Investigation of the Temperature Effect on the Sensitivity of Thermal Conductivity Detector

Vladimir I. Platonov
Chemistry Department, Samara University, Samara, Russia
Email: rovvv@yandex.ru

Dmitry A. Uglanov, Sofia S. Dostovalova, and Sergei V. Zaika
Heat engineering and heat engines Department, Samara University, Samara, Russia
Email: dmitry.uglanov@mail.ru, {sophiadost, xak-s}@mail.ru

Abstract—**Thermal conductivity detector for use in gas dynamic express-analyzers and high-speed chromatography systems is being developed by chemistry department in cooperation with other Samara University departments. This article is devoted to investigating the effect of temperature on detector sensitivity. Silicon underlying with resistive chromium layer was used as a sensitive element of the detector. The temperature dependence of the sensitive element resistance was defined for different chromium film thicknesses. The film thickness which provides the highest sensitivity of the detector was found. Also optimal output channels configuration in the gas chromatograph detector was determined. It provides uniform temperature fields distribution at constant gas-flow rate.**

Index Terms—**thermal conductivity detector, sensitive element, element resistance, film thickness, output channels configuration, temperature distribution**

I. Introduction

Gas chromatography is a method of separation and physicochemical analysis of substances based on substances movement along the sorbent layer in the mobile phase flow. Because of different degree of substance solubility, some components are retained in the stationary phase and some pass through the chromatograph column. Then substances are registered by the detector.

One of the major trends in chromatography is that capillary columns are becoming more and more widely used at present, since analysis time could be considerably reduced. Capillary chromatography requires high sensitivity and speed of response, and also a small volume of measuring chamber of detector [1].

Another trend in modern instrument making is miniaturization. Small dimensions and weight of analytical devices and rapidity of analysis make on-site testing with gaining results in real time possible. It is a great advantage of microdevices as it allows to reduce the probability of the sample change during its storage and transportation. Saving of time and cost of sample conservation and transportation is another benefit [2].

Manuscript received March 2, 2017; revised June 13, 2017.

Detector is an important chromatograph element that is needed for measuring the concentration of substances. The operating principle is based on dependence of materials resistance from temperature change. With the change in gas flow thermal conductivity, such as when organic molecules displace some of the carrier gas, quantity of heat is removed from sensitive element increases. It leads to a temperature change, and hence the electrical resistance of the sensitive element. A signal in the form of a potential difference (voltage) appears in the circuitry. The signal is proportional to the concentration of an analyte in a carrier gas [3].

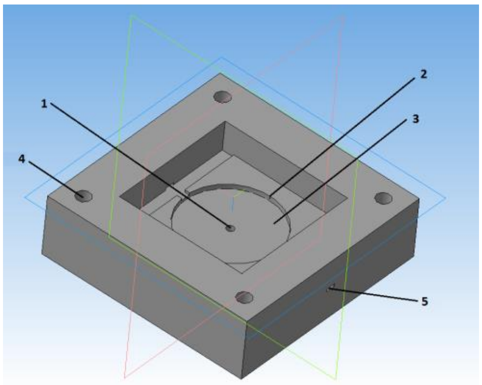

Figure 1. Detector construction: 1 – inlet, 2 – outlet, 3 – working chamber, 4 – fixing hole.

Out of more than forty different types of detectors in gas chromatography thermal conductivity detector is the most widely used detection system in general gas analysis and in environmental testing due to it simplicity and robustness. Also, this detector is not as sensitive such as the flame ionization detector. However, unlike flame ionization detector, thermal conductivity detector has nondestructive character of substance analysis [4]. Moreover, the thermal conductivity detector is uniquely suited for miniaturization, since it is sensitive to the concentrations of substances in the mixture, not the total mass of a sample [5]. Thermal conductivity detector is being developed at Samara University (Fig. 1). For better sensitivity influence of temperature, pressure and other chromatographic process parameters should be

doi: 10.18178/ijmerr.6.4.305-308

eliminated. If it's impossible, these parameters should be constant during all analysis process. Sensitivity of detector is several times higher in the constant temperature mode [6].

II. THE RESISTANCE-TEMPERATURE DEPENDENCE OF THE SENSITIVE ELEMENT

Silicon underlying with resistive chromium layer was used as a sensitive element of the detector (Fig. 2). Chromium layer was deposited by magnetron deposition method. Then copper contacts were formed on the resistor surface.

