Metrological parameters of semiconductor sensors of hydrogen sulfide SCS-H₂S with membrane coatings based on tungsten and copper oxides

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Abstract. The paper shows the possibility of using metal oxides W and Cu as a gas-sensitive material of a semiconductor hydrogen sulfide sensor. The results of studying the following metrological parameters of SCS-H₂S are presented: calibration characteristic, selectivity, measurement range and basic error, the effect of pressure on the values of the input signal and the sensor's resistance to concentration overloads. The principle of operation of the developed semiconductor hydrogen sulfide sensor is to change the electrical conductivity of the gas-sensitive layer as a result of sorption of hydrogen sulfide.

1. Introduction
Globally, hydrogen sulfide is one of the main priority environmental pollutants and chemical sensors are used in studies to determine and monitor it. Today, scientific research is underway to develop sensitive and selective thermocatalytic and semiconductor hydrogen sulfide sensors and to select the optimal compositions of gas-sensitive materials for these sensors [1, 2]. Therefore, the development and research of highly sensitive and selective hydrogen sulfide sensors is important. Interest in hydrogen sulfide sensors is undoubtedly caused by their demand. The results obtained in [3] made it possible to develop a selective semiconductor hydrogen sulfide sensor SCS-H₂S designed to monitor the amount of H₂S in a gas mixture.

The use of semiconductor hydrogen sulfide sensors involves a variety of technological, medical and environmental tasks, where constant monitoring of the presence of components in gas environments is required. Gas sensors based on semiconductor elements attract considerable attention of specialists due to their extremely high sensitivity to the composition of the gas phase, simplicity of design and the ability to integrate into information systems. As a gas-sensitive material of the semiconductor layer for detecting micro-concentrations of gases, metal oxides are mainly used [4, 5].

We have shown the possibility of using metal oxides W and Cu as a gas-sensitive material of a semiconductor hydrogen sulfide sensor [3]. The principle of operation of the developed semiconductor hydrogen sulfide sensor is to change the electrical conductivity of the gas-sensitive layer as a result of sorption of hydrogen sulfide [6, 7].
2. The experimental procedure and the results obtained

The paper discusses the results of studying the following metrological parameters SCS-H2S: calibration characteristic, selectivity, measurement range and basic error, the effect of pressure on the value of the input signal and the resistance of the sensor to concentration overloads.

2.1. Calibration characteristic of a semiconductor hydrogen sulfide sensor is as following

The dependence of the SCS-H2S signal on the concentration of hydrogen sulfide was established in the range of its concentrations from 10 to 750 mg/m$^3$ by passing a gas mixture of hydrogen sulfide and air through a developed sensor. In the experiments performed, each test point in the measuring range was characterized by six values: three for direct and three for reverse measurement cycles.

The analytical signal of the sensors was monitored with a B7-35 voltmeter after establishing a constant value (at least 1 min, after applying a standard mixture to the device). As a result of the experiments, it was found that the temperature dependence of the resistance of the semiconductor sensor is, as a rule, nonlinear. Practice shows that this type of dependence is not entirely convenient for basic research in order to manufacture and test the sensor and gas analyzer. It is more convenient to present the sensor conductivity in a normalized form or in logarithmic coordinates.

The normalized calibration characteristic of hydrogen sulfide sensors based on tungsten and copper oxides with an operating temperature of 350°C is shown in figure 1.

![Figure 1](image)

**Figure 1.** Dependence of the analytic signal of the sensor ($\sigma_{\text{gas}}/\sigma_{\text{air}}$) on the amount of the determined component ($C_{\text{H}_2\text{S}}$) in the gas supply 1-SiO$_2$-WO$_3$; 2-SiO$_2$-WO$_3$-1%CuO; 3-SiO$_2$-WO$_3$-5%CuO; 4-SiO$_2$-WO$_3$-10%CuO.

