Method for determining the concentration of unknown combustible gas

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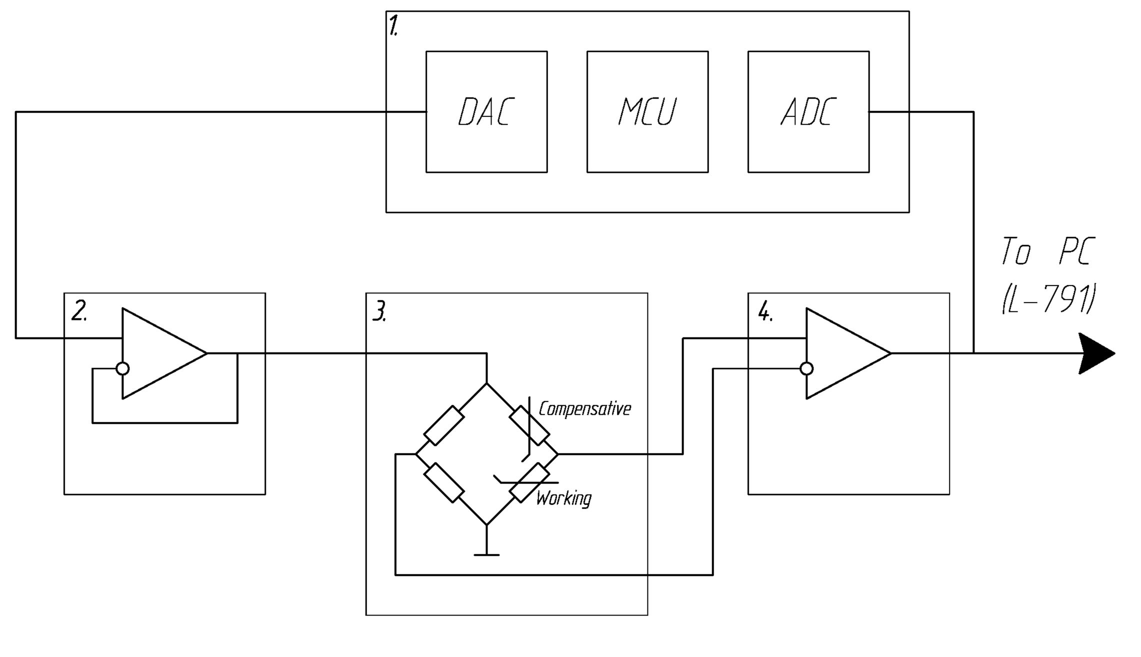
Introduction

It is known that catalytic sensors have different sensitivities to different combustible gases. Usually gas analyzers are calibrated by methane and not suitable for measuring other flammable gases. Correction is needed to get real concentration of other gases. In this paper it is shown that sensor sensitivity to one particular gas alters with sensor temperature and each gas has its own rate of reducing the sensitivity with a further increase of temperature. It allows us to calculate the concentration of unknown flammable gas. Applying this method decreases measurement error from 30-40% to 5-10% for hydrocarbons.

Approach

As methane catalytic sensors produced by "NTC IGD" Ltd were chosen (Figure below). Sensors represent a platinum coil of cast micro wire with quartz insulation. A core diameter is 10 μm and insulation thickness is 2 μm. A principle of operation of such sensors based on flameless burning (oxidation) of combustible gas on the catalytic active surface and measuring the amount of released heat, which is proportional to the concentration of combustible gas.

