Investigation of Nanofilm Influence on Optical Sensor's Characteristics

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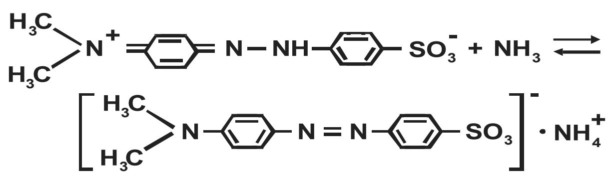
A particular place among optical methods of analysis is occupied by chemical sensors based on effect of frustrated total internal reflection and thin films of substances, which alter their optical features under effect of environment contents. It is known, that some organic substances are sensitive for gases micro-concentrations at a room temperature, for example, organic dyes [1]. Many pH dyes have been inserted in sol-gels for the pH sensing and acid-base gases including CO_2 and NH_3 [2-4]. The fundamental opportunity for creation of optical NH_3 sensor based on the film of 4-[4-(dimethylamino)phenylazo]benzenesulfonic acid sodium salt (Methyl Orange), immobilized within Nafion® have been presented in [5,6].
The interaction of ammonia containing in the air with dye molecules in accordance with the scheme:



The maximum of absorbance spectrum of the film drifts to the short wave range from $\lambda_{max} = 522$ nm to $\lambda_{max} = 464$ nm in the presence of ammonia. Therefore according to Fresnel's law, the intensity of reflected light under the angle close to critical increases on the wave-length equal to 522 nm. The influence of matrix nature on primary parameters of optical NH_3 sensor was investigated in this work. Films of Nafion® and SiO_x were investigated as matrixes. The sensitivity, dependence of sensor signal on humidity and dynamic parameters of sensors were determined.

EXPERIMENTAL

A design of a chemical optical sensor is presented in Figure 1. The principle of sensor working bases on the dependence of reflected light intensity on absorption spectrum of sensitive film. The sensor consists of prism from optical glass with refraction index equal to 1,518 at the wave 546,07 nm. The angle of prism top must be such in order to pitch angle is a few bigger then critical. Thin (200 μm x 1 cm^2) rectangular plate made from same glass was mounted on the side opposite bigger angle. The good optical contact must be between prism surface and glass plate. The sensitive layer includes the Methyl Orange, immobilized in matrix. It was formed on outside surface of plate. The light source was fixed on the other side. We used the light-emitting diode L-53 GSBT with wave-length of λ_{max} = 530 nm. Intensity of the reflected beam from sensitive layer/ glass plate border was measured by a silicon photodiode which was fixed on the opposite side. The sensor was placed in a flow-through measuring cell.

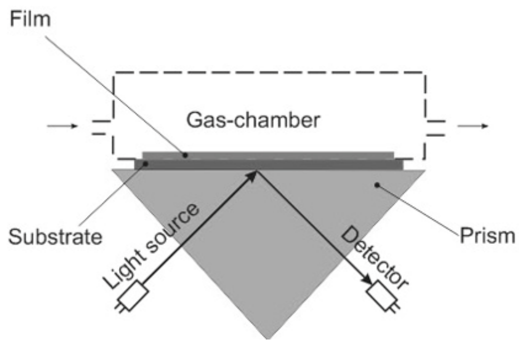


Figure 1. An optical sensor's design.

A specially designed microprocessor unit was used to take measurements. The properties of the sensor were examined on sample gas mixtures using a dynamic blender “Environics-4000” (Environics, USA); the Dräger test ampoules (Dräger, Germany) were employed. The temperature was varied in the range 0 / +60 ^{o}C with accuracy equal to ±0,5^{0}C at temperature influence investigations on sensor’s response. All remaining measurements were made at room temperature. The humidity influence was estimated in range 5 – 80% of relative humidity, at that the given humidity value was maintained with accuracy equal to ±2% relative humidity.

The Nafion® film with Methyl Orange was deposited by centrifuge from solution. Initial solution was 5% mass. Nafion® in ethyl alcohol (H-form, Aldrich, USA) and diluted with water in the ratio 1:9 vol. On the base this solution saturated with Methyl Orange (Laverna, Russia) solution was prepared. Then films were dried during 24 hours in the air.

