

## Development of an Approach to Increase Hydrogen Measurement Selectivity

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Hydrogen monitoring in industrial premises, when other gases are also present in air, is an urgent task. For safety reasons, it is necessary that a hydrogen sensor provides measurements at the lowest possible temperature. In this paper, we propose an approach to the selective measurement of the concentration of hydrogen, which is part of multicomponent hydrocarbon mixtures. Binary and ternary mixtures of hydrogen with methane, propane, and butane were used in this study. The traditional method is based on measuring the catalytic sensor response, and a new method that is based on measuring the amount of heat released during hydrogen combustion was used to solve the problem of selectivity. An industrial catalytic sensor was used for the measurements. It was shown that for the selective measurement of hydrogen in hydrocarbon mixtures, it is necessary to reduce the sensor temperature below 200 °C. Measurements of hydrogen concentration and a comparison of results were carried out at 105 °C. Such a low operating temperature is an excellent result for a catalytic sensor. It is shown that the method based on measuring the amount of heat released during hydrogen combustion is more accurate than the traditional method, and the average error was 7.7%.

### 1. Introduction

One of the promising areas of “green” energy is the use of hydrogen as an environmentally friendly fuel.<sup>(1)</sup> However, the use of hydrogen is faced with the problem that it is very difficult to transport it over long distances because it could embrittle the steel and welds used to fabricate the pipelines and could leak through pipeline junctions owing to its high fluidity.<sup>(2)</sup> In addition, it is extremely explosive in a wide concentration range: from 4 up to 75 vol.% for a hydrogen–air mixture and from 4 to 96 vol.% for a hydrogen–oxygen mixture.<sup>(3)</sup> Therefore, hydrogen is

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mainly produced only in places where it is consumed. To monitor hydrogen leaks, it is important to have efficient gas analyzers that can detect hydrogen in its pre-explosive concentration range (from 0 to 4 vol.%).

Available hydrogen leak detectors can be classified according to the type of transducer they use. The main transducers used in instruments for gas analysis include electrochemical,<sup>(4)</sup> semiconductor,<sup>(5)</sup> and catalytic sensors.<sup>(6,7)</sup> Each type of sensor has its own advantages and disadvantages, which determine their fields of application. The electrochemical and semiconductor sensors are most effective in the ppm range of hydrogen concentrations, and the catalytic ones, in the pre-explosive concentration range (0.1–2 vol.%).

In many technological processes, hydrogen is not present in its pure form and is one of the components of a hydrocarbon mixture. In particular, options for transporting hydrogen are considered as part of methane–hydrogen mixtures or their usage as fuel.<sup>(8)</sup> Therefore, it is necessary to monitor the concentration of hydrogen in multicomponent mixtures of flammable gases.

Gas analyzers with catalytic sensors are among the most common devices for monitoring the presence of flammable gases in air. One of the features of catalytic sensors is that they react only to flammable gases, but, at the same time, they do not have selectivity, since all flammable gases are oxidized on the sensor. Therefore, it is impossible to extract the response to hydrogen from the response to the hydrocarbon mixture using a catalytic sensor for flammable gases and volatile organic compounds. Moreover, it is important to note that the sensitive element of a catalytic sensor requires heating to a temperature of 300–400 °C, and the reaction of hydrogen with oxygen itself is accompanied by the release of heat.

For safety reasons, the hydrogen catalytic sensor must have low operating temperature as possible in order not to accidentally cause a hydrogen–air explosion, for which only 20 μJ of energy suffices. In addition, the hydrogen sensor must be small and consume as little power as possible, and its sensing temperature must be low (ideally, at temperatures near room temperature), for safety reasons.

These requirements are the motivation for the ongoing development of hydrogen sensors. Many research groups are working to develop low-power catalytic hydrogen sensors with improved parameters by optimizing their design and manufacturing technology.<sup>(7,9,10)</sup>

Note that catalytic hydrogen combustion is actively studied, since compared with conventional hydrogen–air combustion, it exhibits higher safety and efficiency and ultralow NO<sub>x</sub> emissions.<sup>(11,12)</sup> At the same time, the low-temperature catalytic combustion of hydrogen is known from the literature<sup>(13)</sup> and is even considered as a method of initiating the ignition of combustible hydrogen–hydrocarbon mixtures in internal combustion engines.<sup>(14)</sup> However, the possibility of low-temperature measurements of hydrogen, until recently, was considered in catalytic sensors only from a perspective point of view since traditional measurements involve heating the sensor to a temperature at which the response saturates.

