



Increase of catalytic sensors stability



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ABSTRACT

The design and main technical characteristics of a typical catalytic sensor are described. The main drawbacks related to the lack of stability due to natural ageing and poisoning of sensing elements by catalytic poisons are defined. It is suggested to provide a restricted access of the analyzed gas mixture into the reaction chamber by diffusion through a calibrated hole to increase the stability of sensor.

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1. Introduction

In flammable gases detection practice the sensors based on thermochemical (catalytic), semiconductive and infrared gas analysis technologies are most commonly used. Of these three types of sensors the catalytic sensors that are characterized by a simple design, low weight and small size, low power consumption [1], require a simple process and a simple equipment for their production and have lower price are the most widely used. Small size with low power consumption allows catalytic sensors to be used in wireless solutions [2].

Catalytic sensors are used in different types of fixed and portable gas analyzers and gas detectors designed for monitoring of flammable gases and vapours concentration in the air of production facilities (in coal mines, during the natural gas and oil production and transportation, at chemical plants and oil-processing plants) as well as in the air of habitable rooms where natural gas is used as domestic gas.

Total production of catalytic sensors in the world stands at millions of units a year.

2. Commercial catalytic sensors and their deficiencies

Catalytic sensors produced by different manufacturers are rather similar in design and consist of two sensing elements (active and compensating) connected into a bridge-type measuring circuit and placed into a reaction chamber in which the analyzed atmosphere enters by diffusion through the gas exchange sintered metal filter.

The general view of a sensor of this type (DTK-3) produced by the Scientific and Technical Center of Measuring Gas Sensors (STC IGD) is shown in Fig. 1, where 1 is the ring limiting the damping area; 2 is the sensor body; 3 is the layer of epoxy compound; 4 is the bush securing the block of contact pins; 5 is one of two sensing elements; 6 is the block of contact pins; 7 is the reaction chamber cap with a calibrated hole; 8 is the gas exchange sintered metal filter; 9 is the calibrated hole; 10 is the damping area; 11 is one of two reaction chambers.

The sensor DTK-3 is supplied with direct current $I=50$ mA, $U=2.8$ V, the power of sensor under static conditions (W) is 140 mW. The characteristic dimension of sensing element shaped as a hollow cylinder is 0.3 mm, the hollow diameter is 0.2 mm, the diameter of measuring-heating spiral is 0.25 mm, the diameter of glass-insulated platinum microwire strand is 0.01 mm. The mass of the sensor is 2 g.

The unique feature of the DTK-3 design is a built-in multiple protection of sensing elements against the effects of speed and fluctuations of ventilation flow as well as against the dust contained in the atmosphere being monitored. It is provided by consecutive

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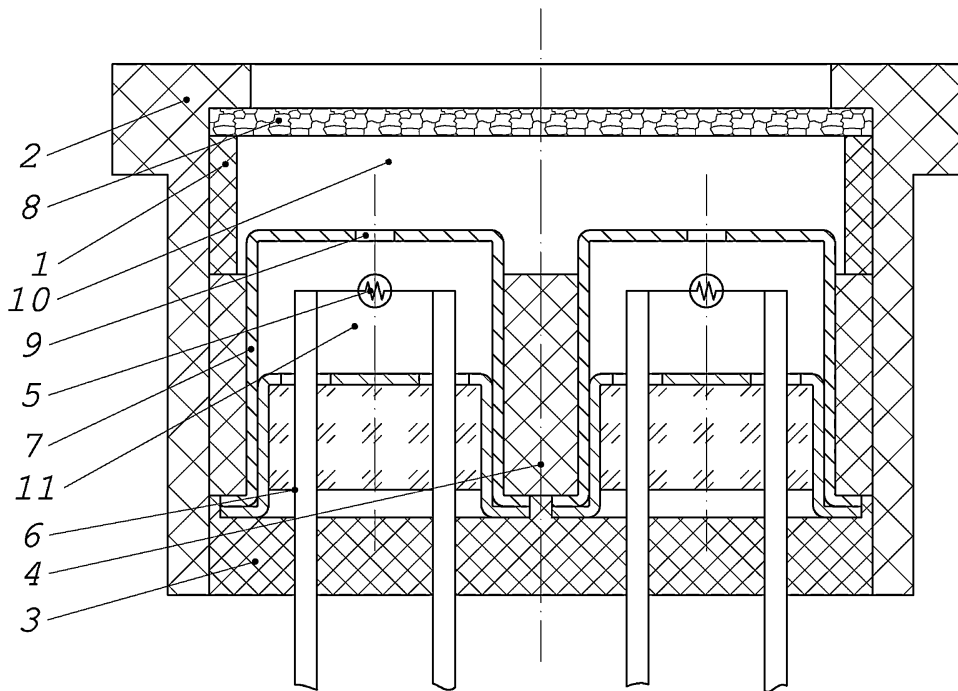