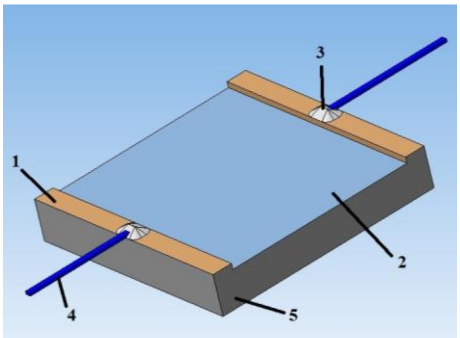

Figure 2. Three-dimensional model of the detector sensitive element: 1 – copper contacts; 2 – chromium layer ; 3 – solder; 4 – contact wire; 5 – silicon underlying.

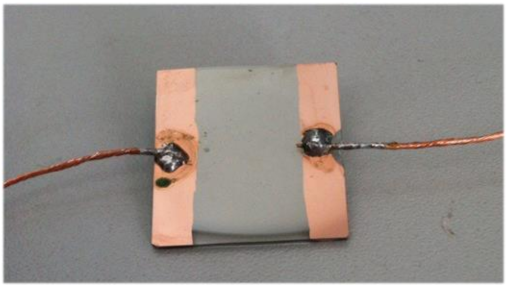

Figure 3. Photo of the sensitive element.

The temperature dependence of the sensitive elements resistance was defined for different chromium film thicknesses (Fig. 3). It was found that the film thickness of 20 nm provides the highest sensitivity of the detector, since it ensures greater resistance change at the temperature changes by 1 degree (Fig. 4).

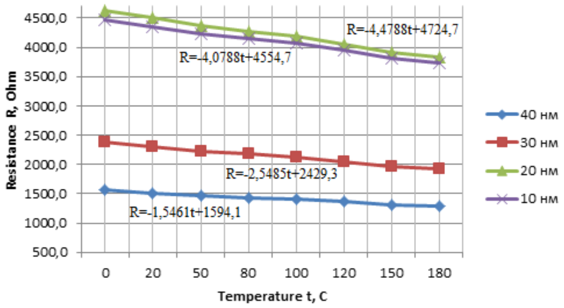

Figure 4. The temperature dependence of the film resistors resistance for chromium layer thicknesses 10, 20, 30, 40 nm.

Another factor affecting the results of the chromatographic analysis is temperature fields distribution in the gas chromatograph detector. Output channels configuration in the gas chromatograph detector should provide uniform temperature fields distribution at constant gas-flow rate [7].

III. OUTPUT CHANNELS CONFIGURATION IN THE GAS CHROMATOGRAPH DETECTOR

The purpose of research is temperature fields computation in the gas chromatograph detector at using a mixture of air and hydrogen (Cv_H2=10%, 90%) for different output channels configuration at constant gas-flow rate F=100 ml / min.

According to the requirements of the carrier gas for thermal conductivity detector, the thermal conductivity coefficient of the carrier gas must be much larger than that of the sample. The thermal conductivity coefficient of H2 and helium are all relatively large, but H2 as a carrier gas is more economical and widely used [5].

A plate (20x20 mm) covered with a layer of chromium (thickness up to 100 nm) is attached to detector. Electricity (I=2 ma; U= 10 V). Heat flow through a plate q=50 W/m2. Inlet pressure – 110 kPa. Outlet Pressure – 100kPa.

The thermophysical properties of air-hydrogen mixtures (Cv_H2=10, 90%) were determined (Table I).

TABLE I. THE THERMOPHYSICAL PROPERTIES OF AIR-HYDROGEN MIXTURES (CV_H2=10, 90%)

Mixture parameter	Unit of measure	C_{v_H2} = 10%; C_{v_air} = 90%	C_{v_H2} = 90%; C_{v_air} = 10%
density	kg/m^3	1,135	0,206
heat capacity	J/kg K	1142,98	6213,17
flow rate	kg/s	$1{,}895\ 10^{-6}$	$0{,}344\ 10^{-6}$
viscosity	kg/m s	$1{,}7894\ 10^{-5}$	$8{,}96\ 10^{-6}$
heat-conductivity coefficient	W/m K	0,0242	0,0172

Three-dimensional models of the gas duct for configuration with two and four output gas channels were built in SolidWorks (Fig. 5-Fig.6) [8], [9].

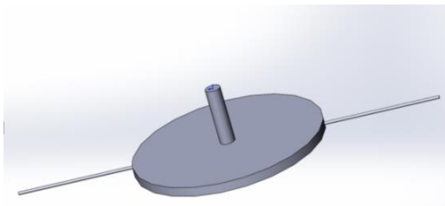

Figure 5. Three-dimensional model of the gas duct with two output gas channels.

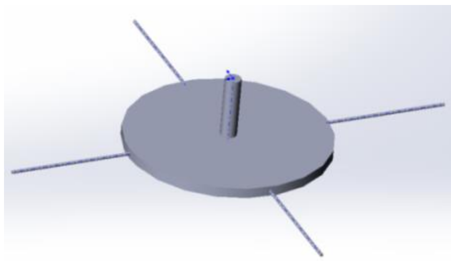

Figure 6. Three-dimensional model of the gas duct with four output gas channels.

