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An algorithm for selective determination of components of C_3H_8-H_2 and H_2-CH_4 gas mixtures in the study of temperature dependence of electrical conductivity of a semiconductor sensor based on SnO_2

© S.A. Kazakov[1], A.A. Dugin[1], T.S. Gagiev[1], M.A. Grevtsev[1], A.V. Sokolov[2], O.A. Arefieva[3], A.Yu. Shishkin[3], V.N. Khvorov[3]

[1] Ioffe Institute,
194021 St. Petersburg, Russia
[2] OOO NIIIT,
123592 Moscow, Russia
[3] AO NPO PRIBOR,
199034 St. Petersburg, Russia
E-mail: kazakov59@mail.ioffe.ru

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This paper proposes an algorithm for processing measurement data of the temperature dependence of electrical conductivity of a SnO_2-based gas sensor in order to determine the concentrations of individual components in C_3H_8-H_2 and H_2-CH_4 mixtures. For this purpose, the sensor was calibrated for hydrogen, methane, and propane using metrologically reliable gas mixtures in dry air; the obtained concentration dependences were used to determine the coefficients of cross-sensitivity of the sensor to a particular component of the gas mixture. Using the well-known independent component method, linear equations were compiled for the studied two-component gas mixtures, the solutions of which satisfactorily describe the sensor signals obtained in the experiments.

Keywords: electrical conductivity, adsorption, gas sensor, semiconductor, selectivity.

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Resistive-type semiconductor gas sensors may respond to a variety of gases and have the potential capacity to detect multi-component gas mixtures. The output data of a working sensor are typically one-dimensional and represent the ratio of conductivities of the test gas and air. Owing to a wide response range of the sensor, identical responses may be produced by multi-component gases mixed in different proportions. It is hard to discern the types and concentrations of components of a multi-component gas mixture if one relies solely on one-dimensional measurement data from a sensor operating at a constant working surface temperature. Temperature modulation provides an opportunity to expand the range of data from the sensor. This method helps obtain new useful data for detection, but still struggles with determining the types and concentrations of gas mixture components [1]. This is attributable to the fact that sensors have a wide range of responses, combining data on several types of gases within the dynamic response curve [2,3]. In other words, the mixing of gas types and concentration data makes it difficult to identify a multi-component gas mixture.

In order to establish the relation between preliminary calibrations of a sensor and its readings in the process of measurement of the specified components of volatile compounds in mixtures with hydrogen, the semiconductor sensor based on SnO_2 was pre-calibrated for detection of methane, hydrogen, and propane against metrologically reliable gas mixtures prepared using PGS cylinders and a „Mikrogaz-FM12" gas mixing unit [4]. This approach allowed us to obtain concentration dependences for a number of detected components and calculate the coefficients of cross-sensitivity of the sensor to a particular component of the gas mixture. Figures 1, *a, b*, and *c* present the preliminary calibration data for hydrogen and the power-law calibration curves for determining the coefficients of cross-sensitivity of the sensor to methane.

The temperature at which cross-sensitivity to another component of the gas mixture is determined corresponds to its temperature maximum of sensitivity to the original component (hydrogen). For example, this temperature for methane as a concomitant component is $\sim 500\,^\circ$C. Figures 2, *a, b*, and *c* present the preliminary calibration data for methane and the power-law calibration curves for determining the coefficients of cross-sensitivity of the sensor to hydrogen.

The obtained data allow us to compile a system of equations for determining the concentrations of trace hydrogen and methane components in a model experiment where a two-component gas mixture of methane and hydrogen in a concentration ratio of 10 : 1 is supplied to the gas-sensitive element. Experimental data obtained in measurements of the temperature dependence of conductivity of the sensor based on SnO_2 are shown in Figure 3. Different concentrations of the gas mixture components were set via exponential dilution.