Fig. 1. General view of thermocatalytic sensor DTK-3.

passage of gas mixture being analyzed through the gas exchange filter, damping area and calibrated hole. And the performance of the active sensing element (the quantity of flammable gas oxidized per a time unit in the volume of the reaction chamber, mol/s/l) is set to a greater value than the diffusion flow capacity of the calibrated hole. This sensor design has been developed to implement the dynamic operating mode and to extract diagnostic data from artificially generated transient processes. In addition, this sensor design has been used and is still in use in portable devices operating in pulsed power-saving mode.

Since the inception of low-temperature catalytic sensors with sensing elements which were based on platinum-group metals pulverized on the carriers with highly ramified surface [3–5], the sensors developers and manufacturers have been improving the technology of sensing elements and sensor design [6–8].

These improvements cover the materials and composition of the catalyst carrier, the heater, the methods of sensing elements production, the methods and procedures of output signal measurement, and the sensor operation optimization as a whole.

Despite of the progress in improvement of sensor parameters and performance characteristics allowing this type of sensor to compete with the sensors based on other principles of gas analysis, the problems relative to natural ageing of sensing elements and their poisoning by catalyst poisons remain difficult to solve.

Natural ageing means a variation with time of the structure of the carrier and the catalyst of a sensing element resulting in irreversible porosity degradation, pore sticking, fissuring, reduction of the total surface of the carrier, reduction of active catalyst sites bringing about a progressive sensitivity loss.

The rate of progressive sensitivity loss increases as the size and weight of sensing element decrease.

The aim of the present article is to find engineering solutions allowing reducing the rate of natural ageing and catalyst poisoning enhance sensor operation stability and increase calibration intervals for sensing elements with lower size and weight.

3. The approaches to solving the problem and the results obtained

One of the possible engineering solutions is the restriction of the analyzed gas mixture access by diffusion into the reaction chamber of the sensor in static mode to the values at which the sensing element performance is two or more times as high as the throughput rate of the calibrated hole.

In this case, under conditions of general decrease of output signal due to underutilization of potential performance capability of the sensing element, the capability margin of the sensing element arises. If a constant diffusion flow enters the reaction chamber, this capacity margin will automatically compensate for the sensitivity loss caused by natural ageing and poisoning of sensing element with catalyst poisons.

The sensitivity loss will be compensated until the capacity margin of sensing element is exhausted.

The theoretical and experimental studies in support of the suggested engineering solution are described below.

Using methane detection in the analyzed air atmosphere as an example, consider the variation in time dt of methane concentration dC_k in the reaction chamber (during its filling) due to diffusion flow of methane–air mixture from the analyzed atmosphere through a small-size plain hole for the conditions when the sensing element located inside the chamber is off. We will apply a differential equation of gas diffusion assuming that methane concentration in the methane–air atmosphere is low:

$$\frac{dC_k}{dt} = -D \frac{(C_k - C_a)}{l} \frac{1}{V} S \quad (1)$$

where C_k is the methane concentration in the reaction chamber, mole fractions; C_a is the methane concentration in the atmosphere being analyzed, mole fractions; D is the methane diffusion factor in the air, m^2/s ; S is the cross-section area of the hole, m^2 ; V is the reaction chamber volume, m^3 , l is the plain hole length, m .