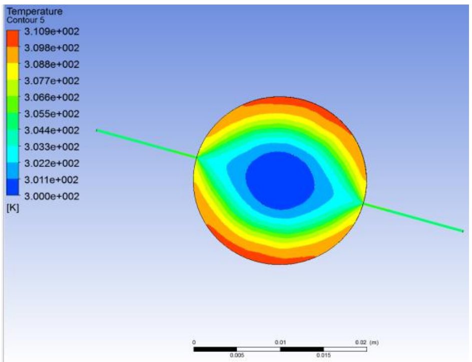

Figure 7. Temperature fields for configuration with two output channels (Cv_H2=10%).

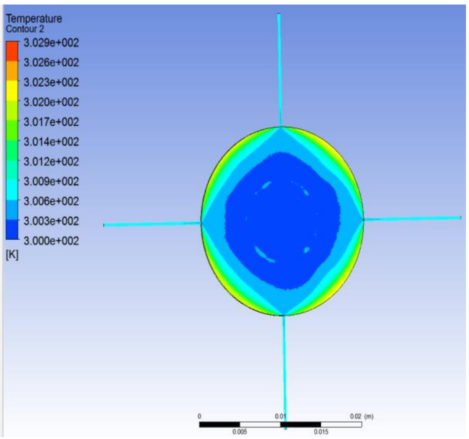

Figure 8. Temperature fields for configuration with four output channels (Cv_H2=10%).

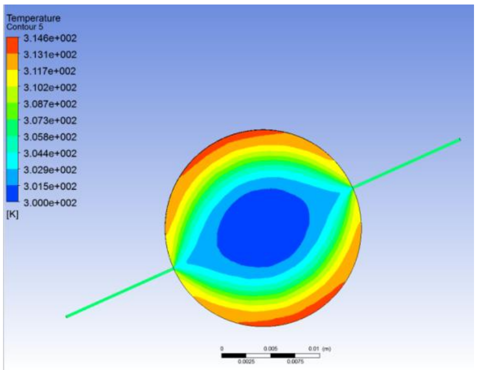

Figure 9. Temperature fields for configuration with two output channels (Cv_H2=90%).

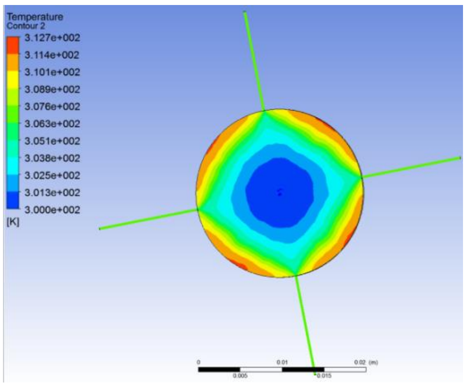

Figure 10. Temperature fields for configuration with four output channels (Cv_H2=90%).

Then the finite-element mesh was imposed using ANSYS Meshing. Mesh element size is 0,65 µm, amount of elements in model is 10,7 million.

Temperature fields calculation was made by means of ANSYS for different output channels configuration and mixtures (Fig. 7-Fig.10) [9].

Table II shows ranges of temperature for different mixtures and output channel configurations.

TABLE II. TABLE OF TEMPERATURE RANGES

Mixture	T, K	Configuration	
		2 output channels	4 output channels
C_{v_H2} = 10%; C_{v_air} = 90%	Tmin	300	300
	Tmax	310,9	302,9
C_{v_H2} = 90%; C_{v_air} = 10%	Tmin	300	300
	Tmax	314,6	312,7

Optimization parameter allows to compare different configurations of output channels (Table III).

TABLE III. TABLE OF OPTIMIZATION PARAMETER VALUES

Mixture	Optimization parameter	Configuration	
		2 output channels	4 output channels
C_{v_H2} = 10%; C_{v_air} = 90%	$\frac{T_{max}}{T_{min}}$	1,0363	1,0096
C_{v_H2} = 90%; C_{v_air} = 10%	$\frac{T_{max}}{T_{min}}$	1,0486	1,0423

IV. CONCLUSIONS

1. The highest sensitivity of the detector is provided by film thickness of 20 nm.

2. More uniform temperature distribution detector is provided by configuration with four output channels. It also allows to reduce the maximum temperature in the detector which is important to provide the sensitivity of the device.

The next stage of the research will be prototyping gas chromatograph detectors with different configurations of the output channels and carrying out the experiment.

