Development and research of metrological characteristics of selective thermocatalytic methane (natural gas) sensor

Kh G Sidikova¹, I E Abdurakhmanov², N I Mumunova¹, O N Kholboev¹ and E Abdurakhmanov²

¹ Jizzakh State Pedagogical Institute, Jizzakh, 140100, Uzbekistan
² Samarkand State University, 15, University blv. Samarkand, 140104, Uzbekistan

E-mail: tunikom57@mail.ru

Abstract. In this work, the catalyst (0.75In₂O₃-0.25 Ag₂O и 0,25Fe₂O₃-0,75 Ni₂O₃) for selective and highly sensitive methane sensor was selected. Selective natural gas thermochemical sensors have been developed using selected catalysts. In a wide range of parameters, the influence of various parameters was studied and optimal conditions providing the highest thermochemical sensor signal were established.

1. Introduction
The methane explosions are one of the most dangerous types of accidents at domestic and industrial facilities. Therefore, today special attention is paid to the creation of express and inexpensive chemical sensors for reliable and unambiguous control of natural gas leaks and accumulations [1-4]. The analysis of the development of gas sensors in industrialized countries has shown that the most perspective for the prevention of explosion hazard is the use of thermocatalytic and semiconductor sensors [5, 6]. This circumstance determines the relevance of research aimed at the development of express, sensitive and selective sensors that provide reliable control of explosion hazard of gas mixtures of closed environmental systems. With the introduction of new technologies and the development of analytical control, the requirements for the sensitivity and selectivity of methods for determining substances increase. Considering those mentioned above, the development of new highly effective sensors of fire-explosive gases, in particular, methane, remains an actual problem.

2. The work aims
To develop sensitive, selective thermocatalytic sensors of methane (natural gas) using nanomaterials obtained with the use of sol-gel process and to create on their basis highly effective signaling and gas analyzers of natural gas.

3. The experimental part
It presents the results of preparation and certification of standard gas mixtures H₂, CO, CH₄ and natural gas with air. The used gas-air mixtures in work were prepared by the manometric method according to the standard SEV 4981-86 (group B 19). It consists ofa gradual dosage of separate gas components in a cylinder. The content of the component in the gas mixture (Xi) in percent is calculated by the formula:

\[ X_i = \frac{V_i}{V_{tot}} \times 100 \]
where \( P_i \) is the partial pressure of the 1st component. \( P \) is the total pressure of the mixture. New, more precise determination of methane content in the mixture was carried out by the gas chromatographic method.

In scientific literature and practice, it has traditionally been considered that widely used thermochemical sensors (TCS) do not provide selectivity in determining individual components of the mixture of gases. Therefore, the problem of providing selectivity of TCS is an actual one. One of the possible methods to ensure the TCS selectivity is the use of sensitive elements (SE), containing catalysts with a different activity to the components of the gas mixture. In this regard, the main task in the development of selective TCS CH\(_4\) is the selection of catalytic systems SE.

Aiming at the development of sensitive and selective TCS for determination of CH\(_4\) (methane, natural) gas, the regularities of oxidation of H\(_2\), CO and CH\(_4\) on different catalysts were studied. The oxidation degree of the combustible component was controlled by the removal of the mixture chromatogram before and after gas passage through the catalyst layer. In the course of experiments in the temperature range, 100-350\(^\circ\)C, the catalytic characteristics of a number of individual and binary metal oxides were studied: Ga, In, Ag, Cr, Mn, Fe, Co, Ni, Cu and Zn. In the presence of catalysts, oxidation of H\(_2\), CO and CH\(_4\) occurs mainly in terms of thermodynamics in the most advantageous direction with the formation of carbon dioxide and water vapor:

\[
\begin{align*}
\text{H}_2 + \frac{1}{2}\text{O}_2 &= \text{H}_2\text{O} + 286 \text{ kJ} \quad (1) \\
\text{CO} + \frac{1}{2}\text{O}_2 &= 2\text{CO}_2 + 283 \text{ kJ} \quad (2) \\
\text{CH}_4 + 2\text{O}_2 &= \text{CO}_2 + 2\text{H}_2\text{O} + 892 \text{ kJ} \quad (3)
\end{align*}
\]

These reactions are accompanied by a large thermal effect and are almost irreversible. It follows from the results of the experiments that Ag\(_2\)O and In\(_2\)O\(_3\) are among the most active catalysts of oxidation of CH\(_4\) and natural gas. In the temperature of 2000\(^\circ\)C in the presence of Ag\(_2\)O and In\(_2\)O\(_3\), the transformation of natural gas is 86 and 98 %.