Let us set $\tau = (l \cdot V)/(D \cdot S)$ and call it a time constant of diffusion filling process of the reaction chamber.

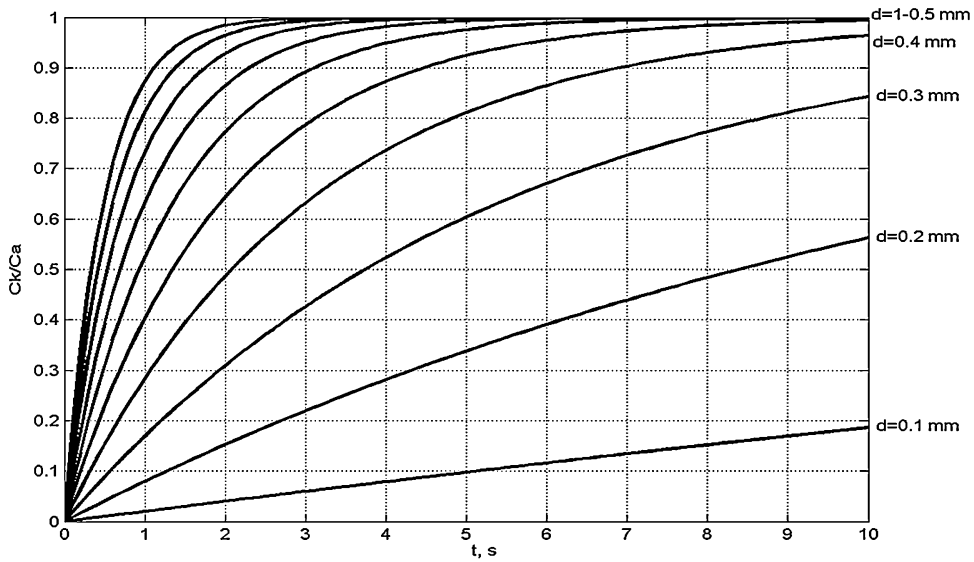


Fig. 2. The dependence of relative methane concentration C_k/C_a during filling of the reaction chamber on the time t for various values of $d=0.1-1.0$ mm.

Then Eq. (1) will be:

$$\frac{dC_k}{dt} = -\frac{C_k - C_a}{\tau} \quad (2)$$

Separating the variables for integration, we have:

$$\frac{d(C_k - C_a)}{(C_k - C_a)} = -\frac{dt}{\tau} \quad (3)$$

Upon integration we obtain:

$$(C_k - C_a) = C \cdot \exp\left(\frac{-t}{\tau}\right) \quad (4)$$

where the constant C is calculated based on initial data: at $t=0$, $C_k=0$.

Finally we obtain:

$$C_k = C_a \left(1 - \exp\left(\frac{-t}{\tau}\right)\right) \quad (5)$$

Let us calculate the time constant

$$\tau = \frac{l \cdot V}{D \cdot S} = \frac{l \cdot V \cdot 4}{D \cdot \pi d^2} \quad (6)$$

for various diameters d ranging from 0.1 mm to 1.0 mm of the plain inlet hole in the reaction chamber. The reaction chamber volume V is 33.5 mm^3 , the length of the calibrated plain hole l is 0.2 mm.

To calculate the methane–air interdiffusion factor under normal conditions (at a temperature of 20°C and a pressure of 1 atm) the following formula will be used:

$$D = \frac{3}{8} \sqrt{\left(\frac{\pi RT}{2\mu_{12}}\right)} \frac{1}{n\sigma_{12}} = 1.76 \times 10^{-5} \text{ m}^2/\text{s} \quad (7)$$

where

$$\mu_{12} = \frac{m_1 m_2}{m_1 + m_2}, \quad \sigma_{12} = \pi \left(\frac{d_1 + d_2}{2}\right)^2$$