ACKNOWLEDGMENT

This work was supported by the Ministry of Education and Science of the Russian Federation in the framework of the implementation of the Program ‘‘Research and development on priority directions of scientific-technological complex of Russia for 2014– 2020.

REFERENCES

[1] I. A. Platonov, P. K. Lange, I. N. Kolesnichenko, and V. I. Platonov, “The dynamic characteristics of a thermal conductivity microdetector for gas analyzers,” *Measurement Techniques*, vol. 58, no. 6, pp. 724-728, 2015.

[2] I. Platonov, V. Platonov, M. Gorunov, and E. Novikova, “Planar microchromatographic systems for the rapid analisis of gas mixtures,” in *Proc. 30th International Symposium on Chromatography*, Salzburg, Austria, 2014, p. 2.

[3] D. Cruz, J. P. Chang, S. K. Showalter, *et al*., "Microfabricated thermal conductivity detector for the micro chemLab," *Sensors and Actuators B*, vol. 121, pp. 414–422, 2007.

[4] K. Chen and Y. E. Wu, "Thermal analysis and simulation of the microchannel flow in miniature thermal conductivity detectors," *Sensors and Actuators A*, vol. 79, pp. 211–218, 2000.

[5] J. Sun, D. Cui, X. Chen, L. Zhang, H. Cai, and H. Li, "Design, modeling, microfabrication and characterization of novel micro thermal conductivity detector," *Sensors and Actuators B: Chemical*, vol. 160, no. 1, pp. 936-941, December 2011.

[6] I. A. Platonov, Y. I. Arutyunov, and P. K. Lange, "Quick-response thermal conductivity detector for gas chromatography," *Information-Measuring and Control Systems*, vol. 1, no. 8, pp. 97-102, 2013.

[7] V. V. Biryuk, A. B. Tsapkova, and A. A. Shimanov, "Numerical modeling of cyclone machine for cleaning gas generator gases," *Key Engineering Materials*, vol. 685, pp. 153-157, 2016.

[8] S. O. Nekrasova, D. A. Uglanov, and A. A. Shimanov, "Comparative analysis of calculation models of pulse tube thermoacoustic refrigerator," in *Proc. 4th International Conference for Young Scientists High Technology: Research and Applications*, Trans Tech Publications Ltd, 2016, pp. 3-7.

[9] S. O. Nekrasova, E. A. Zinovyev, and A. I. Dovgyallo, "Numerical investigation on a 70 Hz pulse tube micro-cryocooler, international conference on oil and gas engineering," *Procedia Engineering*, vol. 152, pp. 314-320, 2016.

Dr. Vladimir I. Platonov is an Associate Professor in the Chemistry Department, Samara National Research University named after Academician S. P. Korolev (Samara University), Russia, and conducts research in the areas of gas and liquid chromatography and chemistry. Associate Professor Platonov received Ph.D. at Samara University, Russia in 2013. From 2013 till now he is a senior researcher in the Chemistry Department. He has published more than 20 journal paper in his research fields.

Dr. Dmitry A. Uglanov is an Associate Professor in the Department of Heat Engineering and Heat Engines, Samara National Research University named after Academician S.P. Korolev (Samara University), Russia, and conducts research in the areas of cryogenics, cold-energy systems, cooling systems and energy-saving problems of LNG using. Associate Professor Uglanov graduated as an engineer for laser systems and received Ph.D. at Samara University, Russia in 2003 and 2006, served as assistant of the Heat Engineering and Heat Engines till 2009. From 2009 till now he is Associate Professor in the Department of Heat Engineering and Heat Engines. He is also a Vice-Dean of Institute of Engine and Power Plant Engineering and Member-Correspondent of International Academy of Refrigeration. He has published more than 60 journal paper in his research fields.

Sofia S. Dostovalova is a PhD-student in the Department of Heat Engineering and Heat Engines, Samara National Research University named after Academician S. P. Korolev (Samara University), Russia, and conducts research in the area of heat-and-mass transfer. PhD-student Sofia Dostovalova graduated as an engineer at Samara University, Russia in 2014. From 2014 till now she is a junior researcher in the Department of Heat Engineering and Heat Engines. She has published more than 15 journal papers in her research field.

Sergey S. Zaika is a PhD-student in the Department of Heat Engineering and Heat Engines, Samara National Research University named after Academician S. P. Korolev (Samara University), Russia, and conducts research in theareas of cryogenics and cooling systems. PhD-student Sergey Zaika graduated as an engineer for aviation engines at Samara University, Russia in 2015. From 2015 till now he is PhD student in the Department of Heat Engineering and Heat Engines. He is also a assistant dean of Institute of Engine and Power Plant Engineering. He has published more than 15 journal papers in his research fields.