EXAMINATION OF THIN FILMS OF PHTHALOCYANINEAS
FROM THE POINT OF VIEW OF THEIR APPLICATION IN NO₂ SENSORS

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invited paper

In the group of new sensory materials, phthalocyanineas posses very attractive physical and chemical properties. For some years, phthalocyanineas are investigated for applying in acoustic as well as in optic gas sensors.

This work analyzes the possibility of using the surface plasmon resonance systems for lead phthalocyanineas investigations for NO₂ sensor applications.

Keywords: surface plasmon resonance, dioxide nitrogen detection, lead phthalocyjanine

1. INTRODUCTION.

Technical progress in air monitoring appliances aims at the development of such systems that could be widely applied in industrial and environmental surveying. The application is determined by the necessity to control the concentration of heavily toxic substances. Nitrogen compounds produced during the burning process can be mentioned among them. [1]. Their toxicity and quantity among gas poisons (mainly NO₂) trigger off the need to look for new technical solutions for the production of nitric oxide sensors [1, 2]. Among several new measurment techniques for toxic gases [2] in the group of optical methods particular attention should be paid at the surface plasmon resonance method.

The idea implemented in a plasmon sensor makes use of the changes in optical parameters of the phthalocyanine layer caused by the change in the concentration of NO₂. The changes are recorded by means of plasmon resonance phenomenon (SPR) [3,4]. The phenomenon of plasmon surface resonance is connected with the presence of surface plasmon wave related to the oscillation of charge density in a metal layer. Such a wave can occur and stay on the surface of the distribution

of two substances: metal-dielectric, when the incidence of electromagnetic wave takes place on the surface. The idea of a plasmon sensor performance means that the propagation constants SPW (β_{SPW}) and the propagation constant of optical electromagnetic wave are equalized (β_{e-m}) [5]. To achieve that, exciting electromagnetic wave is directed at the border of these two media distribution through material of a bigger refractive index (e.g. glass, plastic) at a proper angle $\theta_i(\omega_1)$ characteristic for a given frequency (light wave length) . Such matching of wave vectors guarantees the resonance transfer of electromagnetic energy from the incident wave to the surface plasmon wave. Surface plasmon resonance occurs as resonance absorption of optical energy of the incident wave. As a result, the changes in the optical parameters of a medium tested can be detected by the analysis of a mutual interaction between the SPW wave and optical one by means of the measurement of optical wave concentration.

The target herein is to examine the reaction of phthalocyanine layers of a various composition placed on a gold film to the influence of nitrogen dioxide in order to define sensitivity characteristics. The research on the regeneration process of layer structures with phthalocyanines, once they had stayed in the atmosphere of NO_2 for a long time has been carried out as well. The tests were conducted for the concentrations of 100 ppm of NO_2 in nitrogen for two various structures of lead phthalocyanine.

2. EXPERIMENTS

2.1. METER CIRCUIT.

In our investigations the optical experimental set-up, presented in [6] was used. Tested samples, in the form of thin layered structure, (Fig.1) on the goniometric table as been placed. The sample, from the one side with prism and from the second one with the chamber was coupled. To the chamber, the tested gases with known concentration were pumped. In our set-up the source of white light was used. From the source, the light went by optical fiber and by polarizer, to the prism. Nest, the light was reflecting from sensing surface and it was hitting to the optical detectors and simultaneous to the spectrometer. In computer, the signal was registered.

In this way, the polarized light (p-polarization) by shining of the layered structure (Fig.1) has been generating the surface plasmon wave in it. The electric field of the plasmon wave has been penetrating the region, where the particles of tested gas were adhered.

The spectrometer has been registering the changes of light intensity for various wavelength as a function of gas concentrations. By applying the goniometer table in the experimental set-up there were possibility of simultaneous light intensity measurements as a function of light wave lengths and a function of angle changes of tested sample and light direction.

The rate of gas flow during the measurements might be changed in wide range but in our experiments it was constant and equal 1l/min, for all fests. The set-up is fully automated and all measurement processes by adequate numerical programs were controlled.

2.2. REACTION OF A SENSOR FILM WITH PHTHALOCYANINE ON THE BASIS OF GOLD AFTER EXPOSURE TO NITROGEN DIOXIDE.

In the experiment sensor structures made of a glass base (sodium and calcium glass) with a deposited gold film and phthalocyanine film were used. The films of gold and phthalocyanine were laid by means of vacuum evaporation technique. The layer of gold was 45 nm thick while that of phthalocyanine was in the range of from 15 to 100 nm. Lead phthalocyanine was tested in the experiment. Fig. 1 presents examined film structure.