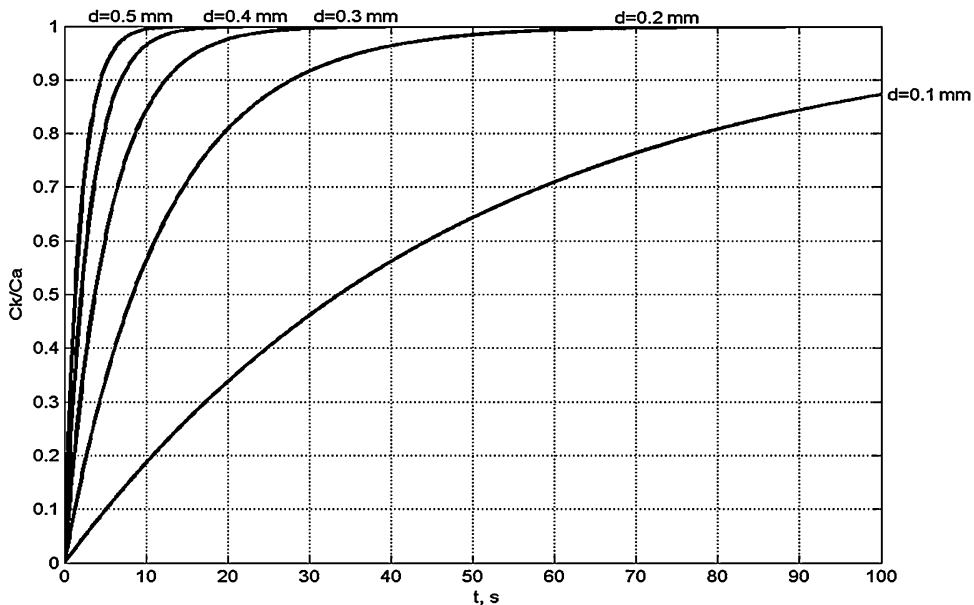


Fig. 3. Relative methane concentration in the reaction chamber C_k/C_a as a function of time t for $d=0.1-0.5$ mm.

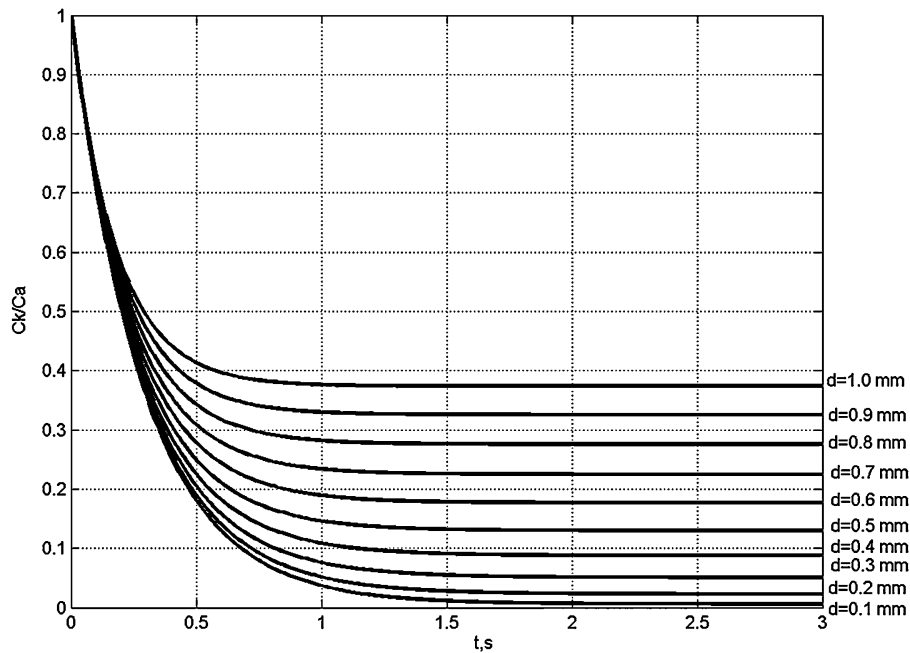


Fig. 4. Relative methane concentration C_k/C_a as a function of time t for various $d=0.1–1.0$ mm during simultaneous methane diffusion through the hole in the reaction chamber wall and its burning inside the chamber on the walls of catalytically active surface of sensing element.

