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Multi-element gas sensor based on surface plasmon resonance: recognition of alcohols by using calixarene films

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Abstract. This work is devoted to development of a multi-element gas sensor based on surface plasmon resonance (SPR) to recognize some alcohols. As sensitive layers capable to change their optical properties when interacting with volatile alcohol molecules, we investigated bulk-porous sorbents – calixarenes (tret-butyl-calix[4,6,8]arenes (C[4]A, C[6]A, C[8]A), tetra-amyl-calix[4] resorcinolaren (C[4]Re). Each calixarene was studied to obtain its kinetic concentration SPR characteristics for interaction with ethanol, isopropanol and penthanol vapors. To realize SPR measurements, the sensitive calixarene films ($d \sim 100$ nm) were deposited on a gold film ($d \sim 45$ nm) by using the method of thermal evaporation in vacuum. Experimental multi-element SPR device was designed as based on the analysis of TV image obtained for the studied array of calixarene films and tested using saturated ethanol vapors.

Keywords: Surface plasmon resonance, imaging gas sensor, sensor array, calixarene films, alcohols.

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1. Introduction

In the recent decade, the problem of recognizing odors transform into real challenge to physicist, chemists and engineers [1]. While camcorders and microphones became excellent artificial organs for sighting and hearing, olfaction remains unattainable for changing it with artificial sensors. Up-to-date gas-analytic systems “electronic nose” consist of an array of sensors that being in contact with a complex mixture of volatile molecules generates a set of electric signals suitable for further input to computer and logical processing [2]. But sensitive materials in these devices do not reveal specific high-selective interaction traditionally inherent to biochemical sensor systems. These materials are characterized by low-selective cross-reactivity. It means that each element of this array responds to various studied chemical reagents to some extent [3].

When analyzing complex molecular interactions in gas medium, the most popular sensor arrays are based on optical principles of transduction. There arise new reports of designing such devices for food and fragrance industries, for solving ecological tasks, development of new drugs, and even for space investigations [4 – 8].

Optical transducers use light absorption effects [9], reflection [10], diffraction [11], interference [12], optical fibers [13], as well as SPR [14]. To design a sensor array, one can use, for example, the spectrum of optical absorption for a thin organic film, which can change when being in contact with studied gas mixture and defines its color. It is visual estimation of this effect that was used in creation of the miniature “artificial nose” for one-shot application [15]. However, a noticeable change in the absorption spectrum of this organic film sorbing gas molecules is usually related with strong chemical transformations and, as a rule, is non-reversible. Thereof, this method did not get any further development.

Recently in our work [16], successfully realized was the method for digital registration of changes in color components (RGB) inherent to interferentially colored calixarene thin films. The essence of this method consists in changing the thickness and refraction index of organic films when binding the studied volatile molecules, which causes color changes. Measuring the refraction coefficient and thickness of the molecular layer, one can draw a conclusion of the type of molecules in ambient atmosphere. This method showed

rather high sensitivity and specificity in the course of detecting volatile molecules of some alcohols.

However, measuring the reflection amplitude for three wavelengths is not the most sensitive method to determine the thickness and refraction index for organic films. Sensitivity of the SPR effect to changes in the refraction index is at least one order higher. For instance in [17], the authors demonstrate the possibility to measure a difference in refraction indexes for dried air and helium by using the SPR method. This method is based on the energy transfer from an optical beam to a surface evanescent wave propagating parallel to a metal/dielectric interface, and this coupling is very sensitive to a local change of the refractive index of the dielectric medium, induced for example by the surface hybridization of biomolecules. One of the ways to realize the SPR sensor array is to measure variations of the reflection coefficient at some fixed wavelength and angle of incidence on 2D surface by using CCD camera [18].

However, application of SPR to register the refraction coefficient and thickness of the organic film array is not a trivial task. The matter is that, when depositing the organic film on a plasmon-supporting gold layer, the SPR angle is shifted by tens degrees, which causes the necessity to specially choose the prism design. Some additional difficulties arise when trying to create an SPR array, since in this case one should choose the thickness and refraction index of this organic film in such a manner that the SPR angle would be approximately the same for all the samples. Only in this case registration of SPR signal changes becomes possible in the mode of fixed angle. In creation of multi-element sensor arrays based on the SPR effect, one problem more is to choose material of a sensitive organic film. This sensitive material should be porous to increase the adsorption volume, noticeably expand when adsorbing molecules-analytes and have different selectivity with regard to various classes of volatile molecules.

