh A, Eshkobilova M E and Abdurakhmanov E 2015 Determination of natural gas in atmospheric air and technological gases Ecological systems and devices 9 11-5

[6] Abduraxmanov E, Sultanov M, Daminov G and Tillayev S 2014 Determination of carbon oxide in exhausts of vehicles by thermocatalytic method Open Access Library Journal 1 1-4 doi: 10.4236/oalib.1100406

[7] Abdurakhmanov E, Sattarova M J, Murodova Z B and Abdurakhmanov I E 2015 Influence of external factors on the analytical signal of a highly sensitive ammonia gas analyzer VG-NH3 Chemical Industry 1 142-5