Table 1

The relationship between the time–constant of the diffusion filling of the reaction chamber τ and the diameter of the calibrated plain inlet hole d for the constant reaction chamber volume, V .

d (mm)	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
τ (s)	48.50	12.10	5.40	3.00	1.94	1.35	1.00	0.76	0.60	0.49

Let us draw Table 1 using the calculated values of the time constant τ (d).

Note that τ is the time period during which the methane concentration in the reaction chamber C_k will be equal to 0.63 of methane concentration in the atmosphere. During 2τ time methane concentration C_k will reach $0.86 \approx 0.9$ of C_a and in 3τ period methane concentration C_k will be as high as $0.95 C_a$. The dependence of relative methane concentration in the reaction chamber C_k/C_a on the time is shown in Fig. 2.

As follows from Fig. 2, if the hole diameter is from 1.0 mm to 0.7 mm, the time of the chamber filling is less than 3 s, if $d=0.5$ mm it is about 10 s. This relationship for smaller diameters d of calibrated holes is presented in Fig. 3, where you can see a significant increase of filling time with the decrease of diameter d .

For the calibrated hole diameter d of 0.1 mm (Fig. 3) the filling time of the reaction chamber is more than 100 s. It is not admissible, as there is a requirement that the response time shall not exceed 30 s. For the adopted reaction chamber volume V of 33.5 mm^3 the calibrated holes with a diameter $d=0.3$ mm and more meet this requirement.

Under static operating conditions, simultaneously with methane diffusion into the reaction chamber, methane burning (oxidation) on the surface of active sensing element takes place in it.

For pre-explosive methane concentrations in the air, because of excess of oxygen, all methane molecules reaching catalytically active surface of the sensing element are immediately oxidized, and the actual reaction rate only depends on the rate of diffusion transfer of methane molecules to this surface, therefore the flow being oxidized is equal to methane flow to the surface.

Let us determine the variation in time dt of methane concentration dC_k in the reaction chamber due to methane burning (oxidation) using the following equation:

$$\frac{dC_k}{dt} = -D^* \frac{(C_k - C_o)}{l_k} \frac{1}{V} S_k \tag{8}$$

where $D^*=6.118 \times 10^{-5} \text{ m}^2/\text{s}$ is the methane diffusion factor at determining temperature $t=250^\circ\text{C}$ which is equal to the average temperature near the catalytically active surface; $S_k=0.283 \text{ mm}^2$ is the geometric surface area of the sensing element; $l_k=0.15 \text{ mm}$ is the boundary layer thickness; C_o is the methane concentration on the catalytically active surface, mole fractions.

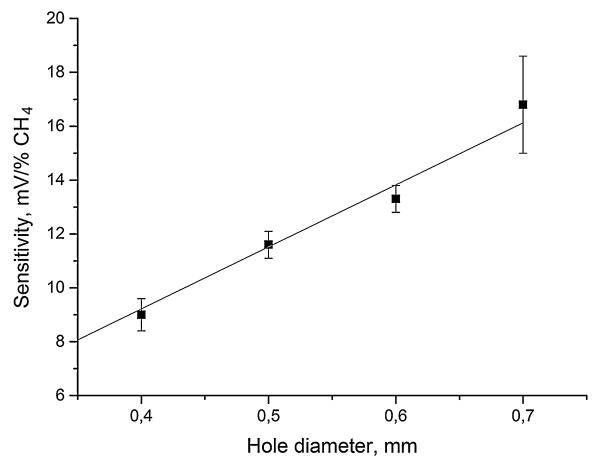


Fig. 5. Depending of sensor sensitivity from the diameter of the hole.