When applied to gas analysis, the independent component analysis (ICA) model [5] stipulates that the overall conductivity signal from a sensor obtained under simultaneous influence of components of a gas mixture on a semiconductor material is the algebraic sum of the effects of each com-

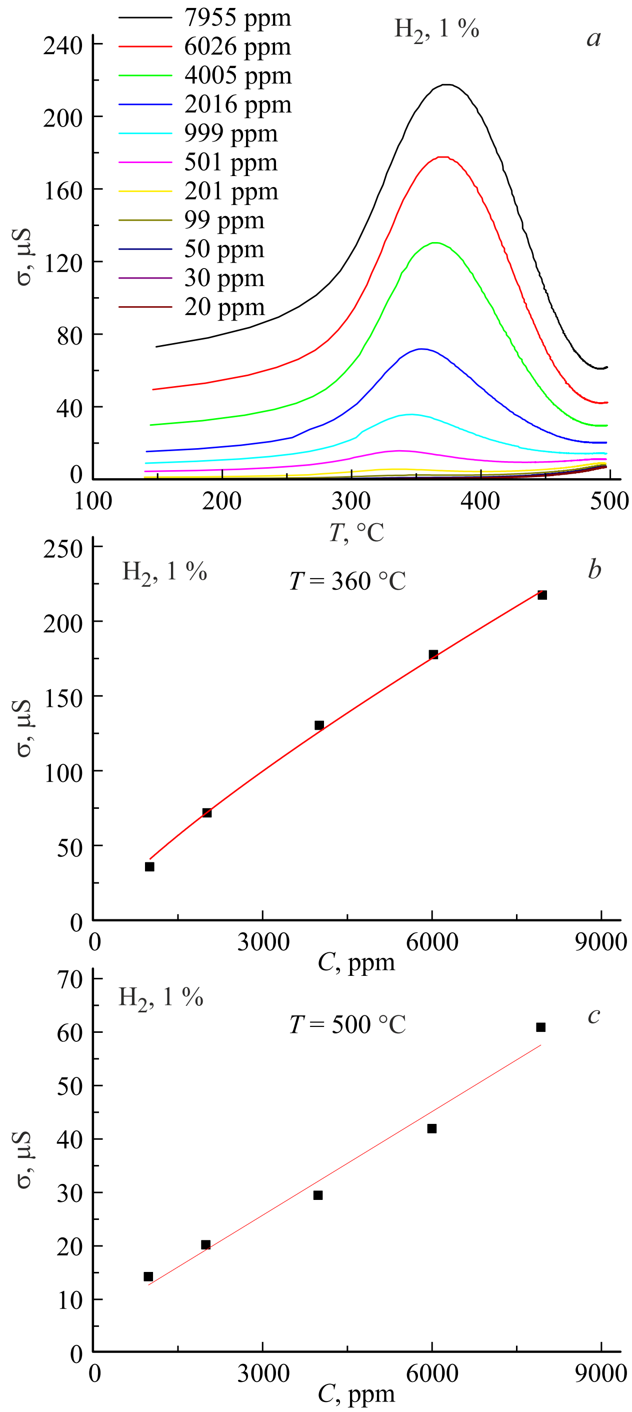

Figure 1. Experimental data on sensor conductivity obtained while hydrogen was supplied (*a*); concentration dependences at temperatures of 360 °C (*b*) and 500 °C (*c*).