The purpose of this study is to not only develop methods for the low-temperature measurement of hydrogen, but also solve the problem of its selective measurement in hydrocarbon mixtures. The selective detection of hydrogen in a hydrocarbon mixture is a non-trivial task that has not been solved so far, particularly in the case of catalytic sensors. The

solution to this problem will have a significant contribution to the development of gas analysis methods and their practical applications.

The novelty of this work lies in the fact that by varying the temperature of the catalytic sensor, we can suppress the reaction of the catalytic combustion of hydrocarbons and, at the same time, maintain an effective hydrogen combustion reaction. It is important to note that an industrial catalytic sensor is used, which, under normal conditions, does not have selectivity to hydrogen or other hydrocarbons.

In this work, two methods are used to measure hydrogen concentration: the traditional approach based on the sensor response after its stabilization (Method I) and the measurement of the response during the combustion of hydrogen inside a sensor housing (Method II). This choice is made because of the following reasons. The traditional method is the main method of determining the concentration of combustible gases. It has many modifications, which, however, do not change its essence, namely, a change in sensor temperature during catalytic gas combustion.<sup>(15)</sup> Method II is based on the amount of heat released during the combustion of a known volume of gas.<sup>(16)</sup> This method is not widely used. The main advantage of the method is that it can be used for the rapid evaluation of the explosiveness of the environment having an unknown gas composition using a typical catalytic sensor. The method does not require the identification of the types of hydrocarbons, their quantity and concentration. A more detailed discussion of the methods is provided in the next section.

This article is organized as follows. In Sect. 2, we introduce the methods and the approach to low-temperature measurement. In Sect. 3, we mainly present and discuss the experimental results of selective hydrogen measurement in two- and three-component mixtures. Finally, conclusions are given in Sect. 4. A detailed study of catalysts for catalytic hydrogen sensors was previously carried out.<sup>(6)</sup>

## 2. Materials and Methods

### 2.1 Sensor and experimental setup

Catalytic sensors were the pellistors manufactured by Scientific and Technical Center of Measuring Gas Sensors.<sup>(17)</sup> Each catalytic sensor has a heating coil made of a platinum microwire in quartz-shaped insulation and covered with a highly porous  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> layer. Depending on the design, the catalytic sensor can have working and reference elements or it can only have the working element. The working element was impregnated with the catalytic metal salts of palladium chloride (PdCl<sub>2</sub>) and platinum acid (H<sub>2</sub>PtCl<sub>6</sub>) with the Pt:Pd = 1:3 molar ratio. The sensor design is presented in more detail in Ref. 16. Calibration gas mixtures (CGMs) of hydrogen and hydrocarbons indicated in Table 1 were taken as initial gases.

The formation of mixtures consisting of binary and ternary components was carried out using a laboratory setup that includes gas cylinders with CGM, a diffusion gas chamber, two test boards with a set of sensors, and a computer for data processing (Fig. 1). The flow of gas mixtures coming from the cylinders was varied using flow regulators of the LZM-6T type. Multicomponent gas mixtures were formed in the gas chamber. After measurements were taken,

Table 1  
Concentrations of target gases in air.

CGM type	Hydrogen H <sub>2</sub>	Methane CH <sub>4</sub>	Propane C <sub>3</sub> H <sub>8</sub>	Butane C <sub>4</sub> H <sub>10</sub>
Concentration in air, vol.%	0.96	0.47	1.01	0.666

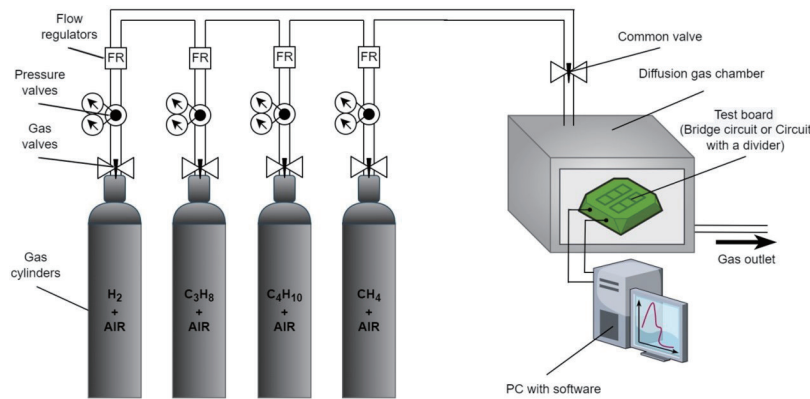


Fig. 1. (Color online) Block diagram of measuring installation.

the gas chamber was purged with air to remove the previous gas mixture. A measuring board with an installed set of sensors was placed in the chamber. For data transmission, the board was connected to a computer. After that, the obtained measurement results were processed.