Solution of the above problems is the aim of this work.

2. Experimental setups and materials

2.1. SPR sensor instrumentation

To study adsorption properties of sensitive organic films for sensor arrays, we used the single-channel device BIOSUPLAR-201, developed in V. Lashkaryov Institute of Semiconductor Physics (NAS of Ukraine) in cooperation with Mivitec GmbH-Analytical μ -Systems (www.micro-systems.de). This device provides measurements of the total SPR curve in the angle configuration that corresponds to the Kretschmann scheme [19] with mechanical scanning the angle of incidence within the range 18 degrees in air (12 degrees in glass) and accuracy 5 arc seconds as well as the possibility to make absolute calibration by the angle. Excitation of surface plasmons (SP) in thin gold film is

realized using the p-polarized laser beam ($\lambda = 670$ nm) and a glass prism (refraction index $n = 1.61$, base angle 65° , base face 20×20 mm²). It allows to register SPR curves within the range of incidence angles 56 to 68 degrees (in glass). It is this range where the SPR minimum is located, if depositing a sensitive organic film with the thickness 50 – 200 nm on gold. Measured in these experiments as a device output signal was the angle position of the SPR minimum during adsorption and desorption of molecules-analytes.

The multi-channel SPR sensor is developed and constructed using the same principle, but without automated scanning by the angle. The idea of this multi-channel SPR analyzer is to realize visualization of the SPR response for each sensing element by using TV camera. The optical scheme of this device is shown in Fig. 1. The central unit of the experimental facility is the glass prism ($n = 1.51$) with the base angle 70° and base face 60×120 mm. The base face of the prism is equipped through immerse liquid with the SPR chip containing several sensors and flow-through cuvette to input-output a studied sample. The prism is located on a rotating goniometric table with a special pantograph providing equality of angles of incidence and reflection within the range $55 - 75^\circ$. All the system of sensors is illuminated with a broad uniform beam of p-polarized light ($\lambda = 0.65$ μ m) and a fixed angle of incidence. A stationary image of the sensor surface is captured by a black-and-white CCD camera.

The developed facility allows to use recent achievements in the field of TV technologies, computer input and analysis of images. The essential advantage of this method is the possibility to simultaneously test all the cells of the multi-element sensor. Besides, there arises the opportunity to study dynamics of the process with further analysis of every its stage and the static image recorded in the corresponding time moment. The system for processing the image consists of three main components, namely: electronic TV camera, device for input and registration of video frames as well as computer soft to process the image. Used in this facility is the CCD camera Spacecam 300 operating in the mode of receiving white-and-black images with the resolution corresponding to 250,000 pixels. The system of automatic gain control (AGC) in this camera was switched off, which gave the possibility to calibrate the facility. To input and register the video frames, we used a specialized universal serial bus (USB). The white-and-black image captured with the camera one could observe at the computer display and register it in a definite moment. For high-speed processing and storage of images, we used a specific soft.

2.2. SPR detector element

As a sensitive element of the SPR sensor, we used gold films with the thickness (45 ± 5) nm on the glass substrate of the size $20 \times 20 \times 1$ mm and refractive index $n = 1.515$. Glass substrates were mechanically cleaned and

chemically processed with further washing in distilled water by using an ultrasonic bath. Then these were finished using glow discharge directly before deposition. Metal layer was deposited by thermal evaporation in vacuum (BYII-4 facility, residual vapor pressure $4 \cdot 10^{-4}$ Pa, speed of sputtering 40 to 50 Å/s). To improve adhesion, we used a thin chromium layer (~ 1 nm). To increase stability, the chips were annealed at $T \sim 120^\circ\text{C}$ [20]. The gold layer was covered with thin organic films consisting of calixarenes sensitive to studied analytes. Optical contact of these SPR chips with the glass prism was achieved using immerse liquid with the same refraction index.