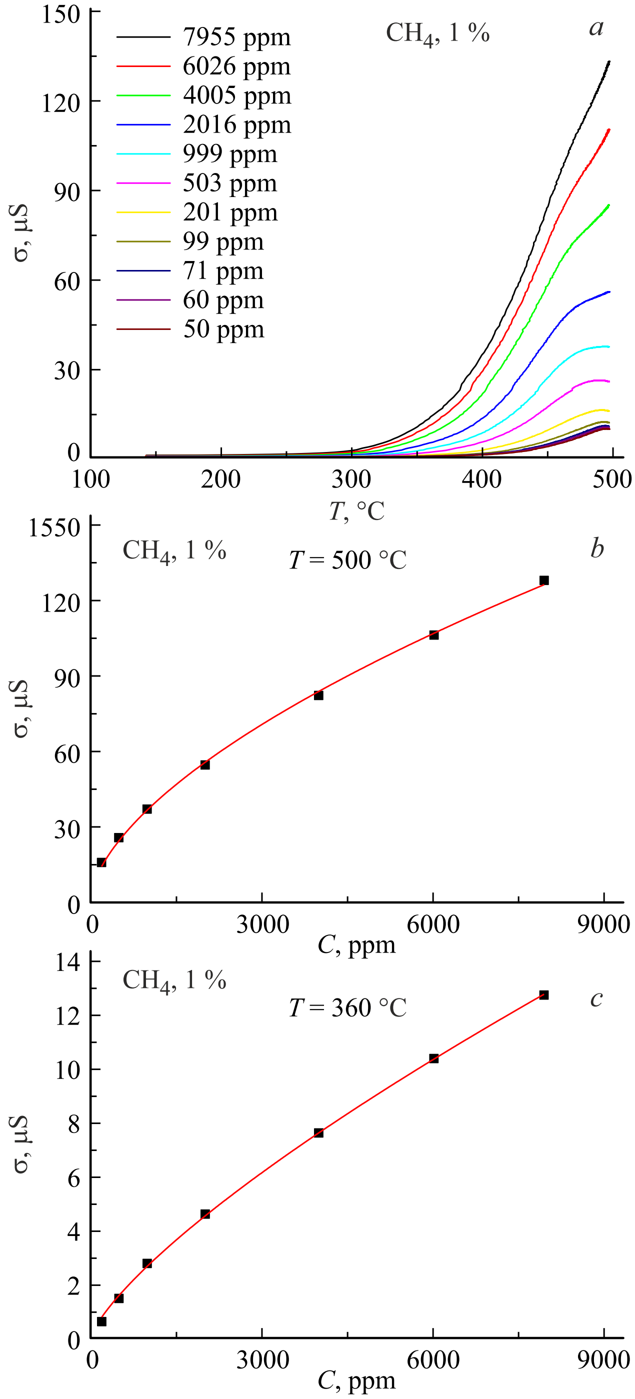

Figure 2. Experimental data on sensor conductivity obtained while methane was supplied (*a*); concentration dependences at temperatures of 500 °C (*b*) and 360 °C (*c*).

ponent on the electronic subsystem of this semiconductor (model of energy-independent chemisorption centers [6]). The general form of system of equations (1) is as follows:

$$\begin{cases} k_{11} \cdot C_1^{n_{11}} + k_{12} \cdot C_2^{n_{12}} = a \cdot s_1 + b \\ k_{21} \cdot C_1^{n_{21}} + k_{22} \cdot C_2^{n_{22}} = f \cdot s_2 + d \end{cases}, \tag{1}$$

Table 1. Numerical values of coefficients of the system of equations

System H_2/CH_4					
k_{11}	0.14803	n_{11}	0.81336	a	0.5217
k_{12}	0.01517	n_{12}	0.74984	b	7.0155
k_{21}	0.2444	n_{21}	0.5849	f	0.9352
k_{22}	0.5861	n_{22}	0.59844	d	8.8508
System C_3H_8/H_2					
k_{11}	0.60865	n_{11}	0.59794	a	0.7211
k_{12}	0.3499	n_{12}	0.6566	b	−13.757
k_{21}	0.2345	n_{21}	0.6701	f	0.5553
k_{22}	0.83154	n_{22}	0.62414	d	−2.2458

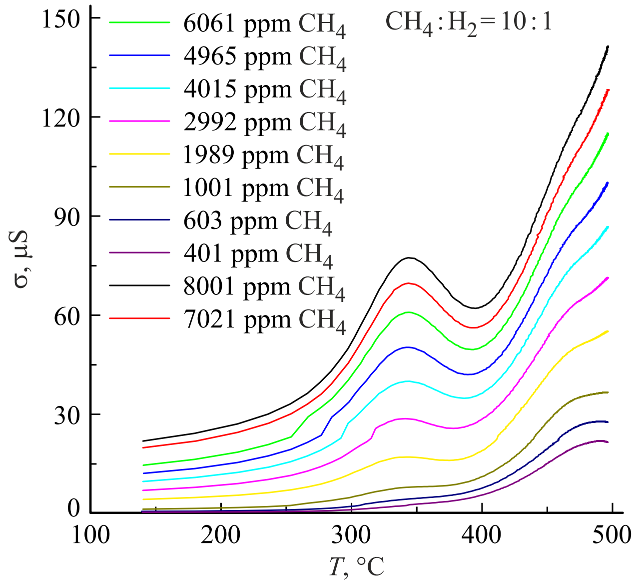

Figure 3. Experimental data on temperature variation of conductivity of the sensor based on SnO_2 that were obtained while the methane–hydrogen mixture was supplied.