Further research of binary oxide mixture selectivity indicates the possibility of using 0.75In\(_2\)O\(_3\)-0.25 Ag\(_2\)O and 0.25Fe\(_3\)O\(_4\)-0.75 Ni\(_2\)O\(_3\) as a catalyst for measuring and comparative SE of selective TCS to determine CH\(_4\) (natural gas) in the presence of H\(_2\) and CO, which are often encountered with natural gas, in the atmospheric air of mines, process gases, vehicle exhaust gases, etc. In the presence of H\(_2\)O and In\(_2\)O\(_3\). The principle of operation of TCS is the free combustion of CH\(_4\) on the catalyst surface and measurement of the amount of heat released in this process. TCS CH\(_4\) consists of two SE and two constant resistors. The scheme of switching on the sensitive elements of the developed TCS CH\(_4\) is shown in figure 1.

At influence of molecules CH\(_4\) on a surface of the catalyst of a measuring element its oxidation according to the equation (3) occurs. When heat is released, the resistance R of the helix changes, which is determined by the formula:

\[
R = R_0 (1 + \alpha \Delta T) \quad (4)
\]

where \( R_0 \) - helix resistance at \( T = 25^\circ C \); \( \alpha \) - temperature coefficient of platinum wire resistance, \( \Delta T \) - helix temperature change. The oxidation reaction rate of CH\(_4\) (W, mol/s) in the kinetic region is usually represented as a function of the volume of molar concentrations of CH\(_4\) (C\(_{CH4}\)) and O\(_2\) (C\(_{O2}\)).

\[
W = k \text{Fe}_3 \text{f}(\text{CCH}_4\text{CO}_2) \quad (5)
\]

where \( k \) is the speed constant, s\(^{-1}\); Fe- the active surface, m\(^2\). Oxidation of CH\(_4\) is accompanied by simultaneous adsorption of O\(_2\) and CH\(_4\) by the catalyst surface, and the reaction rate is affected by the concentration of CH\(_4\) and O\(_2\). It should also be noted that if the concentration of CH\(_4\) exceeds 9%, the...
limiting component in the mixture, which determines the reaction rate, is an oxidizer - O₂ of air. Using the developed catalysts (0.75In₂O₃-0.25Ag₂O and 0.25Fe₃O₄-0.75Ni₂O₃), we have produced TCS, providing a selective determination of CH₄ in the presence of CO and H₂ (figure 2).

Figure 1. Scheme of switching on the thermocatalytic methane sensor sensors (R1 - comparative SE, R2 - measuring SE, R3 and R4 - constant resistors, U₁ - voltmeter for signal control, U₂ - sensor power supply source).

Figure 2. Photo (a) and scheme (b) of selective thermocatalytic methane sensor (1 - hull, 2 - protective cap, 3 - porous titanium mesh, 4 - metal stands, R₁ - measuring SE with 0.75In₂O₃-0.25Ag₂O catalyst, R₄ - comparative SE with 0.25Fe₃O₄ catalyst.

The output signal of the measuring sensitive element (MSE) of the sensor (catalyst: 0.75In₂O₃-0.25Ag₂O) is proportional to the total concentration of combustible gases (H₂, CO, CH₄), the output signal of the comparative sensitive element (CSE) is proportional to the concentration of the mixture of CO and H₂ without the selective defined component (CH₄), and the difference between the signals of the first and second elements is proportional to the concentration of CH₄.

