Identification of organic compounds using a multisensor detector based on SnO$_2$ films in gas chromatography

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Abstract. The possibilities of using a semiconductor multisensor device as a detector for gas chromatography are considered. Semiconductor films of various compositions were investigated for their performance as sensors, the optimal composition for inertia and sensitivity was established. The basic parameters of the detector were determined: sensitivity, linear dynamic range, detection limit. The applicability of the detector for solving typical problems of capillary gas chromatography is shown. Two methods for the identification of organic compounds using a detector based on three sensors have been proposed.

1. Introduction

The use of tin dioxide film sensors for analyzing various compounds in gaseous media began in the mid-1960s [1]. Currently, they are among the most common types of gas sensors [2]. The principle of their operation is based on the increase in the electrical conductivity of the film when the gaseous substance contacts the surface of the sensor. This effect is the result of several processes, among which the most important are gas adsorption and its effect on the surface Fermi levels of a semiconductor film. With increasing temperature, oxidation of volatile substances begins with sorption. This leads to the generation of new charge carriers in the surface layer of the film and opens up possibilities to the detection of organic compounds. Since the mid-1970s there studies in which sensors of this type are connected with simple gas chromatography [3]. It turned out that this type of sensor has a higher inertia compared to typical gas chromatography detectors (flame ionization, thermal conductivity detector). In addition to this drawback, there is the problem of the correct interpretation of the analytical signal of an individual sensor and the choice of its processing algorithm. This is necessary to create a universal and effective approach to the identification of organic compounds using this type of detector. An important task is the selection of such additives to tin dioxide and such film formation methods that would provide a set of selective, stably operating and low-inertia film sensors suitable for the analysis of multicomponent organic mixtures [4].

Proposed in [5, 6], a thermocatalytic detector based on tin dioxide with additions of transition metals can be used to perform typical analyzes in gas chromatography using both packed and capillary columns. As an illustration, Figure 1 shows the peak of hexane on two film sensors of different composition. The sensor signals differ in height and width, which can be explained by the different intensity of charge carrier generation processes and the difference in sorption / desorption times of organic compounds. Such a difference in the signals can be used to identify the components of the analyzed mixture.
Figure 1. Analytical signal of 1 ml of saturated vapor of hexane on a pair of sensors (SnO₂-ZnO and SnO₂-Gd₂O₃)

2. Experimental part

SnO₂ films were deposited by pyrolytic decomposition. The glass tubes, with diameter of 2mm, were used as the substrate. Solutions for application were prepared by dissolving tin (IV) chloride in ethanol followed by the addition of nitrates of doping metals (Cu, Zn, Ni, Ag, Gd, Ce). The mass concentration of tin in the solution was 1% by weight. The ratio of tin to metal was 100:3. The process of film deposition occurred in two stages. In the first stage, the substrate was wetted with a solution and ethanol was evaporated at 120 °C for 5 minutes. After that the substrate was calcined in a muffle furnace at a temperature of 720 °C for 5 minutes and cooled to room temperature. The deposition process was repeated 3-5 times since, with a smaller number of depositions, the conductivity of the film remained too low for use as a sensor. In some cases, to improve the properties of the sensor, doping was carried out simultaneously with two oxides (MeₓOᵧ + Ag₂O), the amount of silver used was 10% of the amount of Me [7]. After the films were deposited, silver-coated steel wire was attached to opposite sides of the substrate and the film was incorporated into a measuring circuit.

Sensors (3 pieces) were placed in a quartz tube located in the heater. The output of the chromatographic column is connected to the bottom of the tube through a side entrance made of air flow (50 ml / min.). Oxygen is necessary for the rapid restoration of the working surface of the sensor, it also acts as a make-up gas. The temperature of the thermostat during the experiments was equal to 450 °C, which ensured optimal selectivity and response of the sensors. The detector circuit is shown in Figure 2. The system was mounted on an Agilent serial gas chromatograph.

The measuring circuit of the detector is shown in Figure 3. It consists of a variable resistance, a sensor and a DC source with a voltage of 4.5V. All elements are connected in a series electric circuit. The magnitude of the voltage drop across the variable resistance was used as a signal, which was recorded using an ADC with a frequency of 10 Hz.
Chromatogram processing was carried out in several main stages. At first, the chromatogram was manually labeled using a program written in C#. The primary dependence of the voltage drop on time was converted into the relative electrical conductivity of the sensor according to the formulae:

$$\frac{R}{R_0} = \frac{E}{U_0 - 1}/\left(\frac{E}{U_{\text{max}}} - 1\right)$$

where $E$, $U_0$ and $U_{\text{max}}$ - the EMF of the power source, the recorded voltage at the peak base and at the maximum of the peak, respectively. An example of conversion is shown in Figure 4.

After recalculation, the main parameters (height and width at half height) were extracted from the chromatogram for each peak. The text of the program is written in the programming language Python.
3.7.1. The coordinate of the intersection point between half-width and peak was determined by interpolation at two adjacent points. Since the electrical conductivity of the sensor in the absence of the signal was minimal, $y_{\text{min}}$ was taken as 1.