2.3. Sensitive materials

To construct gas sensors, commonly used are such materials as: phtalocyanines [21], macro-cyclic compounds [22, 23], metal-proteins [24], calixarenes [25]. The latter possess apparent advantages, as compared to metal-proteins and phtalocyanines, due to their porous structure and high value of expansion coefficient in the course of adsorption [26, 27].

In [28], the authors studied four ways to deposit calixarene layers onto substrates of gas sensors, namely: “thin and thick drop”, Langmuir-Blodgett (LB) technique, “air-brush”, thermal evaporation in vacuum. Their investigations showed that, regardless of the method of deposition, adsorption capability of calixarene films to alcohol molecules within the thickness range 50 to 1,000 nm remains practically the same and is in proportion to the film volume. To prepare sensor arrays, they usually used the method of thermal evaporation in vacuum, as it provides the highest uniformity of the film in thickness under the condition of thermal stability for this material.

In this work, as sensitive materials of a multi-sensor array we investigated thin calixarene films: tert-butyl-calix[4,6,8]arenes (C[4]A, C[6]A, C[8]A) and tetra-amyl-calix[4]resorcinolaren (C[4]Re) synthesized in the Institute for Organic Chemistry, NAS of Ukraine (Kyiv). Molecules of these materials are closed compositions of several phenol rings with the cage dimensions 0.63 (1.36) nm for C[4]A up to 0.79 (1.8) nm for C[8]A. The thickness of the order of 100 nm was chosen as optimal, because this calixarene film thickness provides the shift of the SPR angle to the range $55 - 60^\circ$, which is suitable to the chosen prism dimensions. Since this class of calixarene films is thermally stable, the films were deposited using thermal evaporation in vacuum without heating the substrate (BYII-4 facility, residual vapor pressure $4 \cdot 10^{-4}$ Pa, speed of sputtering 1 nm/s). Thickness calibration of films was carried out using atomic force microscopy.

2.4. Analytes

Used in this work as analytes were the following alcohols: ethanol, penthanol and isopropanol of super-high purity. To study concentration dependences, we used saturated alcohol vapors dilute with dry cleaned air. Dilution was realized using a special syringe of 20 ml capacity made of material inert to the studied substances.

3. Results and discussion

3.1. SPR investigations of calixarene films

Development of this multi-element SPR sensor for recognition of alcohols was begun from studying the sensitivity and specificity of calixarene films towards studied analytes. With this aim, the samples with

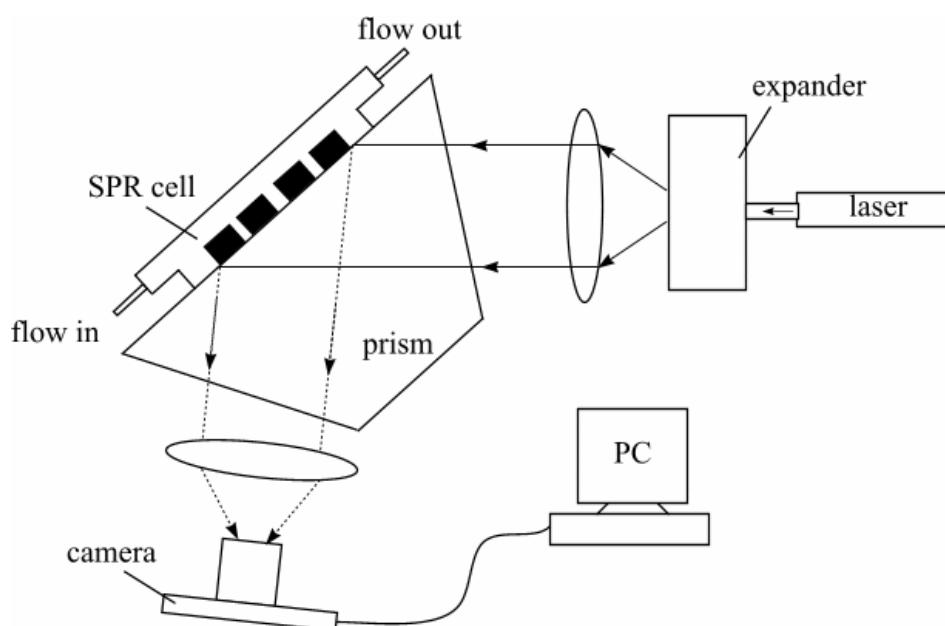


Fig. 1. Scheme of the experimental SPR setup.

calixarene (C[4]A, C[6]A, C[8]A, C[4]Re) films were one-by-one placed to the cell of the single-channel device BIOSUPLAR-201, and the kinetics of changes in the angular position of SPR minima with time were recorded when injecting ethanol, pentanol and isopropanol vapors in various concentrations as well as after pumping with pure air. The obtained kinetic curves are shown in Fig. 2.