As follows from the data presented, in a wide range (50-1000 mg/m$^3$), the dependence of the signal of the SCS-H$_2$S semiconductor sensor on the concentration of hydrogen sulfide in the SGM has a linear character. A method for increasing the sensitivity of a semiconductor hydrogen sulfide sensor based on the use of a gas-sensitive material based on SiO$_2$/WO$_3$-10% CuO is proposed. It was found that in the range of concentrations of hydrogen sulfide 50-1000 mg/m$^3$ the dependence of the signal on the amount of hydrogen sulfide is linear.

The found values of the basic, absolute, and reduced errors of the developed sensors are much smaller than their permissible values according to GOST. Therefore, the developed sensors can be used to monitor the content of hydrogen sulfide in objects of various objects.
2.2. Selectivity of a semiconductor H2S sensor

The most important characteristic of gas analytical instruments is the selectivity of determining the component of the analyzed gas mixture. In the semiconductor sensors developed by us, the selectivity of determination is ensured by the selection of optimal temperatures and the corresponding catalysts. A study of the selectivity of hydrogen sulfide determination by the developed sensors was carried out using certified gas mixtures according to the requirements of GOST, presented to gas analytical devices for closed ecological systems and chemical industry facilities. The selectivity of the semiconductor hydrogen sulfide sensor was determined in the presence of hydrogen, carbon monoxide, and methane at a temperature of SCS-H2S 350°C using standard gas mixtures.

The experiments were carried out at a temperature of 20±2°C and a pressure of 730±10 mm Hg. The average results obtained when establishing the selectivity of SCS-H2S are presented in table 1.

Table 1. Results of the selectivity test of the semiconductor sensor of hydrogen sulfide TCS-H2S-3M (n=5, P=0.95).

| Composition of the gas mixture mg/m³ | Found hydrogen sulfide mg/m³ |
|-------------------------------------|-----------------------------|
|                                     | SCS-H2S No 1 | SCS-H2S No 2 | SCS-H2S No 3 |
|                                     | \( \bar{x} + \Delta x \) | \( \bar{x} + \Delta x \) | \( \bar{x} + \Delta x \) |
| H2S-563±air (remaining)             | 560±3         | 566±5         | 565±3         | 1.4 |
| H2S-563±H2-604±air (remaining)      | 562±2         | 562±4         | 562±3         | 1.6 |
| H2S-563±CO-830±air (remaining)      | 559±3         | 565±3         | 562±4         | 1.6 |
| H2S-563±CH4-540±air (remaining)     | 560±4         | 564±4         | 564±5         | 1.4 |

As follows from the data obtained, the presence of carbon monoxide, hydrogen, and methane in the analyzed mixture of H2S in the studied concentration range does not affect the value of the output signal of the hydrogen sulfide sensor. The sensor in the studied concentration range makes it possible to selectively determine H2S. The error in determining SCS-H2S due to unmeasured components does not exceed 1.2%.

Thus, a sensor has been developed that provides selectivity for determining hydrogen sulfide in multicomponent gas-air mixtures, which simultaneously contain hydrogen, carbon monoxide and methane (natural gas). Such mixtures include gaseous emissions of industrial enterprises producing metal sulfides, paints, artificial silk, sugar, asphalt, leather products, atmospheric air of mines, livestock complexes, sewer pipes, wells, etc. In all cases, the value of the relative standard deviation (Sr) for the account of unmeasured components does not exceed 0.05. Changing the flow rate of the gas mixture in the studied interval (5-50 l/h) does not significantly affect the output signal of the sensor. The output signal of the sensors also does not depend on the location in space and the angle of inclination, which allows us to classify the developed sensors (according to GOST-13320-82) as independent.