Testing of developed sensors included special experiments connected with the selection of the optimal value of supply voltage, establishment of dynamic, graduation and other characteristics of the sensor, and also with detection of the degree of its selectivity and stability. The highest sensor signal by CH₄ is observed at the supply voltage of 2.6V. Comparison of the sensor signal values according to CH₄ and natural gas showed that the supply voltage providing the highest TCS signal in identical conditions for natural gas (2.8-3.0V) is higher than for methane (2.6V). The developed sensor has a response start time (t₀.₁) of 3-4 s, a constant time (t₀.₆₃) of no more than 9 s, a readout time (t₀.₉) of 13 s and a full time of the analytical signal output (tₚ) of the sensor within 17-18 s, which once again confirms the possibility of using the developed sensors for rapid control of natural gas content. Dependence of the sensor signal...
on methane concentration in the studied concentration range (from 0.1 to 5.0 % vol.) is straightforward (table 1).

**Table 1.** Dependence of TCS signal on CCH₄ in the gas mixture (n=5, P=0.95).

| CCH₄ % vol. | Sensor signal, mV | S | Sr·10^2 |
|-------------|-------------------|---|---------|
| 0.1         | 6.2±0.1           | 0.08 | 1.3     |
| 1.0         | 63.0±0.3          | 0.24 | 0.4     |
| 2.0         | 127.0±0.9         | 0.72 | 0.6     |
| 3.0         | 186.1±1.7         | 1.37 | 0.7     |
| 4.0         | 256.4±3.2         | 2.58 | 1.0     |
| 5.0         | 323.3±2.8         | 2.25 | 0.7     |

The results of the experiments testify to the identity of the signal dependence of the developed TCS on the concentration of CH₄ and natural gas. This confirms the possibility of using the developed TCS to control the explosive concentration (in the range of 0-5.0 % rpm) of natural gas in the atmospheric air of domestic and industrial premises and the interior of vehicles. The influence of the content of unmeasurable components on the determined value of the sensor output signal was studied in the presence of H₂ and CO.

Two types of the sensor were used in the experiments. TCS-1 - sensor containing the catalyst on the measuring and compensating element and TCS-2 - sensor containing the catalyst only on the measuring element. As follows from the results (table 2), TCS-1 practically does not feel H₂ and CO in the studied concentration range. The signal of the sensor according to CH₄ under the same conditions (1 % mixtures of H₂, CO and CH₄) is 36.8 times more than the signal of H₂ and 159.3 times more than the signal of CO. In contrast to TCS-1, a sensor without a compensating sensor element (CSE) is sensitive to H₂ and CO. The signal of this sensor 1% to H₂, CO and CH₄ is 103.9 mV, 29.1 mV and 97.0 mV, respectively. Therefore, TCS-1, in contrast to TCS-2, is characterized by high selectivity. TCS-1 also provides selectivity of natural gas determination in the presence of H₂ and CO. Error of detection of sensors due to unmeasurable components does not exceed 2.0%. Verification of methane sensor stability in time was carried out under normal conditions during 1000 hours of continuous operation at natural gas concentration -1.00 % in air. As the experiments have shown, the sensor signal is stable during the regulated interval. The results of check of measuring range and basic error of the sensor with measurement limits of 0-5.0 % vol. are presented in table 2. Table 2 presents the results of the measurement range check and the basic error of the sensor with 0-5.0 % vol.

**Table 2.** The results of determination of the TCS-CH₄ error (range 0-5,00 % vol.).

| CCH₄ in the mixture, % vol. | found CH₄, % vol. | Basic error (Δ) | Prim. Priv. error.(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                   |

In the studied interval, the signal dependence on concentration has directly proportional character and the basic reduced error of the sensor with ranges 0-5.0 % vol. was 0.2 - 1.4 % accordingly (Table 2.20). The additional error of the sensor caused by the temperature change does not exceed 2 % and is less than the basic error of the device itself (table 3).
Table 3. Additional error (γ_d) of TCS in the interval of temperature from -10 to +40 °C (n=5, P=0,95).