## 2.2 Methodology

Method I: The traditional method of measuring combustible gases, particularly hydrogen, involves using a Wheatstone bridge circuit [Fig. 2(a)].<sup>(15)</sup> The working ( $R_{act}$ ) and reference ( $R_{ref}$ ) elements were connected in one arm of the bridge, and the other arm contained two precision resistors with a resistance of 10 k $\Omega$ .<sup>(18)</sup> A voltage ( $U_{supply}$ ) is applied to the Wheatstone bridge circuit, which induces the heating of the working element to the temperature at which the combustible gas “burns”. In this case, the heat released as a result of the flameless oxidation of combustible gas molecules on the surface of the catalytic sensor will lead to an increase in the heater temperature of the working sensor and cause an imbalance in the bridge.<sup>(19)</sup> The measurements are carried out after the sensor response in the gaseous environment stabilizes.

Gas analyzers with such a measurement scheme are usually calibrated to two concentration points that lie within the pre-explosive concentration range, in pure air and in air containing the analyzed gas with a predetermined concentration. A measured response voltage ( $U_{out}$ ) is the voltage between two points of the bridge circuit diagonal. Figure 2(b) (black lines) shows the dependence of the response voltage ( $U_{out}$ ) on the supply voltage ( $U_{supply}$ ) in two CGMs of hydrogen. It is seen that the response voltage is practically proportional to the hydrogen concentration at different supply voltages (0.6 and 2.8 V) [Fig. 2(b), blue lines]. If the analyzed medium contains more than one combustible component, all the contained molecules will

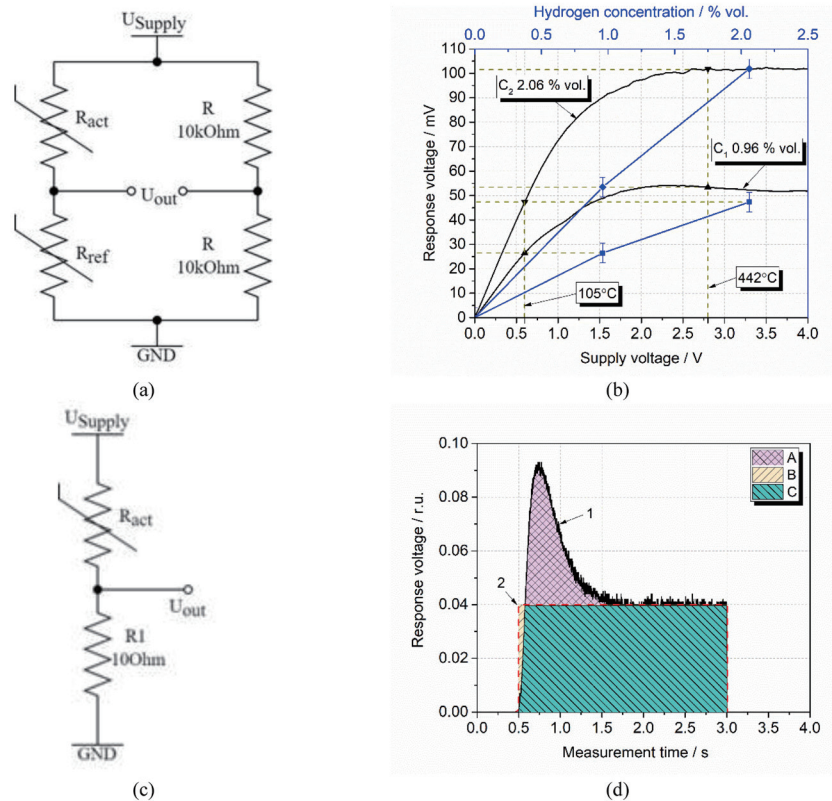


Fig. 2. (Color online) (a) Measurement bridge circuit (Method I), (b) dependence of response voltage on supply voltage in two CGMs of hydrogen, (c) measurement voltage divider circuit (Method II), and (d) dependence of sensor response ( $U_{out}$ ) on measurement time;  $A$  is the measured area, area  $B$  is needed to find a curvilinear trapezoid, and area  $C$  is the gas leakage.

participate in the catalytic oxidation process. Thus, all components of the gas mixture will affect the heater temperature. As a result, the catalytic sensor has no selectivity to combustible gases and vapors. This limits the scope of its application to only known gases.