Table 2. Results of the dependence of the “SCS-H2S” sensor signal with a measurement range of 0-1000 mg/m³ on the concentration of hydrogen sulfide in the mixture (n=5, P=0.95).

| Introduced hydrogen sulfide, mg/m³ | Hydrogen sulfide found mg/m³ |
|-------------------------------------|-----------------------------|
|                                     | \( \bar{x} + \Delta x \) | S | Sr \( 10^2 \) |
| 50                                  | 51±2                       | 1.61 | 2.15 |
| 100                                 | 98±2                       | 1.61 | 1.64 |
| 250                                 | 249±3                      | 2.41 | 0.67 |
| 500                                 | 496±4                      | 3.22 | 0.63 |
| 750                                 | 757±5                      | 4.02 | 0.53 |
| 1000                                | 992±5                      | 4.02 | 0.41 |
2.3. Test the measuring range and the basic errors of the SCS-H2S sensor

The measurement range of the hydrogen sulfide sensors was tested by supplying a mixture of H$_2$S with air to its input in a certain sequence. The experiments were repeated at least 5 times, the results of the experiments are presented in table 2.

As follows from the data given in table 2, the developed sensor in the studied concentration range has a directly proportional dependence of the signal on the amount of hydrogen sulfide in the mixture. In the concentration range of 50-1000 mg/m$^3$, the Sr value does not exceed 0.022.

When determining the main error of the sensors, a mixture with a certified concentration of hydrogen sulfide vapors in air, which was supplied to the device at a rate of 20±2 l/h, was used as an SGM. The main error ($\Delta$) was determined as the difference between the sensor readings and the true concentration values, referred to the measurement range according to the formula:

$$\Delta=A_t - A_0$$  \hspace{1cm} (1)

where $A_t$ is the concentration of the measured component at the test point of measurement induced on the indicator; $A_0$ is the true concentration of the measured component at the test point. The main reduced errors ($\gamma_{re}$) of the sensors were determined by the formula:

$$\gamma_{re} = \frac{(A_1 - A_0)\times100}{C_f-C_i}$$  \hspace{1cm} (2)

where $C_f$-$C_i$ is the final and initial limits of the measured concentration of the determined components of the gaseous media (1000 mg/m$^3$).

| No | Introduced H$_2$S mg/m$^3$ | Found H$_2$S mg/m$^3$ | Found values of errors | Reachable in accordance with GOST ($\gamma$),% |
|----|--------------------------|------------------------|------------------------|-----------------------------------------------|
|    |                          |                        | Main absolute error ($\Delta$) | Main reduced error ($\gamma$),%   |                                        |
| 1  | 50                       | 51                     | 1                      | 0.1                           | ±5.0                                  |
| 2  | 250                      | 247                    | 3                      | 0.3                           | ±5.0                                  |
| 3  | 500                      | 496                    | 4                      | 0.4                           | ±5.0                                  |
| 4  | 1000                     | 993                    | 7                      | 0.7                           | ±5.0                                  |

As follows from these data, the found error values of the developed sensors are much smaller than the permissible values according to GOST. Therefore, the developed sensors can be used to monitor the content of hydrogen sulfide in objects of various environments. The additional error of the SCS- H$_2$S sensors, caused by a change in the ambient temperature, was tested in the range of -10 - +50°C. In the experiments, PGS was used with a hydrogen sulfide content of 50 and 500 mg/m$^3$ in a mixture.

Influence of the temperature of the gaseous medium for each point on the additional error ($\gamma_{add}$) of the sensor was determined by the formula:

$$\gamma_{add} = \gamma_{main} - \gamma_{norm}$$  \hspace{1cm} (3)

where $\gamma_{norm}$-main error in the calibration characteristic; $\gamma_{main}$ - main sensor error for each measurement. The results of determining the additional error of the sensor due to changes in the ambient temperature showed that the additional error of the SCS-H2S sensor from changes in the temperature of the gas medium is not more than 1.0%, and in all cases it is much less than the main error of the device itself.

2.4. The effect of pressure on the values of the input signals SCS-H$_2$S

Pressure tests were carried out in the range of 600-900 mm Hg. To determine the effect of pressure on the operation of the sensor, the pressure in the sensor chamber was set from 600 to 900 mm Hg (with a difference of 50.0 ± 1.5 mm Hg) and after one hour the readings of the device were recorded while
passing a standard mixture with a hydrogen sulfide content of 250 and 500 mg/m$^3$. The results of experiments to determine the effect of pressure on a useful analytical signal are presented in Table 4.

