Calibration algorithm for semiconductor gas sensors and determination of volatile hydrocarbon concentrations in atmospheric air using Fourier transforms

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Abstract. A calibration algorithm and an algorithm for measuring the concentrations of volatile hydrocarbons in atmospheric air using Fourier transforms for semiconductor gas sensors have been developed. This work presents experimental data on sensor calibrations obtained on certified equipment using gasoline, solvent vapor, toluene, and methane as an example. The calibration carried out by recording measurements of the electrical conductivity of the gas-sensitive layer of the sensor over time, both during heating and cooling samples of sensors based on samarium sulfides and other composite materials. The method of semiconductor gas Fourier spectroscopy that we are developing, the construction principles of which are described in recent publications, is based on the relationship of the obtained calibration characteristics of the sensors of volatile hydrocarbons concentration contained in atmospheric air, with the electrophysical characteristics of samarium sulfide based rare earth semiconductors used as gas sensitive layers.

1. Introduction
A new calibration algorithm and a measurement algorithm for semiconductor gas analysis are proposed in the present work. This allows to unambiguously solve the problem of selectivity of a gas sensor when it is operated in a rather complex multicomponent gas mixture of volatile hydrocarbons contained in atmospheric air [1,2]. The previously proposed method for constructing semiconductor Fourier spectroscopy of gas analysis is based on a modification of the optical methods of Fourier spectroscopy [3,4] and allows one to obtain the spectral characteristic of the sensor from the total change in its electrical conductivity over time when the sensor temperature in the analyzed or calibration gas medium is increased (decreased). The use of Fourier transforms for non-periodic functions makes it possible to extract the amplitude-frequency spectrum of the concentration effect on the semiconductor conductivity of a particular component of the gas mixture from the useful detector signal. The frequency characteristic of the Fourier transform determines the selectivity of the detector, and the absence of a frequency shift is responsible for the stability of its operation. In this case, the amplitude of the selected frequency is responsible for the concentration effect of one or another measured component of the gas mixture.
2. Calibration and processing of experimental data

The paper describes a calibration algorithm for semiconductor sensors of volatile hydrocarbons concentrations on the example of methane, propane, gasoline, solvent vapor, toluene. When calibrating gas-sensitive elements, data were obtained on the change in the conductivity of the sensor over time during its heating or cooling. It turned out that, the distinguished frequency characteristics for these molecules with various concentrations of components in atmospheric air were as follows: for gasoline $\sim 0.0406 \text{ s}^{-1}$ (cooling) and $\sim 0.036 \text{ s}^{-1}$ (heating), for solvent vapor: $\sim 0.459 \text{ s}^{-1}$ (heating), for toluene $\sim 0.208 \text{ s}^{-1}$ (heating).

Consider specific examples. Figure 1 shows the difference signal of the change in the conductivity of the sensor over time (data from the detector are subtracted when the sensor cools in atmospheric air in the absence of gasoline vapors) when it cools down at specified constant concentrations of gasoline (when preparing gas mixtures, certified brands of gasoline vapors and certified equipment for the preparation of calibration gas mixtures).

![Graph showing conductivity changes](image)

**Figure 1.** Change in conductivity with time during cooling of a semiconductor sensor (SmS) at given concentrations of gasoline:

$s5$ – 0.906 vol.%, $s3$ – 0.544 vol.%, $s2$ – 0.363 vol.%, $s1$ – ~0 vol.%

Figure 1 also shows the trend lines in areas with maxima at sensor (SmS) cooling at various concentrations of gasoline contained in atmospheric air. The time extreme point for all the functions presented (and three different concentrations of gasoline) turned out to be the same and the value is approximately $\sim 3125 \text{ ms}$. The Fourier transforms of data for three different concentrations of gasoline and the functions of the trend lines (in the selected time section) are presented below in graphical form (figure 2(a) and figure 2(b)). The points of the extrema in time coincide and are approximately equal to $\sim 3127 \text{ ms}$. 