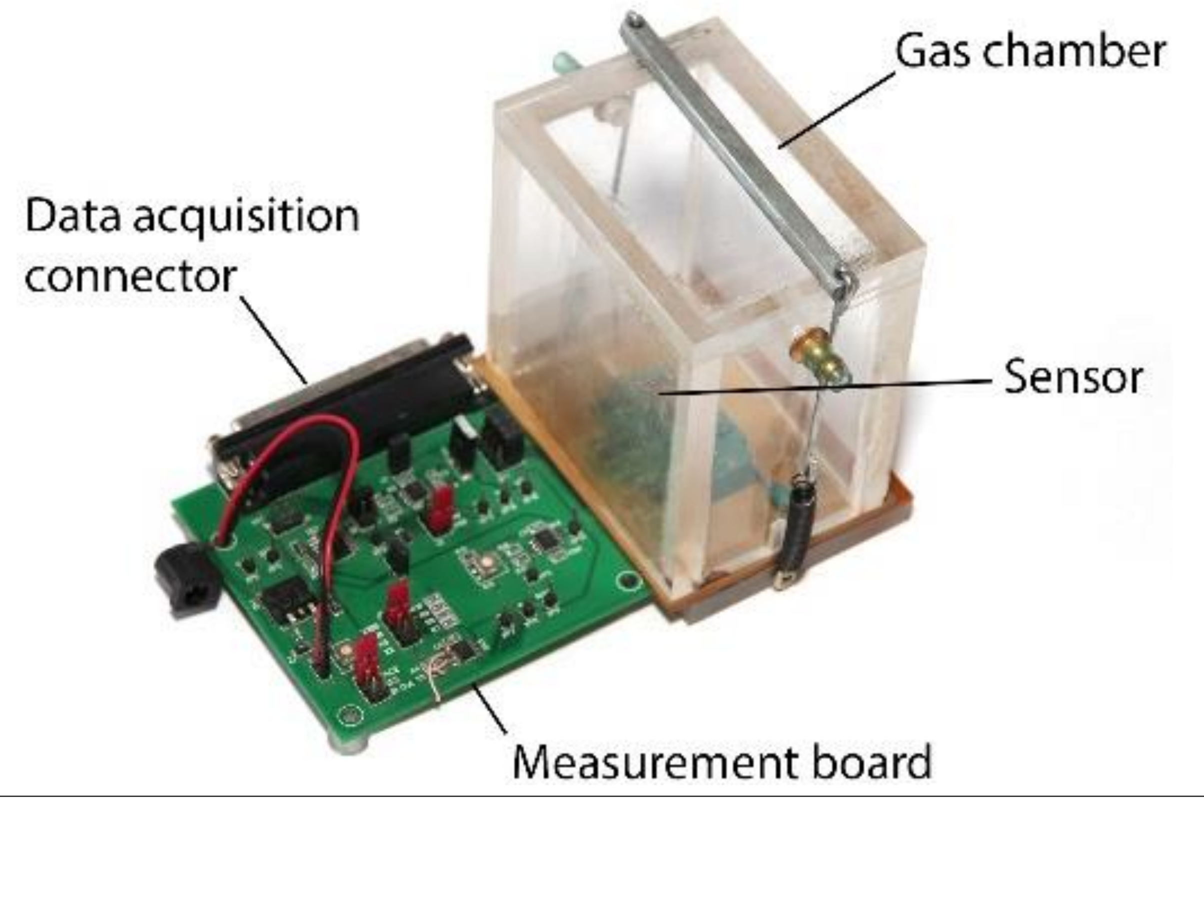
Figure below shows the scheme of test stand. The scheme consists of (1) AduC831 microcontroller with two 12-bit DAC (Digital-to-Analog Convertor) and 8-channel 12-bit ADC (Analog-to-Digital Convertor). DAC is used to set sensor supply voltage. Power supply for sensor is based on (2) an operational amplifier working as a voltage follower. (3) In measuring part, working and compensative sensitive elements are installed in a Wheatstone bridge. (4) Amplifying part is built on the AD8532 working as a differential amplifier. As a data acquisition system there used universal input/output PCI-board L-791 produced by L-card. It has 32 analog input channels with 14-bit ADCs and the sample-rate 400 kHz.



The number of different gas mixtures with air with pre-explosive concentration of flammable gases was used for the experiment. Detailed description of mixtures is presented in the table below.