Method II: The second method is based on measuring the amount of heat released during the combustion of a known volume of combustible gases inside the sensor housing. This method fundamentally differs from Method I. The dynamic measurements are carried out during the combustion of the gas portion inside the sensor housing. Therefore, measurements must be carried out in a periodic mode, which is necessary to recover the atmosphere inside the sensor housing after gas burnout due to the diffusion of a new portion of gas.

Noted that the rate of hydrogen combustion must be much higher than that of its inflow into the sensor housing to ensure correct measurements. To limit the diffusion of hydrogen into the sensor housing, a diaphragm with a hole diameter of 0.2 mm was used. The voltage divider circuit [Fig. 2(c)] is used instead of the Wheatstone bridge circuit.

The advantage of this method is that there is no need to identify gases, their quantities, and concentrations, and it can be used in industry for the quick determination of potentially explosive mixtures in air. This method was used for flammable gas detection and described in more detail

in previous works.<sup>(16,20)</sup> It is necessary to note that Method II is not precise in the case of hydrocarbon mixtures. However, if there is hydrogen in hydrocarbon mixtures, its accuracy should be much higher as the gas type is known. To calculate the heat generated, extended data processing based on integrating the area under the measured dependence of the sensor response on the measurement time is used.<sup>(20)</sup>

Figure 2(d) illustrates Method II. The black line is the dependence of the sensor response ( $U_{out}$ ) on the measurement time in the presence of combustible gas. It can be seen from this dependence that there is a “hump” that is associated with heat released during the burning of gas inside the working chamber of the sensor.

The amount of heat released during the combustion of hydrogen is proportional to the difference between the dependences of the sensor responses in mixtures with ( $U_{mixture}$ ) and without ( $U_{air}$ ) hydrogen, that is, the difference observed in areas [Fig. 2(d), area A]. It is necessary to note that the gas leakage into the sensor housing contributes to the measurement results. This leads to an error in the calculation. However, the leakage can be easily calculated and taken into account by subtracting area C in Fig. 2(d) (area B is needed to find a curvilinear trapezoid).

It is difficult to apply integral calculus to determine the area under the curve after the end of measurements since it will be necessary to store a large volume of experimental points. Therefore, the integration has been replaced by real-time summation.<sup>(20)</sup> Moreover, the higher the sampling rate, the more accurate the result will be. After measurements are taken in air and in the presence of hydrogen, the difference observed in areas under the curve is calculated, which is proportional to the amount of heat generated. Before starting the measurements, the sensor is calibrated by supplying a known concentration of hydrogen. The working sensor ( $R_{act}$ ) is included in the divider circuit with a resistor  $R_1$ , which has a resistance rating of  $10\ \Omega$  [Fig. 2(c)]. The value of  $10\ \Omega$  is given according to a pseudo-bridge circuit, where the role of one of the arms of the bridge circuit is played by the digital-to-analog converter of the microcontroller.<sup>(20)</sup>

### 2.3 Approach to low-temperature measurement

To ensure the selective measurement of hydrogen in multicomponent mixtures of flammable gases, it is necessary to change the approach to measurements, particularly to carry out measurements in the “temperature scan” mode but not at one point at a constant voltage ( $U_{Supply}$ ).<sup>(21)</sup> In this work, temperature scanning was used to determine the optimal temperature for performing the selective measurement of hydrogen in multicomponent mixtures of combustible gases. For this, the response of the sensor was investigated in a voltage range from zero to 4 V with a discrete amplitude step of 50 mV. The duration of each step was 25 s. This allows one to obtain the temperature dependence of the sensor response in a wide temperature range and define the optimal measurement conditions.

The dependence of the sensor response on the applied voltage for hydrogen and some hydrocarbons is shown in Fig. 3. The temperature of the catalytic sensor at the applied voltage is shown on the upper scale in Fig. 3. These dependences, except for hydrogen, are S-shaped curves. The sensor response appears at a certain temperature characteristic of a given gas.