3. Results and discussion

Mixed alcohols and n-alkanes C$_9$-C$_{14}$, as well as solutions of essential oils, were studied as objects. Figure 5 shows an example of a chromatogram of fir essential oil in hexane, obtained on a SnO$_2$-Gd$_2$O$_3$ film sensor. As previously mentioned, the sensors have different responses, namely the heights and widths of the peaks.

![Chromatogram of fir essential oil in hexane.](image)

Figure 5. Chromatogram of fir essential oil in hexane.  
1 - $\alpha$-pinene, 2 - camphene, 3 - $\beta$-fellandrene, 4 - $\gamma$-terpene, 5 - limonene, 6 - bornyl acetate

The choice of the optimal composition of the films was made according to their sensitivity and inertia. For this, the sensors were calibrated for three substances (ethanol, hexane, acetone). The detection limit was calculated as a triple noise value multiplied by the sensitivity of the sensor. Linear dynamic range (LDR) was determined graphically from calibration curves. Films with the addition of ZnO, CuO, NiO turned out to be the most sensitive. It was also found that the addition of Ag$_2$O as the second dopant improves the inertial properties of the SnO$_2$-CuO and SnO$_2$-NiO films. The measurement results are presented in Table 1. It may be noted that, in terms of the LDR, film detector is similar to an electron capture, but at the moment gives way to serial detector sensitivity. Insufficient sensitivity can be corrected by the signal amplifier, but even in this form, the system is applicable for quantitative analysis.

| Sensor   | Sensitivity, conventional units of area / mg | Detection limit, g | Linear range |
|----------|---------------------------------------------|--------------------|--------------|
| Sn-Zn    | 512                                         | $1,7 \cdot 10^{-5}$ | $10^2$       |
| Sn-Cu(Ag)| 335                                         | $0,5 \cdot 10^{-5}$ | $10^2$       |
| Sn-Ni(Ag)| 423                                         | $0,4 \cdot 10^{-5}$ | $10^2$       |
To identify compounds in the mixture, it was proposed to use the difference in peak heights and their half widths, as well as additional chromatographic information in the form of retention indices. In order to eliminate the influence of the amount of substance and the velocity of the carrier gas on the identification features, we did not use the heights and half widths themselves, but their relations for two different sensors. As it turned out, within the linearity domain, the ratio of heights remains constant. Similarly, when the carrier gas speed changes, the ratio of half widths of peaks remains constant. Thus, if there are three sensors, we can calculate two independent height ratios and two independent half-width ratios. Considering the various combinations of such relationships, we sought to select such variants in which the entire set of the studied substances differs in the best way. In other words, the image of the figurative points of the compounds in the coordinates of the corresponding set should be as far as possible from each other, not depend on the quantities taken, and demonstrate a logical change in the homologous series.

In total, 5 different dependencies were investigated as potentially interesting variants: $H_1/H_3 - H_2/H_3$, $H_1/H_3$ - Retention index, $W_1/W_3 - W_2/W_3$, $H_1/H_3 - W_1/W_3$, where $H_n$ and $W_n$ are the height and half width of the signal of the $n$-th detector. As a result, it was found that the dependencies $W_1/W_3 - W_2/W_3$ and $H_1/W_1 - H_2/W_2$ do not allow the identification of substances due to the imposition of the figurative points of different classes of organic substances. The dependences of $H_1/H_3 - H_2/H_3$ and $H_1/H_3$ - Retention index (Fig. 6) showed themselves in the best way. As you can see, the identification signs of each substance are grouped in certain areas on the plane, and with increase in the molecular weight of alcohols, the figurative points of the compounds are gradually removed from the origin.

![Image](image1.png)

**Figure 6.** Figurative points of alcohols on the signal relationship plane.

![Image](image2.png)

**Figure 7.** Figurative points of alcohols in the three-dimensional coordinate system.

The accuracy of identification can be significantly increased if retention indexes are used as the third parameter (Fig. 7). This technique is quite common in gas chromatography.

### 4. Conclusions

Thus, on the basis of the proposed data, we can draw a conclusion about the applicability of multisensor systems for solving typical problems of capillary gas chromatography. Its main advantage is the ability to identify compounds in mixtures. The proposed approach allows for the most qualitative separation of the figurative points of various compounds. However, the current design of the detector is not sensitive enough, which can be corrected through rational selection of the film composition, as well as the use of amplifying circuits.
References

[1] Seyama T, Kato A, Fujishi K and Nagatani M 1962 Anal. Chem. 34 1502
[2] Barsan N, Koziej D and Weimar U 2007 Sens. Actuators B 121 18–35
[3] Beling S, Bläser G, Bock J, Heinert L, Traxler M and Kohl D. 1998 Sens. Actuat. B. 52 15
[4] Eranna G, Joshi B C, Runthala D P and Gupta R P 2004 Solid State Mater. Sci. 29 111–188
[5] Povarov V G and Lopatnikov A I 2016 Journal of Analytical Chemistry 71 901-906
[6] Povarov V G, Lopatnikov A I, Geib D S, Bulatova A V and Razgonyaev A O 2013 Journal of Analytical Chemistry 68 300-304
[7] Madler L, Roessler A, Pratsinis S E, Sahm T, Gurlo A, Barsan N and Weimar U 2006 Sens. Actuators B 114 283–295