Table 2
Time constant $\tau_k/(\tau + \tau_k)$ as a function of diameter of calibrated inlet plain hole d .

d (mm)	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
$\tau_k/(\tau + \tau_k)$	0.006	0.023	0.051	0.088	0.13	0.177	0.225	0.276	0.326	0.374

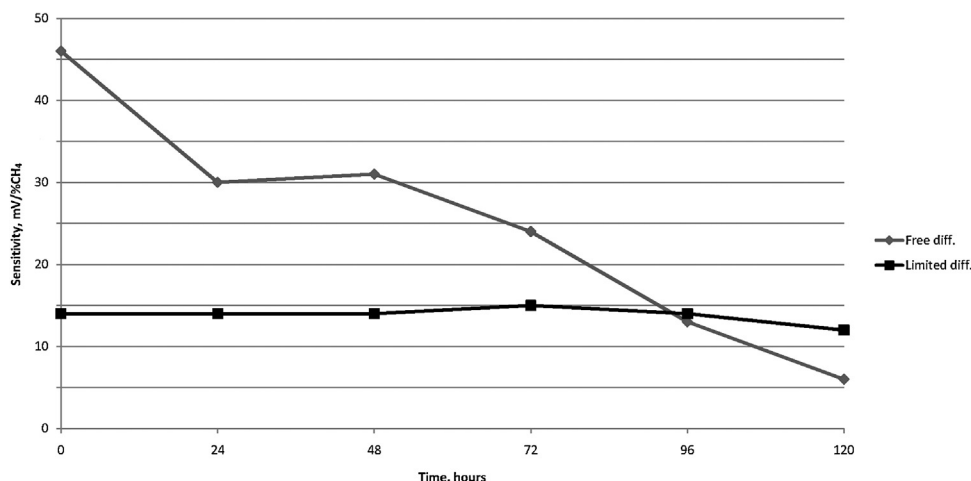


Fig. 6. Hastened ageing of catalytic sensors.

Introducing the constant τ_k which characterizes molecular diffusion of methane towards the surface of the sensing element, we obtain the following equation

$$\tau_k = \frac{l_k \cdot V}{D \cdot S_k} = 0.29 \text{ s} \quad (9)$$

The variation in time of methane concentration C_k during simultaneous methane diffusion and burning (oxidation) on the sensing element surface is described by the following equation:

$$\frac{dC_k}{dt} = -\frac{(C_k - C_a)}{\tau} - \frac{(C_k - C_o)}{\tau_k} \quad (10)$$

On actual sensing elements $C_o = 0$ as methane completely oxidizes on the catalytically active surface. In this case the solution of Eq. (10) with the initial data: $t=0, C_k = C_a$, results in the following relationship:

$$C_k = C_a \left(\frac{\tau_k}{\tau + \tau_k} + \frac{\tau}{\tau + \tau_k} \cdot \exp\left(-\frac{t(\tau + \tau_k)}{\tau \cdot \tau_k}\right) \right) \quad (11)$$

Let us draw Table 2 using the calculated values of time constant $\tau_k/(\tau + \tau_k)$ as a function of d .

The relationship between the relative methane concentration C_k/C_a and the time t (3) for various $d=0.1$ – 1.0 mm during simultaneous diffusion of methane through the hole in the reaction chamber wall and its burning (oxidation) on the surface of catalytically active surface of sensing element is shown in Fig. 4.

Table 3
The average sensitivity of ten sensors within 8 month.

	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov
Standard (mV/%CH ₄)	31.2 ± 2.0	24.3 ± 1.7	20.0 ± 1.5	19.2 ± 1.4	18.5 ± 1.4	17.6 ± 1.5	16.9 ± 1.2	16.1 ± 1.1
Restricted diffusion (mV/%CH ₄)	12.0 ± 0.8	12.0 ± 0.8	12.0 ± 0.7	12.2 ± 0.8	11.8 ± 0.6	11.9 ± 0.6	11.8 ± 0.7	11.9 ± 0.6

$p < 0.05$.

Table 4
Poisoning of the sensors with calibrated hole.

	Initial	Poisoning 1	Poisoning 2	Poisoning 3	Poisoning 4
Sens (mV/%CH ₄)	12.0 ± 0.4	11.8 ± 0.3	11.5 ± 0.3	11.1 ± 0.4	10.8 ± 0.3

$p < 0.05$.

A graph of dependence of the sensor sensitivity from the hole diameter is shown in Fig. 5. Four caps with different calibrated holes within the diameters range of 0.4–0.7 mm as the most frequently used ones were tested with a number of sensors with different sensitivities in the range of 28–43 mV/%CH₄. The sensitivity varies linearly in the specified range.