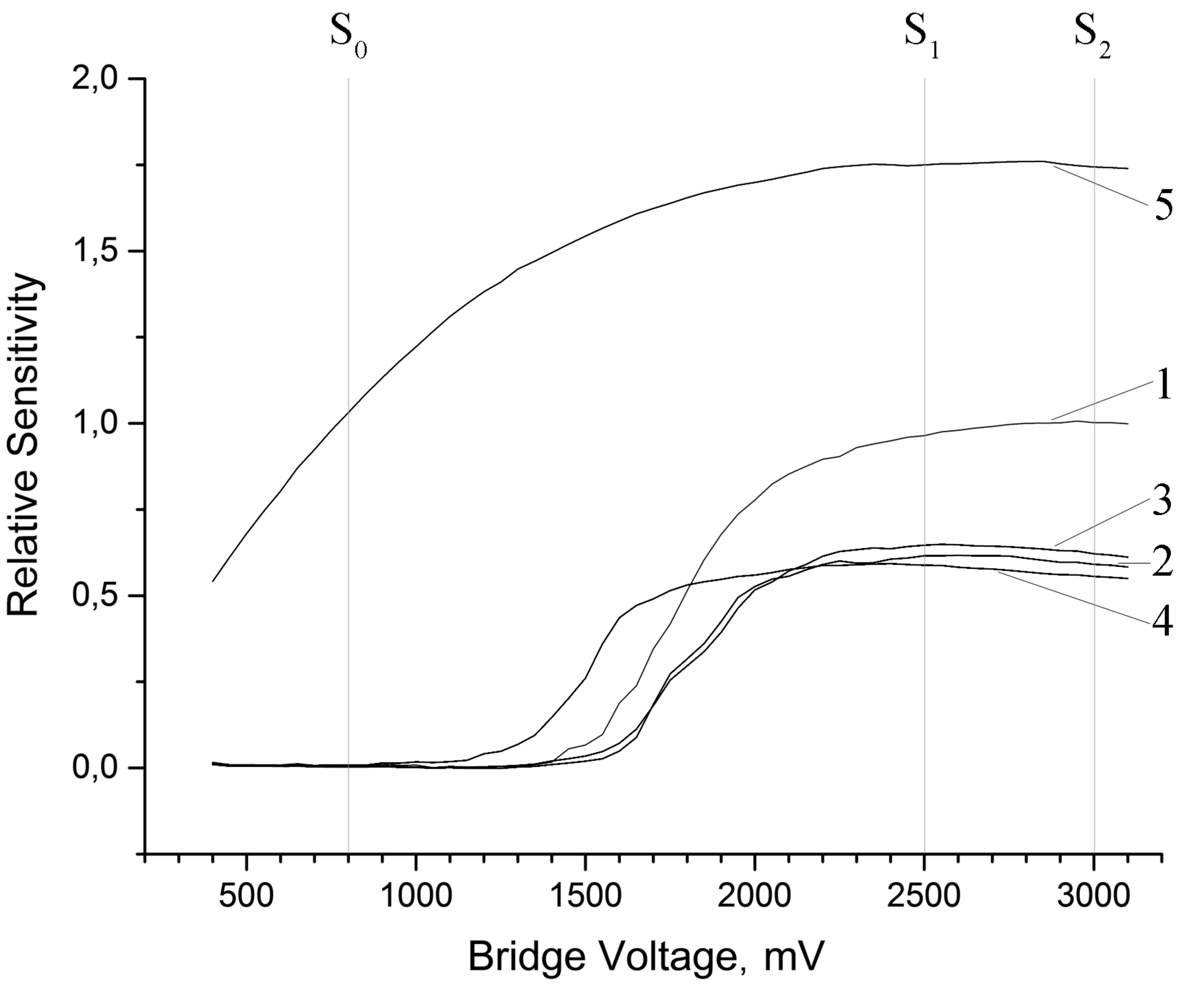
Gas	Concentration, % v/v	LEL, % v/v	Concentration, % LEL
CH_4	1.01 %	4.4 %	23 %
C_3H_8	1.01 %	1.7 %	59 %
C_4H_{10}	0.665 %	1.8 %	37 %
C_6H_{14}	0.485 %	1.24 %	39 %
H_2	0.96 %	4 %	24 %