where $k_{11} \cdot C_1^{n_{11}}$ and $k_{22} \cdot C_2^{n_{22}}$ are the concentration dependences of sensor conductivity for hydrogen at a sensor temperature of 360 °C and for methane at a temperature of 500 °C, respectively; $k_{12} \cdot C_2^{n_{12}}$ is the cross-sensitivity of the sensor to methane at a temperature of 360 °C; $k_{21} \cdot C_1^{n_{21}}$ is

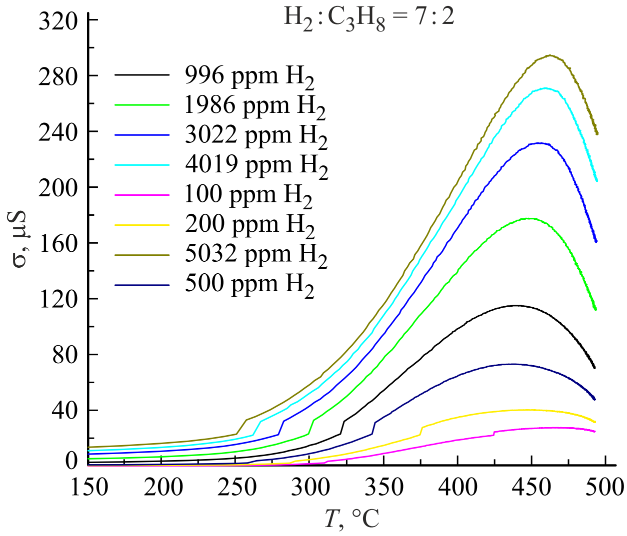

Figure 4. Experimental data on temperature variation of conductivity of the sensor based on SnO_2 that were obtained while the hydrogen–propane mixture was supplied.

the cross-sensitivity of the sensor to hydrogen at a methane temperature of 500 °C; s_1 is the sensor signal magnitude at the optimal hydrogen detection temperature of 360 °C; s_2 is the sensor signal magnitude at the optimal methane detection temperature of 500 °C; and a, b, f, d are the correction factors determined on verifying the calibration against gas mixtures. The numerical values of coefficients of this system are listed in Table 1.

The results of calculations performed for the presented model concentration range of the two-component gas mixture of methane and hydrogen agreed with the experimental data; the error in determination of individual components did not exceed 5 %. The results are listed in Table 2.

Figure 4 presents the experimental data on temperature variation of conductivity of the sensor based on SnO_2 that were obtained while the two-component mixture of hydrogen and propane in a concentration ratio of 7 : 2 was supplied.

A comparison of calculated and experimental data revealed that the error in determining the concentrations of hydrogen and propane did not exceed 20 %. The results are presented in Table 3.

Table 2. Comparison of experimental and calculated data for the methane–hydrogen mixture

Experiment		Calculation		Error, %	
$C(CH_4)$, ppm	$C(H_2)$, ppm	$C(CH_4)$, ppm	$C(H_2)$, ppm	CH_4	H_2
8001	800	8249	772	3.1	3.5
7021	702	6976	691	0.6	1.6
6061	606	5844	594	3.6	2
4965	497	4726	497	4.8	0.1
4015	402	3813	402	5.0	0.03

Table 3. Comparison of experimental and calculated data for the hydrogen–propane mixture

Experiment		Calculation		Error, %	
$C(H_2)$, ppm	$C(C_3H_8)$, ppm	$C(H_2)$, ppm	(C_3H_8), ppm	H_2	C_3H_8
5032	1438	4581	1420	9	1.3
4019	1148	4053	1225	0.8	6.7
3022	863	3291	896	8.9	3.8
1986	567	2238	514	12.7	9.3
996	285	806	301	19.1	5.6

The obtained results demonstrate that the proposed algorithm allows for selective determination of atmospheric air components by solving a linear system. One necessary condition for this is a significant difference in the optimal detection temperatures of individual components of the mixture. This may be achieved by producing gas-sensitive materials of various compositions [7].

Conflict of interest

The authors declare that they have no conflict of interest.

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