**Table 4.** Results of determining the concentration of hydrogen sulfide at various pressures (n=5, P=0.95).

| Pressure of the gas mixture, mm Hg | Sensor signal, ($\Delta \sigma/\sigma_{air}$) rel. |
|-----------------------------------|-----------------------------------------------|
|                                   | $\bar{x} + \Delta x$ | $\text{Sr} \times 10^2$ | $\bar{x} + \Delta x$ | $\text{Sr} \times 10^2$ |
| 600                               | 2.57±0.02             | 0.88                      | 3.26±0.9              | 0.69                      |
| 700                               | 2.58±0.02             | 0.86                      | 3.28±1.7              | 1.32                      |
| 800                               | 2.57±0.02             | 0.89                      | 3.27±1.8              | 1.40                      |
| 900                               | 2.59±0.03             | 1.32                      | 3.26±0.9              | 0.71                      |

As follows from the data presented, in the studied range, a change in the pressure of the gas medium practically does not affect the value of the sensor output signal.

**2.5. Resistance of the device to concentration overloads**

A test of the stability of the hydrogen sulfide sensor against overloads by concentration was carried out with a hydrogen sulfide content of 2500 mg/m$^3$ in the mixture. As a control mixture, a gas mixture was used, where the concentration of hydrogen sulfide is 500 mg/m$^3$. At this concentration, the SCS-H$_2$S output signals were compared before and after exposure to the overload mixture for 20 min. The recovery time of the normal operation of the SCS-H$_2$S sensor was determined by its output signal in the zone of the main error. The results of the experiments showed that the developed hydrogen sulfide sensor in the studied concentration range withstands overloads under the tested parameters (Table 5).

**Table 5.** Results of testing the stability of SCS-H$_2$S against concentration overloads (n=5, P=0.95).

| No  | Concentration of hydrogen sulfide in the mixture. | Output signal before and after air. overload, mg/m$^3$ (vol.%) | Primary absolute error | Permissible value of main error in accordance with GOST |
|-----|--------------------------------------------------|---------------------------------------------------------------|------------------------|---------------------------------------------------------|
|     | $C_{H_2S}$                                     | Before air charge                                             | After air charge       |                                                         |
| 1   | -500 mg/m$^3$                                  | 506±5                                                        | 512±5                | 6                                                       | ±0.25%                                                  |
| 2   | -2500 mg/m$^3$                                 | 2497±9                                                       | 2504±6               | 7                                                       | ±0.25%                                                  |

The value of the additional error SCS-H$_2$S under the influence of overload concentration on the operation of the device does not exceed 0.03 vol. %

**3. Conclusion**

Thus, our results made it possible to develop a selective semiconductor hydrogen sulfide sensor SCS-H$_2$S designed to automatically monitor the concentration of hydrogen sulfide in gas samples. Assessment of the metrological characteristics of the developed SCS-H$_2$S sensor was carried out in accordance with GOST 52033-2003.

During the experiment, the following were determined: measurement ranges; basic absolute, relative, reduced and additional errors when changing environmental parameters. It was found that in the ranges of concentration of hydrogen sulfide 50-1000 mg/m$^3$ the dependence of the signal on the amount of hydrogen sulfide is linear. The found values of the basic absolute and reduced errors of the developed sensors are much smaller than their permissible values according to GOST. Therefore, the developed sensors can be used to monitor the hydrogen sulfide content in objects of various environments. The additional error of the sensor due to changes in the ambient temperature is 0.7% and in all cases is much less than the basic error of the device itself.
The total additional error of the sensor due to changes in temperature and pressure of the gas medium in all cases was not more than ±1.5%. The stability of the hydrogen sulfide sensor to overloads of the concentration of hydrogen sulfide was tested at a hydrogen sulfide content of 2500 mg/m³ in the mixture. The experiments showed that the developed hydrogen sulfide sensor in the studied concentration range withstands concentration overloads, and its signal in the studied time interval remains stable over the entire range of changes in the concentration of hydrogen sulfide in the air.

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