Testbed



Experimental results

To get sensor response at different temperatures the following method was chosen. After pouring the chamber with the calibration gas mixture the stand was turned on. Bridge supply voltage was varied from 400 mV (200 mV for working element) to 3100 mV (1550 for working element) in increments of 50 mV. Between measures there was a 10 sec pause to complete transients. The output was recorded for 5 sec after the pause and after that average value was written into memory.



Sensor response under various sensor temperatures. 1 – methane, 2 – propane, 3 – butane, 4 – hexane, 5 – hydrogen.

Figure above presents averaged response of the sensors. At the beginning, when temperature is not sufficient for catalytic reactions, sensitivity of the sensor is zero. Then, after reaching the initial temperature of oxidation reaction, the sensitivity increases with sensor temperature. Oxidation in this zone has kinetic character, as a result the sensitivity is non-linear, i.e. it depends on concentration of the analyzed gas. With increasing temperature, the oxidation becomes diffusive, that is all amount of gas able to reach the surface of catalyst is oxidized. In a diffusion zone a section, where sensitivity does not depend on temperature change, is selected. It is the working temperature of sensing element. Further increase of temperature causes fall of sensitivity associated with both the increase of heat transfer (e.g., by radiation) and the properties of particular reaction, the specific properties of the oxidizing gas (e.g. desorption energy of the fuel component from the surface of the active site of the catalyst).

Corrected signal is calculated using empiric formula:

$$S_R = S_M * exp(F*K) / C_S \qquad (1)$$

where F – the coefficient characterizing the rate of sensitivity decrease for a particular sensor, C_S – the correction coefficient to align results of measurement. F, C_S calculates during sensor calibration by exposing them to calibration gas mixtures with air and must be included in MCU or other data processing means.

Gas	#	S_0, mV	S_1, mV	S_2, mV	C_{def}, % LEL	C_{fl}, % LEL	Δ_{def}	Δ_R
	1	46.26	81.80	83.38	49.25	26.15	97.0%	4.6%
H_2	2	39.68	77.34	78.64	39.31	23.62	57.3%	-5.5%
	3	42.52	71.40	68.43	47.55	23.05	90.2%	-7.8%
	1	0.00	41.52	45.03	25.00	25.00	-	-
CH_4	2	0.00	49.18	51.63	25.00	25.00	-	-
	3	0.00	37.54	37.15	25.00	25.00	-	-
	1	0.00	28.15	27.10	16.94	25.20	-32.2%	0.8%
C_3H_8	2	0.00	28.95	28.45	14.72	22.90	-41.1%	-8.4%
	3	0.00	24.19	22.62	16.11	22.27	-35.6%	-10.9%
	1	0.00	30.09	29.88	18.12	24.19	-27.5%	-3.3%
C_4H_{10}	2	0.00	30.59	29.82	15.56	25.59	-37.8%	2.4%
	3	0.00	24.96	22.87	16.62	25.94	-33.5%	3.7%
	1	0.00	29.21	28.86	17.59	23.89	-29.6%	-4.4%
C_6H_{14}	2	0.00	26.98	25.60	13.71	27.32	-45.1%	9.3%
	3	0.00	21.85	19.43	14.55	27.25	-41.8%	9.0%

C_{def} – default measured concentration, C_{fl} – corrected concentration.
Δ_{def} – measurement error for source results, Δ_R – measurement error for corrected results.

Conclusions

A method of correction of measurement results on catalytic sensors working with various flammable gases using correction factor K characterizing the rate of sensitivity decrease during the temperature increase was described.
Suggested measurement algorithm allows aligning of measurement results for different combustible gases. Measurement error decreases from 90% to less than 10% while measuring hydrogen. For hydrocarbons the error decreases from 30-40% to 0-10%.

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