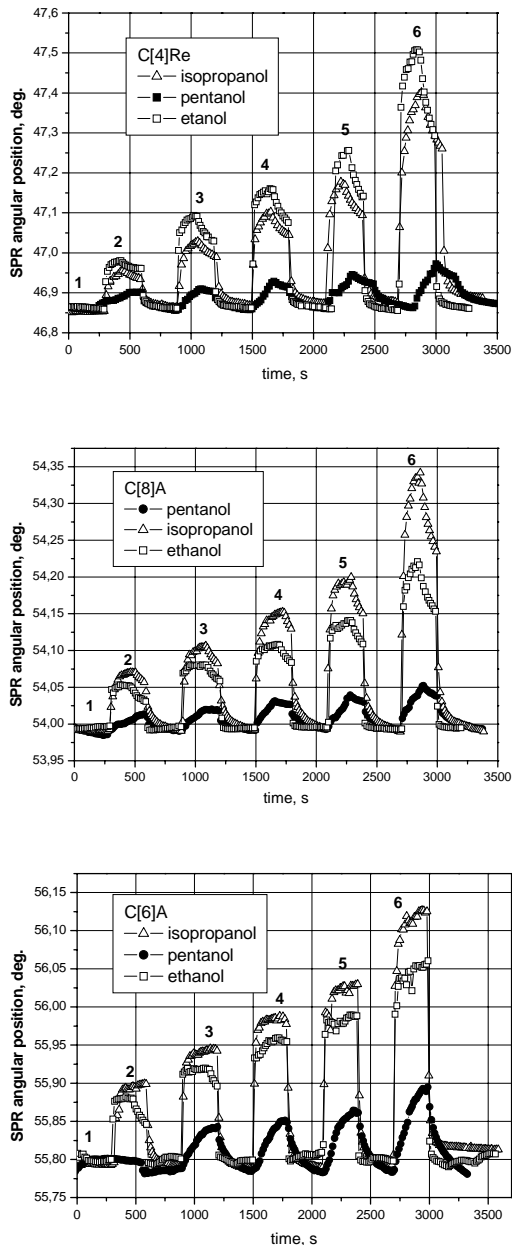


Fig. 2. Relative change of the SPR angle versus time in the cases of letting-to and pumping-out the ethanol, pentanol and isopropanol vapors in various concentrations for the following calixarene films: C[4]A, C[6]A and C[8]A. Changes in the analyte concentration was reached by dilution of alcohol saturated vapors with pure air: 1 – calixarene film under air action; 2 – dilution 1/10; 3 – dilution 2/10; 4 – dilution 3/10; 5 – dilution 4/10; 6 – dilution 6/10.

It can be seen that the SPR response, when alcohols are absorbed by calixarene (C[4]Re and C[8]A) films, has the shape close to the rectangular one: the signal grows to some value and then comes back to its initial value after pumping with pure air. At low vapor pressures (considerable letting down), the top of the signal is rather flat. However, when the concentration grows, the shape of response complicates and demonstrates a pronounced peak. As it was shown earlier in [16], this peak can be related with changes in film elastic constants in the course of adsorption. Contrary to C[4]Re and C[8]A, the C[6]A films demonstrate practically no peak during vapor action. Their response grows slowly in time up to the moment of pumping with pure air. This behavior is related with diffusion of vapors inside the film with time. The maximal amplitudes of SPR minimum shift as a result of alcohol vapor action were obtained with the calixarene C[4]Re.