Films of SiO_x were produced by a method of hydrolytic polycondensation from solutions based on tetraethyl orthosilicate (sol-gel method). Saturated solution with Methyl Orange was used for forming sensitive films by centrifuge.

Films thickness was measured by “ALPHA-STEP 200” (Tencor, USA) and was in the range 100-150 nm.

The signal magnitude of the sensor was determined by the equation:

$$U_s = U_g - U_a,$$

where U_a, U_g - value of the sensor signal in air and in ammonia correspondingly.

RESULTS

Considerably increasing of sensor sensitivity was observed for doped Nafion® film (Figure 2).

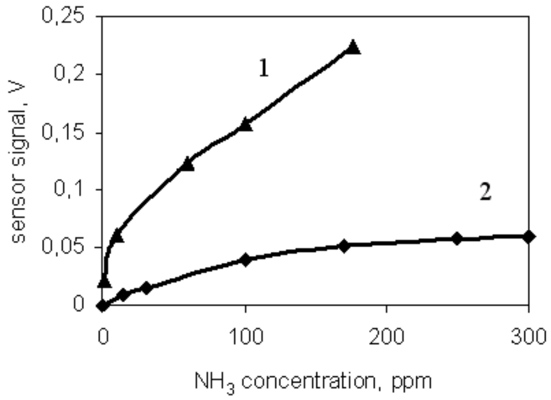


Figure 2. The sensor signal’s dependence on ammonia concentration in air for films based on Nafion® (1) and SiO_x (2) at room temperature and 40% relative humidity.

This fact is evidence of equilibrium constant value of ammonia interaction with organic due in Nafion® more larger than in SiO_x.

At stepped changing of ammonia concentration and constant humidity and temperature the sensor signal front edge may be determined by the equation:

$$U_{s,1} = \sum_i A_i \left[1 - \exp\left(-\frac{t}{\tau_i} \right) \right] \qquad 0 \le t \le t_0$$

Back edge –

$$U_{s,2} = \sum_j A_j \exp\left(-\frac{t - t_0}{\tau_j} \right) \qquad t_0 < t,$$

where t_0 - time which ammonia influence on sensor; coefficients A_i, A_j depend on ammonia concentration in air (Figure 3).

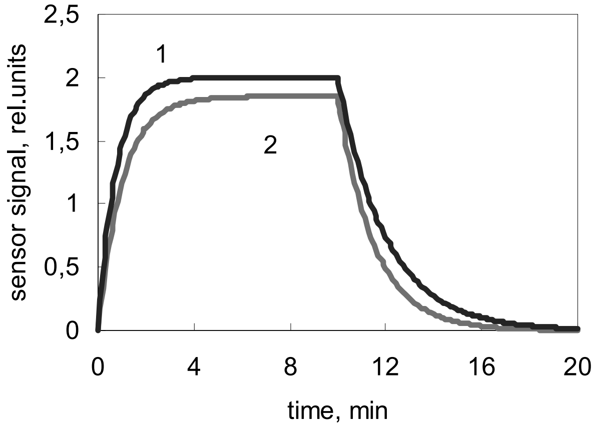


Figure 3. The sensor signal's dependence on ammonia concentration in air for films based on Nafion® (1) and SiO_x (2) at room temperature and 40% relative humidity: ammonia concentration – 10 ppm.

In most cases second and following members of series carry insignificant contribution in sensor signal value. Therefore first member of equation can be used for subsequent calculations in practice. Using this fact the response and recovery time constants were determined. The response time constant for sensitive layer based on Nafion® film three times smaller than for SiO_x (0,4 and 1,2 min correspondingly) at 100 ppm ammonia and 40% relative humidity. Simultaneously recovery time constant for Nafion® film greater approximately as many times than other matrix (17,5 and 5,9 min correspondingly). These results confirm the presence of the considerable dependence of equilibrium constant on the matrix nature.