The experimental evaluation of natural ageing process was performed with acceleration of ageing by additional poisoning of the sensor with vapours of silicone compounds. In addition, the concentration of catalyst poisons and exposure time exceeded significantly the values required by the international standards [9] for the sensor resistance to poisoning by catalyst poisons (exposure for 40 min to methane–air mixture at 1% (v/v) CH₄ in the presence of hexamethyldisiloxane vapours concentration of 10 ppm).

The first tests were performed on two sensors. One sensor had a restricted access of the analyzed mixture to the reaction chamber through the calibrated hole of 0.6 mm in diameter, and another one had a free access of analyzed mixture to the reaction chamber and was only protected against flow fluctuations and dust ingress.

The following test procedure was applied. Both sensors were placed into the test chamber and for 5 days and every day they were on and in working condition for 8 h.

Most of the time the sensors were in clean air, with CH₄ concentration of 1% (v/v) applied on daily basis for 40 min with simultaneous exposure for 15 min to catalyst poison in a concentration of about 500–800 ppm. Then the test chamber was purged

with clean air and kept clean for at least 1 hour. After that, the control measurements of sensitivity were made using 0% and 1% (v/v) CH₄.

The results of the tests simulating natural ageing accelerated by catalyst poisons are given in Fig. 6. The upper curve represents the sensitivity variation of the sensor with free diffusion access of the analyzed mixture to the reaction chamber, and the lower curve shows the sensitivity variation of the sensor with restricted diffusion.

The results obtained show that the sensitivity of the sensor with restricted diffusion virtually does not change and the sensor remains stable during the whole period of accelerated tests (lower curve). During the same period the sensitivity of the sensor with free diffusion (upper curve) decreases under the effect of catalyst poisons by three times, and when it reaches the sensitivity level of the lower curve, the sensitivity loss of both sensors is observed. All this proves that the loss of sensitivity by the sensor with restricted diffusion is inhibited till the capacity margin of the sensing element is exhausted. After that the loss of sensitivity by both sensors is observed.

Another test was to check natural ageing. Ten sensors with similar characteristics were chosen for this experiment. Five of them were standard catalytic sensors, another five were with calibrated holes. All of them were placed into special chamber and were observed for eight months. Every day the sensors were exposed to 1.0–1.5% of CH₄ for 8 h. Table 3 presents the results obtained in this experiment. Signal of the sensors without calibrated hole decreased to 52% of their initial sensitivity, while the sensors with calibrated remained stable during experiment. Thus, the use of restricted diffusion in sensors allows reducing natural ageing rate in comparison with standard catalytic sensors.

And also three sensors were tested to fit requirements of [9]. They were exposed to catalytic “poison” hexamethyldisiloxane (HMDS) with 10 ppm concentration with presence of 1% CH₄ for 40 min. Experiment was carried out 4 times with 2–3 day intervals. Results are showed in Table 4. As could be seen, every sensor has passed the testing. Signal decrease in each experiment is less than 10% needed in the standard.

To summarize the above, using of the calibration hole allows significantly increasing long term stability and improving poison resistance of sensors. Sensors with restricted diffusion access pass [9] tests and are able to work much longer than standard catalytic sensors without significant sensitivity loss. But it's important to note, that sensitivity of sensors with calibrated holes always lower than that of standard sensors.

4. Conclusions

- (1) Based on the analysis of the mass transfer processes during catalytic sensor operation in static mode under conditions of restricted diffusion of analyzed gas mixture the possibility of significant increase of sensor performance stability has been shown.
- (2) The variation of diameter of the calibrated hole which restricts gas diffusion into the reaction chamber of a constant volume

makes it possible to adjust and improve interdependent parameters determining the sensitivity, stability and response time.

- (3) The adjustment of stability becomes possible as under conditions of a stabilized restricted diffusion flow the quantity of combustible component in any concentration coming to the sensing element is far less than the sensing element performance capacity.

As a result, the margin of usable performance capacity of sensing element arises that compensates automatically the loss of performance (sensitivity) of sensing element occurring with time and decreases accordingly.

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Biographies

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