Displayed in Fig. 3 are the concentration dependences for the SPR response amplitude in the case of calixarene C[4]Re film adsorbing volatile molecules of ethanol, pentanol and isopropanol. In practice, the amplitude of SPR responses grows linearly with the concentration of these alcohols. It is noteworthy that the weaker SPR response to pentanol molecules is related with the low pressure of saturated vapors (5 mm Hg) for this heavy alcohol, as compared to isopropanol (40 mm Hg) and ethanol (44 mm Hg). Similar dependences were obtained for calixarene C[6]A and C[8]A films. The results of respective measurements are summarized in Table 1.

Being based on the experimental results of serial measurements of the SPR response corresponding to C[4]Re, C[8]A and C[6]A films adsorbing isopropanol, ethanol and pentanol molecules, one can perform a recognition procedure by application of any mathematical classification method, for example, use statistic methods or neuron networks. To estimate the capability of the chosen array in recognition of the studied alcohols, it is necessary to represent amplitude values of the obtained SPR responses in n -dimensional space of sensors and consider distances between them. To make a preliminary estimation, one can use geometric formalism, i.e., calculate distances between these vectors in some metrics (find the distance function), for instance, in the Euclidean one. Fig. 4 shows geometric constructions for the SPR response amplitudes in Cartesian coordinates for the studied sensor pairs.

Fig. 4 shows a comparison of responses for different sensor pairs to various concentrations of ethanol, isopropanol and pentanol. It can be easily seen that the pairs containing C[4]Re allow to reliably distinguish ethanol and isopropanol regardless of the concentration within the letting down range 1/10...6/10. At the same time, pentanol cannot be practically recognized.

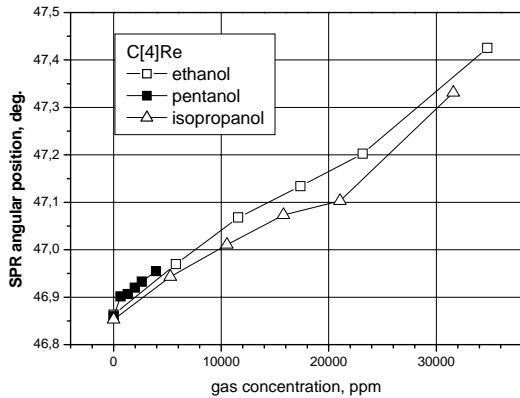


Fig. 3. Amplitude values of the SPR angle shift versus the concentration of the studied alcohols when the latter act on the calixarene C[4]Re films.

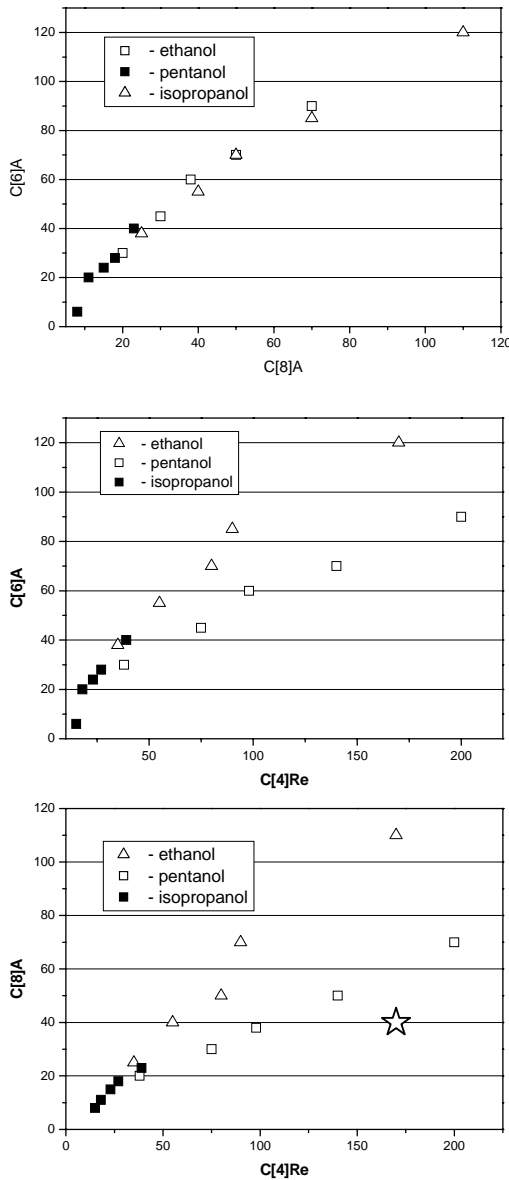


Fig. 4. Comprision of SPR response amplitudes for various alcohols in Cartesian coordinates when using sensor pairs.