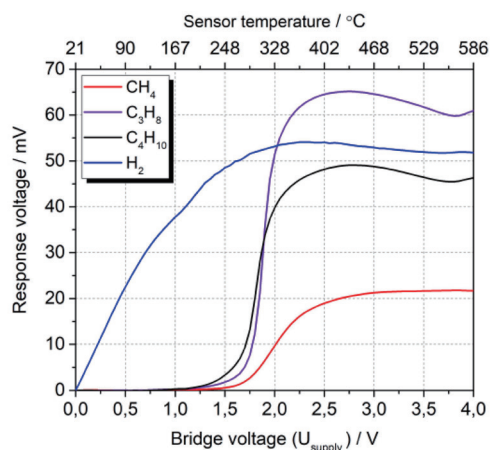


Fig. 3. (Color online) Sensor response to applied voltage for hydrogen and hydrocarbons in CGM (Table 1).

Moreover, the magnitude of the response increases rapidly with temperature. At temperatures above 300 °C, the sensor response saturates. This temperature range (above 300 °C) is traditionally a working temperature range for catalytic sensors, since random errors in establishing and maintaining the temperature in this range lead to a minimum error in measuring the response value.

On the basis of S-shaped curves, an assumption was made about the possibility of the selective determination of hydrogen in a flammable gas mixture in a temperature range high enough to start the oxidation of hydrogen and at the same time low enough to start the oxidation of other flammable gases, i.e., in the range from 20 to 200 °C, which corresponds to a heating voltage from zero to 1.2 V, as shown in Fig. 3.

It is important to note that in this temperature range, the catalytic hydrogen sensor has practically zero response for all the studied hydrocarbons. This is because the temperature on the catalyst surface is insufficient to initiate the oxidation of combustible gas molecules. However, the response of the bridge circuit for the hydrogen can be seen even at sufficiently low heating temperatures, which is associated with the high activity of the catalyst containing platinum and palladium.<sup>(6)</sup>

In principle, to determine the hydrogen concentration, one can take any temperature value in the range from 20 to 200 °C. Since the initiation of the explosion of hydrogen–air mixtures requires a very small amount of energy (about 20 μJ), the lower the temperature of the sensor, the safer its use. On the other side, it is necessary to have high sensor sensitivity to hydrogen when the sensor temperature decreases.

In this work, the H<sub>2</sub> concentration was measured at 0.6 V, which corresponds to a temperature of ~105 °C. This voltage was chosen because (1) the temperature is sufficiently high for the complete hydrogen oxidation on the surface of Pt and Pd particles within the lower flammable explosive limit,<sup>(22)</sup> (2) the signal at the output of the bridge circuit is above 25 mV/% and it can be easily processed according to Fig. 3, and (3) the temperature is higher than the water boiling point, which is important for reducing the effect of humidity during measurements.

To validate the hypothesis about selective hydrogen detection in a mixture with flammable gases, measurements were carried out using the two methods described above. To provide the correct measurement, the sensors were calibrated at a voltage of 0.6 V [Fig. 2(b), blue lines], i.e., in the area of rapid change in sensitivity from the voltage, and not in the area of sensitivity saturation, as usual.

### 3. Results and Discussion

#### 3.1 Method I

As mentioned above, the industry uses this method to determine the concentration of flammable gases in a “version” of a constant heating voltage, at which the response of the Wheatstone bridge circuit is measured. In this study, the approach is based on S-shaped curves that were measured in the voltage range from zero to 4 V. The S-shaped curves in mixtures containing two or three flammable gases, in which one of the gases was hydrogen, were obtained. The concentrations of all components in mixtures are summarized in Table 2. The obtained S-shaped curves for two-component gas mixtures are shown in Fig. 4.

By analyzing Fig. 4, it can be concluded that in the 20–200 °C temperature range, the sensor has a response, which is caused exclusively by hydrogen oxidation. Note that the dependences for multicomponent mixtures have a lower response than that for pure hydrogen. This is due to the lower concentration of hydrogen in the mixture.

The concentration of H<sub>2</sub> in the mixture was calculated in terms of the sensor response at 0.6 V. The sensor response, taken at 0.6 V in the mixtures and related to the sensor response at 0.96% hydrogen, is the concentration of H<sub>2</sub> in the mixture. The calculated concentrations are given in Table 2.