| Temperature, °C | γ_addit. at CcH₄: 0,5% | γ_addit. at CcH₄: 2,5% | γ_addit. at CcH₄: 5,0% | γ_addit. at of GOST |
|----------------|--------------------------|-------------------------|-------------------------|---------------------|
| -10            | 0,4                      | 3,0                     | 2,0                     | 5,0                 |
| 0              | 0,2                      | 2,0                     | 2,0                     | 5,0                 |
| +10            | 0,7                      | 1,0                     | 0,7                     | 5,0                 |
| +20            | 0,6                      | 0,3                     | 2,0                     | 5,0                 |
| +30            | 0,5                      | 0,3                     | 0,4                     | 5,0                 |
| +40            | 0,2                      | 0,3                     | 0,7                     | 5,0                 |

The total additional error of TCS-CH₄ due to changes in temperature (-10 - +400C), pressure (600-800 mm Hg) and humidity (40-95%) was 3.5%. The researches have shown that the thermocatalytic methane sensor TCS-CH₄ developed by us on metrological and some other characteristics quite meets the requirements of GOST for this class of devices.

Table 4. Results of comparative estimations, developed sensors.

| Content in a mixture | Sensor signal, mV |
|----------------------|-------------------|
|                      | Sensor-1 | Sensor-2 |
| C_CH₄1%+ air         | 97,0      | 13,0     |
| C_CO1%+ air          | 0,6       | 5,7      |
| C_H₂1%+ air          | 2,1       | 14,6     |
| Selectivity coefficient: |        |
for CO                | 46,2      | 0,9      |
for H₂                | 161,7     | 2,3      |

The results of comparative researches of sensitivity and selectivity, proposed by us in this work (sensor 1) and previously developed and produced sensors (sensor 2) are presented in table 4. As follows from the resulted data, the offered sensor-1 on selectivity much exceed serially let out sensor-2. In the course of experiments also comparative characteristics of developed selective thermocatalytic sensors for the period, 1990-2019 in the laboratory of gas analysis of Samarkand State University have been studied. The results of the experiments are given in the following tables.

Table 5. Comparison of main parameters of selective thermocatalytic methane sensors developed in SamSU Gas Analysis Laboratory during 1990-2019.

| Parameter                  | TCS-1* | TCS-2** | TCS-3*** |
|----------------------------|--------|---------|----------|
| Catalyst composition of MSE and CSE | 75%In₂O₃+25%AgO и 25%Fe₃O₄+ 75%Ni₂O₃ | Pt-CoO-MnO₂/Al₂O₃ и Pt-NiO/Al₂O₃ | Co₃O₄+1% и Pt Co₃O₄+MoO₃ |
| Catalyst preparation method | Sol-gel technology | Precipitation | Precipitation |
| Sensor design              | Dual-Camera | Single-Camera | Dual-Camera |
| Sensitivity by CH₄, μB/%   | 97,0    | 29,0    | 44,0     |
| Expressivity, t₀₉ с. max  | 13      | 12      | 19       |
| Basic error, %            | 1,6     | 1,5     | 1,6      |
| Power supply voltage, mV  | 2,6     | 3,2     | 3,7      |

As follows from the above data, the developed TSC-1 produced using sol-gel catalyst technology: 75%In₂O₃+ 25%AgO and 25%Fe₃O₄+75% Ni₂O₃ is more sensitive than previously developed analogues (TSC-2 and TCS-3).
4. Conclusion
Thus, the composition of the catalyst of sensitive elements and the construction of the thermocatalytic sensor that provides selective control of the explosive concentration of natural gas from the atmospheric air of industrial and residential facilities - utilities. With the use of selected optimal conditions and selective catalysts of measuring and compensating elements of TCS, high sensitivity and selectivity of \( \text{CH}_4 \) determination from the atmospheric air of closed ecological systems are provided. The influence of various factors on metrological, operational and other parameters of thermocatalytic sensors \( \text{CH}_4 \) based on the catalyst: 75%\( \text{In}_2\text{O}_3 \) + 25%\( \text{AgO} \) and 25%\( \text{Fe}_3\text{O}_4 \)+75%\( \text{Ni}_2\text{O}_3 \) is revealed.

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