Table 1. SPR response of C[4]Re, C[8]A, C[6]A films adsorbing the studied molecules

	Pressure of molecular vapors, p/p _s				
	0.1	0.2	0.3	0.4	0.6
Isopropanol					
C[4]Re	35	55	80	90	170
C[8]A	25	40	50	70	110
C[6]A	38	55	70	85	120
Ethanol					
C[4]Re	38	75	98	140	200
C[8]A	20	30	38	50	70
C[6]A	30	45	60	70	90
Pentanol					
C[4]Re	15	18	23	27	39
C[8]A	8	11	15	18	23
C[6]A	6	20	24	28	40

Thus, after the performed experiments one can draw the following conclusions: i) thermally deposited calixarene C[4]Re, C[8]A and C[6]A films demonstrate different sensitivity when adsorbing ethanol, isopropanol and pentanol molecules; ii) C[4]A films do not pronounce any noticeable sensitivity to the studied analytes, therefore the respective curves were not presented in this paper; iii) even using two films - C[4]Re and C[8]A – one can distinguish ethanol and isopropanol as well as determine their concentration.

3.2. Operational demonstration of multi-element SPR gas sensor

To demonstrate operation of the multi-element sensor based on SPR phenomenon, we used a chip containing four calixarene films: tert-butyl-calix[4,6,8]arenes (C[4]A, C[6]A, C[8]A), tetrapenthylyl-calix[4] resorcinolaren (C[4]Re). The sensor chip was fixed on the prism base face via immerse liquid by using a special flow-through cuvette to input-output the studied assay and illuminated with a wide laser beam of p-polarized light ($\lambda = 0.65 \mu\text{m}$) with a fixed angle of incidence (51° in glass). Light reflected from the sensor surface entered to the objective of CCD camera and brought information about the SPR response. Thus, the SPR image could be observed in display and recorded in definite time moments. Processing the held image provided a possibility to determine the value of changes in the intensity of reflected light and, consequently, to obtain quantitative data upon interaction of sensitive films with the studied analytes.

An analyzed gas mixture was supplied to the studied samples via the flow-through cuvette. Monitoring the changes in light reflection from surfaces of all four sensors being under action of ethanol vapors was performed simultaneously. The respective image was recorded at the initial stage with pure air (Fig. 5a), directly after introduction of the studied assay (Fig. 5b),

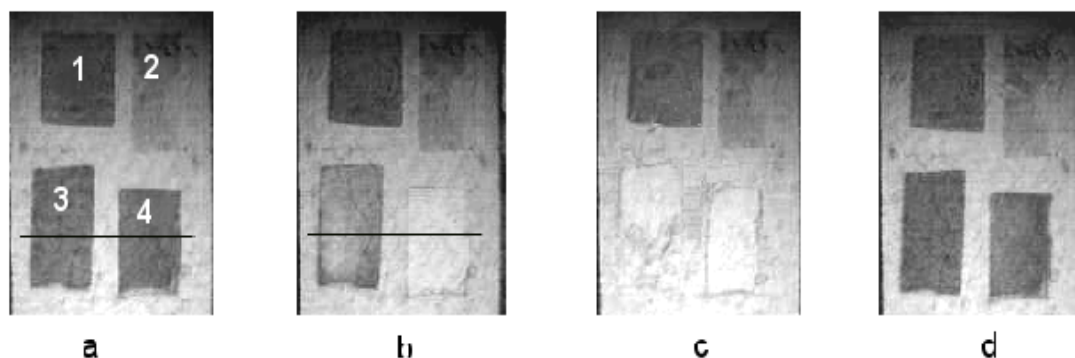


Fig. 5. Time dependence of the ethanol vapor influence on the sensor chip containing four calixarene films: tert-butyl-calix[4,6,8]arenes – C[4]A – 1, C[6]A – 2, C[8]A – 3, and tetra-pentyl-calix[4]resorchinolarene. a – pure air, b – directly after introduction of the studied assay (saturated ethanol vapors), c – in 5 min later, d – after pumping-through with pure air.

in five minutes after this introduction (Fig. 5c), and after pumping with pure air (Fig. 5d). It is seen that the image brightness of the sensors 2, 3 and 4 (C[6]A, C[8]A and C[4]Re, respectively) is changed under action of ethanol vapors, while that of the sensor 1 (C[4]A) remains unchanged. After pumping-through with pure air, the image brightness of all the sensors was recovered. It means that the interaction between calixarene film material and ethanol molecules is reversible, and the studied sensor chip can be used repeatedly.