As seen in Table 2, the experimental values obtained for two-component mixtures coincide rather well with the predetermined values and the error does not exceed 7%. For three-component mixtures, the measured values do not coincide with the predetermined ones, as shown for gas mixture numbers 4–6 in Table 2. This result is difficult to explain. It is possible that this is because there is a strong temperature dependence of the sensor response in this voltage range [about 0.6 V (Fig. 4)]. Therefore, small uncontrolled changes in the temperature of the sensor can lead to large errors in the hydrogen concentration measurements.

Note that catalysts with a molar ratio of Pt:Pd = 1:3 are widely used for catalytic sensors of combustible gases.<sup>(6)</sup> When this type of catalyst is used to monitor hydrogen leaks, hydrogen catalytic oxidation begins at room temperature (Fig. 4). This can be considered as a disadvantage, since it can distort the measurement results. The catalytic combustion of hydrogen at room temperature does not allow one to measure the zero point of the sensor, and thus accurate calibration and subsequent measurements can be difficult to carry out. The fact that the oxidation reaction of hydrogen starts at room temperature is in agreement with earlier works.<sup>(23)</sup>



Table 2  
Gas mixture flow and results of hydrogen measurements using Method I.

Gas mixture number	Gas mixture flow				Specified H <sub>2</sub> concentration in mixture	Measured H <sub>2</sub> concentration at 0.6 V		
	Hydrogen (H <sub>2</sub> )	Methane (CH <sub>4</sub> )	Propane (C <sub>3</sub> H <sub>8</sub> )	Butane (C <sub>4</sub> H <sub>10</sub> )		Component 2	Component 3	
	l/min				vol.%			
1	0.34	–	0.17	–	0.64	0.337	–	0.6
2	0.38	0.25	–	–	0.576	0.188	–	0.545
3	0.42	–	–	0.42	0.502	0.333	–	0.486
4	0.29	0.29	–	0.34	0.305	0.149	0.241	0.447
5	0.21	0.27	0.25	–	0.274	0.174	0.346	0.456
6	0.42	–	0.48	0.19	0.369	0.447	0.115	0.448

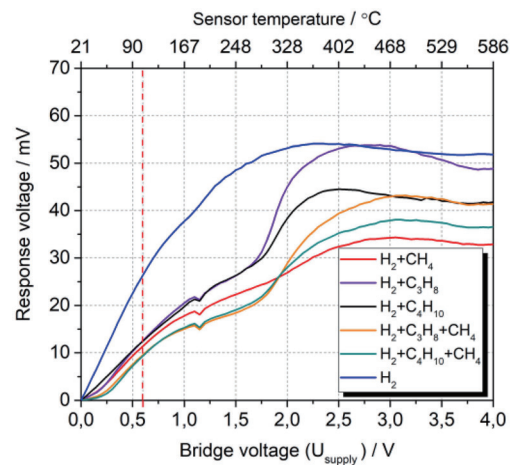


Fig. 4. (Color online) Sensor response to applied voltage for hydrogen (from Fig. 3) and two- and three-component mixtures (Table 2).

### 3.2 Method II

To provide the same sensor temperature range (20–200 °C) in Method II as in Method I, a voltage of 1.1 V was applied to the divider. In this case, part of the voltage dropped across the resistor and a voltage of 0.6 V was applied to the sensor. A pulse duration of 2.5 s was selected experimentally to ensure the complete burnout of H<sub>2</sub> in the sensor housing.

The sensor was preliminarily calibrated for hydrogen in the CGM. Figure 5 shows the experimental dependences of the sensor response during the combustion of hydrogen in a mixture with different hydrocarbons, i.e., in two-component mixtures shown as “Gas mixture number” in Table 3, lines 1–5.

Figure 6 shows the dependences of the difference between the signals obtained during measurements of gas mixtures (Table 3) and air. The integral of the area under the curve of the dependences is proportional to the supplied H<sub>2</sub> concentration.

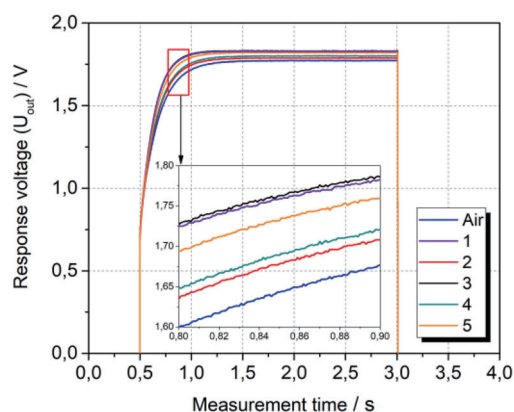


Fig. 5. (Color online) Sensor responses in various gas mixtures (Table 3).