It is possible to determine the frequency spectral characteristics of the processes, while it is clear that there is no frequency shift at different concentrations of gasoline (equations (2)):

$$
S3(\omega) := \int_{3000}^{3250} F3(x, \omega) \cdot e^{-i \omega \cdot x} \, dx
$$

$$
S5(\omega) := \int_{3000}^{3250} F5(x, \omega) \cdot e^{-i \omega \cdot x} \, dx
$$

$$
S2(\omega) := \int_{3000}^{3250} F2(x, \omega) \cdot e^{-i \omega \cdot x} \, dx
$$

Having plotted the square of the amplitude of the real part of the spectral characteristics of the Fourier transforms as a function of frequency (from the definition of Fourier transforms), we can see that for all 3 concentrations the frequency (figure 3) was the same, equal to approximately $\sim 0.036 \text{ s}^{-1}$.

**Figure 2.** The graphical representation: (a) - the Fourier transforms of data for 3 different concentrations of gasoline in atmospheric air; (b) - the function of the trend lines for change in the conductivity difference signal of the gas sensitive element $SmS$.

**Figure 3.** The square of the amplitude of the material part of the spectral characteristic of the sensor, proportional to the concentration of the measured component in the gas mixture (gasoline).
According to the above calculation algorithm for the sensor cooling process, the frequency response of the sensor was calculated during its heating (the equations of the trend lines are given above (equations (4))). The same calculation algorithm (as for cooling, see above) gives the process frequency equal to $\sim 0.040 \text{ s}^{-1}$ (for comparison, we indicate that during cooling the process frequency ($\omega$) turned out to be $\sim 0.036 \text{ s}^{-1}$), which appeared to be fairly close values within the experimental error. This indicates that the optimum temperature for detecting gasoline vapors is the same and can be determined both during heating and cooling of the sensor.

We set up and carried out experiments with the same sensor, but with different other hydrocarbons to confirm the generality of the existing calibration algorithm. The following figure 4 shows the difference signal of the change in conductivity of the sensor over time during its heating at three different concentrations of solvent vapor (certified gas mixtures were used).

![Figure 4](image_url)

**Figure 4.** The trend line of the differential signal of the change in the conductivity of the sensor over time during its heating in solvent vapor at three different concentrations in atmospheric air: $s_7 - 0.423 \text{ vol.\%}$, $s_5 - 0.303 \text{ vol.\%}$, $s_3 - 0.182 \text{ vol.\%}$, $s_2 - \sim 0.001 \text{ vol.\%}$.

The extremum point in figure 4 corresponds to the 170-th millisecond of the process. In this case, the frequency estimate gives a value of $\omega \sim 0.459 \text{ s}^{-1}$, which is approximately an order of magnitude greater than for gasoline vapors (for comparison have the value of $\omega \sim 0.040 \text{ s}^{-1}$ for gasoline vapors, see above). The calibrations for various calibration gas mixtures studied by us for various hydrocarbons contained in atmospheric air are given below. So in the subsequent figure 5 and figure 6 present the corresponding data for the heating process of the sensor based on samarium sulfide and other composite materials (for example, tin oxide doped with lanthanum atoms).
Figure 5. Methane in atmospheric air, differential signal of a sensor during heating of a sensor in a calibration gas mixture:
\[ s_3 = 0.182 \text{ vol.\%}, \quad s_5 = 0.303 \text{ vol.\%}, \quad s_{10} = 0.605 \text{ vol.\%}, \quad s_{15} = 0.906 \text{ vol.\%}. \]

Figure 6. Toluene in atmospheric air, differential signal of a sensor during heating and cooling of a sensor in a calibration gas mixture:
\[ s_2 = 0.121 \text{ vol.\%}, \quad s_3 = 0.182 \text{ vol.\%}, \quad s_4 = 0.242 \text{ vol.\%}, \quad s_5 = 0.303 \text{ vol.\%}. \]