After transformation of the image into digital form and processing the data, one can obtain not only qualitative but quantitative information about interaction of the studied assay with different calixarene films. The program developed by the authors for these analysis allows to find data about reflected light intensities in any image point. With this aim, it is necessary to put the cursor to the point of interest and set a respective command. Besides, it is possible to build a map for the sample with lines of identical reflection intensity.

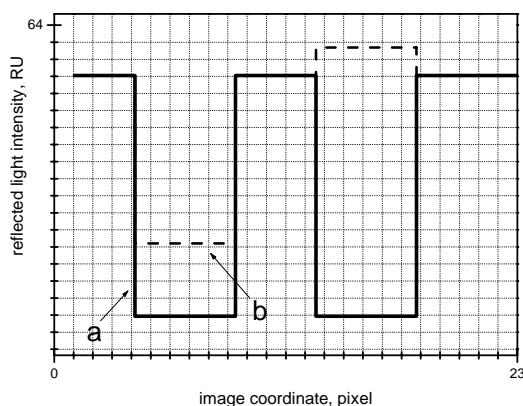


Fig. 6. Distribution of the reflected light intensity along the chosen cross-section of the samples (C[8]A on the left and C[4]Re on the right) in Figs 5a and 5b. The curves: a – sensors under action of pure air, b – sensors under action of saturated ethanol vapors.

Fig. 6 demonstrates the intensity of reflected light in relative units for the sensors 3 and 4 (C[8]A on the left and C[4]Re on the right) versus the image coordinate. The curve *a* corresponds to the initial state of the samples (pure air in cuvette), curve *b* characterizes changes in the light reflection intensity directly after introduction of the ethanol assay with the concentration close to that of its saturated vapors. In Figs 5a and 5b, horizontal lines show the coordinate position of the analyzed profile. It is seen that the signal is increased in both cases. The coordinate of vector that corresponds to augmentation of the signals from the sensors 3 and 4 is shown in Fig. 4b with asterisk. Despite the absence of binding between the measured signals in concentration, the asterisk position is close to the points corresponding to ethanol. In our opinion, this fact proves a technical foundation for the efficiency of creation of multi-channel, high-speed and efficient gas sensor based on the SPR principle.

4. Conclusion

Shown in this work is the possibility to construct the multi-element gas sensor for alcohols, which consists of a surface plasmon resonance transducer and sensor array with cross-reactivity. As sensitive materials for this multi-sensor array, we used thin calixarene films: tert-butyl-calix[4,6,8]arenes (C[4]A, C[6]A, C[8]A) as well as tetra-amyl-calix[4]resorchinolarene (C[4]Re) prepared by thermal evaporation in vacuum. Using the automated single-channel device BIOSUPLAR-201, for each calixarene we studied kinetic concentration characteristics describing interaction with ethanol, pentanol and isopropanol vapors. The calixarene films C[4]A, C[6]A and C[8]A demonstrated different sensitivity and specificity to adsorption of molecules of the studied alcohols. C[4]A films did not pronounce any noticeable sensitivity to chosen analytes. To estimate capability of the investigated sensor array in recognition of analytes, we performed geometrical constructions for

amplitudes of SPR responses to ethanol, pentanol and isopropanol vapors in Cartesian coordinates for pairs of sensors. It has been shown that even using two films - C[4]A and C[8]A – one can recognize ethanol and isopropanol in any concentration as well as to determine the analyte concentration. The obtained results coincide with analogous data of interferential colorimetry for tetrabutyl-calixarene films. It is indicative of reliability of results following from the above experiments and confirm the opportunity to design multi-element SPR gas sensor. Experimental multi-element SPR device has been designed as based on the analysis of TV image obtained for the studied array of calixarene films and tested using saturated ethanol vapors.

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