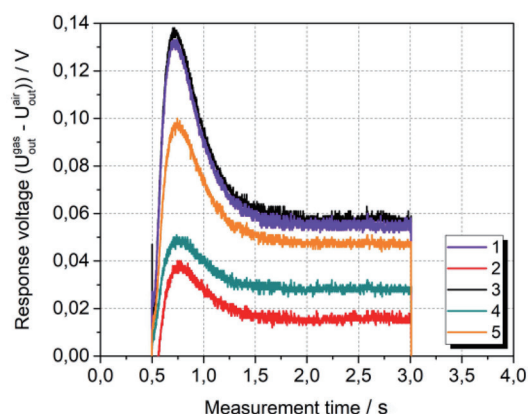


Fig. 6. (Color online) Difference in sensor response between gas mixtures and in air for the same mixtures as in Fig. 5.

Table 3.

Gas mixture flow and results of hydrogen measurements using Method II.

Gas mixture number (Figs. 5 and 6)	Gas mixture flow				Specified H <sub>2</sub> concentration in mixture	Measured H <sub>2</sub> concentration at 0.6 V		
	Hydrogen (H <sub>2</sub> )	Methane (CH <sub>4</sub> )	Propane (C <sub>3</sub> H <sub>8</sub> )	Butane (C <sub>4</sub> H <sub>10</sub> )		Component 2	Component 3	
	l/min				vol.%			
1	0.55	–	0.21	–	0.693	0.281	–	0.639
2	0.34	–	0.63	–	0.334	0.659	–	0.311
3	0.67	0.21	–	–	0.731	0.112	–	0.665
4	0.29	–	–	0.57	0.328	0.439	–	0.305
5	0.29	–	–	0.25	0.517	0.307	–	0.470
6	0.17	0.29	–	0.34	0.202	0.173	0.280	0.188
7	0.25	0.27	0.25	–	0.311	0.165	0.327	0.295
8	0.19	–	0.48	0.19	0.210	0.566	0.145	0.193

Also, the measurements of hydrogen concentration in three-component mixtures have been carried out. On the basis of the data obtained, the hydrogen concentrations were calculated, which are presented in Table 3 (lines 6–8).

A comparison of the specified and measured hydrogen concentration is given in Table 3, which shows that the second method makes it possible to measure the hydrogen concentration in any mixture with an average error of 7.7%. Such results for hydrogen in hydrocarbon mixtures can be considered acceptable.

This may be due to the fact that Method II is based on the combustion of a constant volume of hydrogen inside the sensor housing. As a result of such combustion, a known amount of heat will be released. In this case, the combustion rate should depend on the sensor temperature, but the amount of heat released does not depend on the sensor temperature if the full combustion occurs during the heating pulse duration.

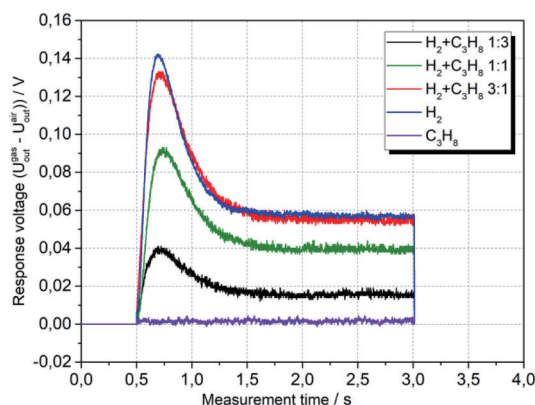


Fig. 7. (Color online) Difference in sensor response between hydrogen–propane CGM and air.

As can be seen from Fig. 6, the combustion of hydrogen, in fact, occurs within one second. In this case, one can expect that the combustion kinetics will depend on the temperature in the 20–200 °C range, but, in any case, all the hydrogen inside the sensor body will “burn out” within 2.5 s, i.e., during the heating pulse duration. Thus, the result of measuring the hydrogen concentration, in this case, does not depend on the sensor temperature, as in Method I. This reduces the measurement error.