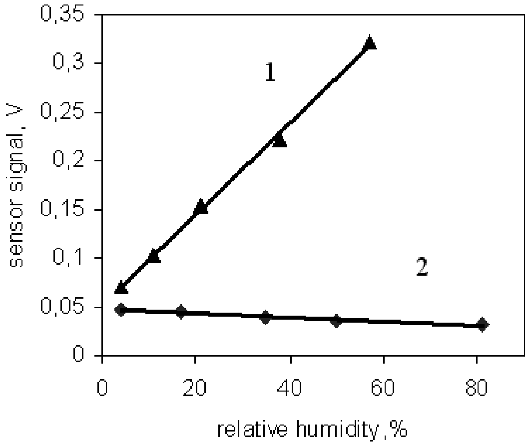


Figure 4. The dependence of sensor signal on relative humidity in 125 ppm ammonia for films based on Nafion® (1) and SiO_x (2) at room temperature.

The humidity increasing considerably raises sensor signal value sensitive layer based Nafion® film (Figure 4) and simultaneously decreases four times response and recovery times. This fact is evidence that adsorption humidity promotes the chemisorption process of ammonia on the film surface.

The results for SiO_x matrix are complicated. On the one hand response and recovery times are decreased in 2-2,5 times. But on the other hand sensor signal decreases simultaneously (Figure 4). Matrix of SiO_x is high porous structure. The adsorption of water in micro- and mesopores brings to fill their. This process accordingly has an influence on optical characteristics of SiO_x films. Hence the losses of light on the film/ environment border decrease.Probably, observed effect compensates influence of humidity adsorption on interaction kinetics of the 4-[4-(Dimethylamino)phenylazo]benzenesulfonic acid sodium salt with ammonia.

The investigations of sensor signal dependence on temperature in the range 0–60 ºC for SiO_x films as they are more thermostable. It was determined that temperature increasing was accompanied by decreasing of sensor's signal. The dependence of sensor signal logarithm on inverse temperature for SiO_x films in 125 ppm ammonia presented in Figure 5.

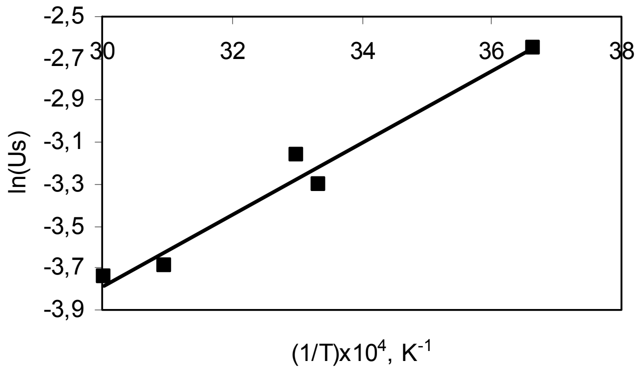


Figure 5. The dependence of sensor signal logarithm on inverse temperature for SiO_x films in 125 ppm ammonia.

The enthalpy of ammonia interaction with the sensitive layer was determined using presented results and it was -14,3 kJ/mol.

As we assumed the temperature increasing resulted in decreasing of sensor time constants for 5-6 times (Figure 6).

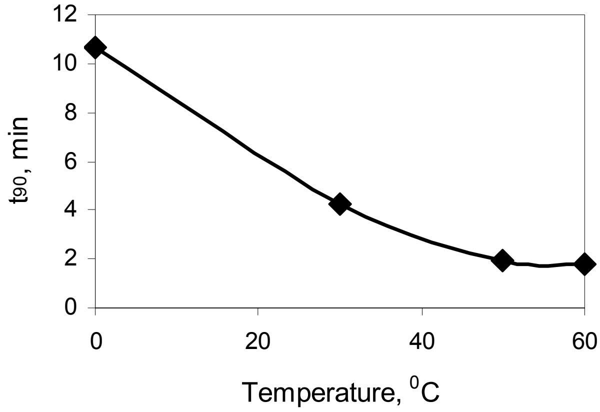


Figure 6. The dependence of response time constant on temperature for SiO_x films in 125 ppm ammonia.

CONCLUSION

The parameters of optical gas sensors considerably depend on matrix nature in which organic due was immobilized. Therefore, the choice of the matrix is ambiguous and complicated. The optimal material brings to significant improvement of sensitivity and dynamic parameters of sensor. Matrix can compensate the negative effect of different factors on sensor signal. For example, correct choice of matrix allows decreasing or eliminating influence of humidity on sensor sensitivity.

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