The found values of the frequency characteristics of the sensor (SmS) in order of magnitude correspond to the values of the rate constants of desorption of typical molecular gases from the surface of oxide semiconductor sensors: \( k_2 \sim 0.05 \text{ s}^{-1} \) [4], which was confirmed by us in the study of other composite materials (in particular, doped tin dioxide lanthanum atoms). It can be assumed that the frequency characteristics of SmS sensors (from an analogy with optical measurements) also correspond to the parameters of the rate constants of reverse chemisorption reactions for the hydrocarbons studied by us. It can be seen from the presented figures that the stability of the spectral characteristics of the sensor is confirmed by the absence of a shift in the characteristic frequency responsible for adsorption.
3. Measurements
The measurement process algorithm seems to be quite simple and convenient for practical use. According to [1], the optimum temperature for detecting impurities corresponds to the extremum point of the sensor calibration equation. A linear relationship is observed between the dimensionless electrical conductivity of the gas-sensitive element in the given coordinates and the concentration of the impurity contained in atmospheric air, which is fully consistent with the mechanisms and concepts for the adsorption of active particles, discussed in detail in [3]. Thus, the measurement algorithm consists in searching for the temperature extremum and in calculating the dimensionless adsorption coordinates of one or another component (selection is determined by the frequency response).

4. Results and discussion
As can be seen, using the presented algorithm for calibrating a gas sensitive element using certified gas mixtures of hydrocarbons (methane, toluene, solvent vapor, gasoline) contained in atmospheric air, it was possible to obtain a system of sensor calibration constants, which allows the algorithm for measuring component concentrations in atmospheric air with a high degree of selectivity. The new measurement process algorithm is a kind of “temperature scanner” of the gas-sensitive layer of the sensor in the measured atmosphere, the concentration “peak” corresponds to the instantaneous equilibrium of the process and determines the selectivity from the calibration: which frequency corresponds to which and there is a measured component. Further, according to the proposed system of sensor calibration constants, the concentration of the measured component of the gas mixture is determined. The presented mathematical apparatus of the measurement algorithm and sensor calibration system completes the construction of semiconductor Fourier spectroscopy of gas sensors, the basic principles of which were described by our team of authors in earlier works.

5. Summary
Further construction of the previously proposed [1,2,3] for the implementation of a new method of gas analysis: semiconductor Fourier spectroscopy is based, first of all, on the analogy with optical measurements and at this stage is connected with the search for the function of one parameter (concentration of the measured component of the gas mixture) at calibration of the gas sensor. Moreover, as is easy to see from Figure 3, a linear relationship between the dimensionless electrical conductivity of the gas-sensitive element in the presented coordinates and the adsorption value named in [4] and the methane concentration in the gas phase contained in atmospheric air is fulfilled.

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References
[1] Kazakov S A, Grevtsev M A and G D Khavrov 2018 The development of semiconductor Fourier spectroscopy principles for the gas analysis on the example of the volatile hydrocarbons concentrations thin-film sensors on based on rare-earth elements Journal of Physics: Conference Series 1135 (2018) 012107
[2] Kazakov S A, Sokolov A V, Grevtsev M A, Sharenkova N V and Kaminskii V V 2018 Scientific Instrumentation 28 137-140
[3] Kazakov S A, Grevtsev M A and Khavrov G D 2018 Proc. Int. Conf. PhysicA.SPb/2018 Principles of construction of semiconductor Fourier spectroscopy for gas analysis on the example of the development of thin-film sensors of volatile hydrocarbon concentrations using rare earth elements (Ioffe Institute, Saint Petersburg), p 191
[4] Myasnikov I A, Sukharev V Ya, Kupriyanov L Yu and Zav'yalov S A 1991 Semiconductor sensors in physico-chemical studies (Moscow: “Nauka” Press) p 327