Some uncertainty can be caused by different heat removals from the sensing element of the sensor at different temperatures. However, the sensitive element is heated to a temperature of only above 100 °C. Therefore, the heat sink will not be highly dependent on the temperature of the sensing element.

For a better explanation of the experimental results presented in Fig. 7, the measurement results of the response of a two-component mixture containing hydrogen and propane are presented. It can be seen from Fig. 7 that there is no sensor response in pure propane. The addition of hydrogen to propane results in a characteristic peak that is associated with the combustion of hydrogen. The intensity of the response increases with hydrogen concentration in the mixture and reaches its maximum in the hydrogen–air mixture.

As mentioned in Ref. 12, Method II is not considered precise in the case of hydrocarbon mixtures. It can be used for the rapid assessment of the explosiveness of combustible gas mixtures of unknown composition. At the same time, for hydrogen–hydrocarbon mixtures, the method showed a better result than the Wheatstone bridge circuit.

#### 4. Conclusion

In this paper, we proposed an approach to the selective measurement of the concentration of hydrogen, which is part of multicomponent hydrocarbon mixtures. Two methods were used to solve the problem: the traditional method based on measuring the catalytic sensor response and a method based on measuring the amount of heat released during hydrogen combustion. The industrial catalytic sensor was used for the measurements.

It was shown that both methods potentially allow selective hydrogen measurement in hydrocarbon mixtures. However, it is necessary to reduce the sensor temperature below 200 °C, while traditionally, the temperature of catalytic sensors is above 300 °C.

The lower limit of the temperature range is determined mainly by the sensor sensitivity. The upper value of the temperature range must be lower than the temperature at the beginning of the “combustion” of hydrocarbons in the target gas mixtures. This value depends on the type of catalyst and hydrocarbon. In this work, the minimum temperature was 105 °C. Such a low temperature was not previously used for the selective measurement of hydrogen in hydrocarbon mixtures. At this temperature, the sensor response was above 25 mV per % of the hydrogen.

Thus, by choosing the measurement temperature, it is possible to adapt the existing gas analyzers with catalytic sensors to measure hydrogen selectively. It is important to note that the results achieved are valid for the Pd/Pt catalyst. For other types of catalyst, it is necessary to carry out similar studies of the temperature dependence of the sensor response to ensure only the “combustion” of hydrogen on the catalyst.<sup>(6)</sup> Further development also requires additional research. In particular, it is necessary to determine the minimal hydrogen sensitivity of the proposed methods.

It is shown that Method II, which is based on measuring the amount of heat released during hydrogen combustion, is more accurate than the traditional one (Method I). The average error in determining the hydrogen concentration is less than 8%. Although Method II is not considered precise in the case of hydrocarbon mixtures,<sup>(16)</sup> such results for hydrogen in hydrocarbon mixtures can be considered good.

In the case of hydrogen, this result is achieved owing to the following reasons. First, a fixed volume of hydrogen, located inside the sensor housing, is burned. This releases a known amount of heat, which is independent of the ignition temperature, i.e., the sensor temperature. Second, because the sensor is calibrated for hydrogen and only hydrogen is burned, hydrocarbons do not burn at the selected temperature.

Method II is suitable for both hydrogen–hydrocarbon and hydrogen–air mixtures. Apart from the measurement principle itself, the difference between Methods I and II is that Method II requires periodic measurements. This is because after the combustion of gases with the sensor, the atmosphere within the sensor housing is to be recovered through the diffusion of a new portion of gas. This fact reduces the energy consumption of the sensor and makes it possible to create gas analyzers with long-term autonomous power supply, which is a trend in flammable sensors.<sup>(24)</sup>

The results can be used for the ignition of hydrogen and hydrogen–hydrocarbon air mixtures in a related field where these mixtures are used for fuel-catalytic ignition.<sup>(14)</sup> Catalytic ignition does not require electrodes and the ignition system, so there is no erosion of the electrodes while the operation time of the catalytic ignition system will be significantly longer than that of a device using a conventional spark plug.

The main promising direction in a new generation of high-performance internal combustion engines is the development of catalysts that provide ignition at low temperatures (<300 °C).<sup>(25)</sup> The results obtained in this study showed that the catalytic combustion of hydrogen begins at temperatures below 100 °C, which potentially indicates the possibility of using Pt-Pd catalysts for the catalytic ignition system with hydrogen as fuel.

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