A measuring stand that enables the measurement of a signal from a detector in the whole spectral range of visible light was used. The stand enabled simultaneous measurements both in the function of a wave length and in the function of sample position angle in one measurement series. The elaborated numerical program allows to present the obtained results in the form of three-dimensional diagrams for dependences of signal size in a detector on the length of wave and sample position angle. The measurements were conducted for various film structures in the presence of nitrogen as carrier gas and next, nitrogen dioxide of a concentration of 100ppm.
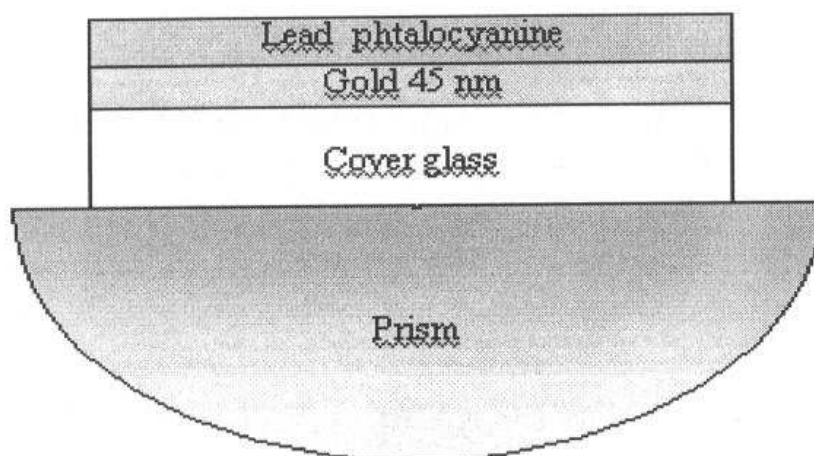

Fig.1. Film structure composition with a sensor film of phthalocyanine.

Fig. 2 presents the results of signal measurements in a detector for a multi-layer structure with phthalocyanine about 50nm thick in the presence of nitrogen dioxide. Fig. 3 shows spatial illustration of sensitivity function of that structure. As a measure for the structure intensity sensitivity to the influence of NO_2 the following formula was assumed :

$$S = \frac{\Delta R}{R_1} = \frac{R_2 - R_1}{R_1} \quad , \qquad (1)$$

where R_1 – signal from a detector during the presence of a sensor film in nitrogen, R_2- signal from a detector during the presence of a sensor film in the mixture of nitrogen and nitrogen dioxide of a tested concentration.
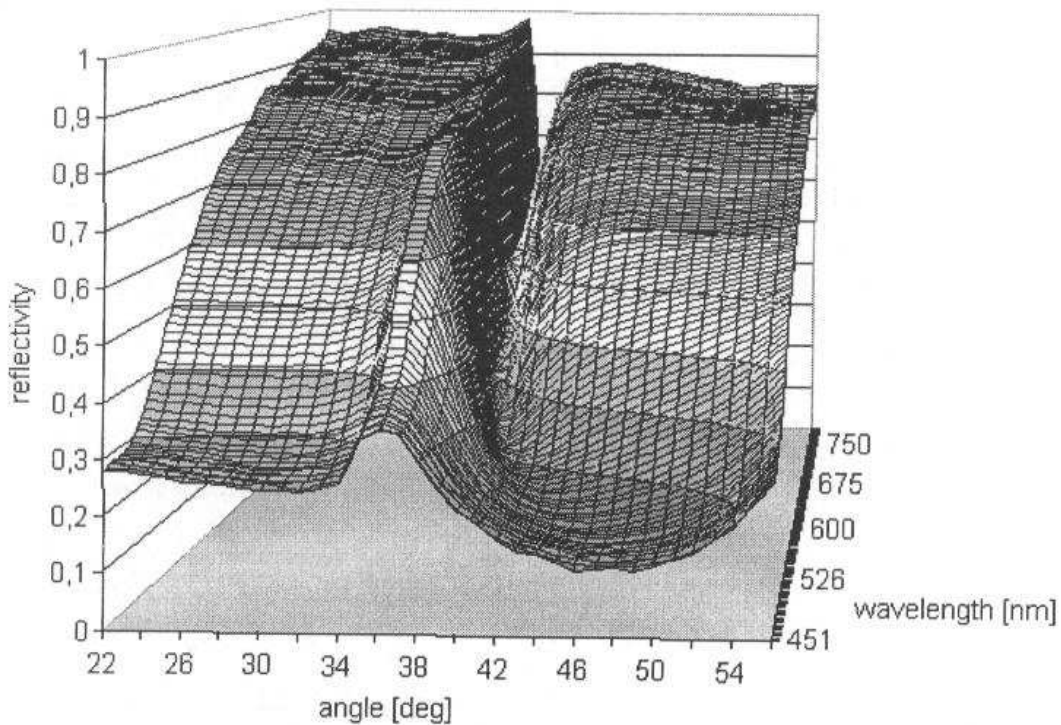

Fig.2. Dependence of signal in a detector in the function of light wave length and incidence angle of detector light. The tests were carried out for the structures: sodium and calcium glass, Au 45 nm, lead phthalocyanine 50 nm, in the presence of air.

Theoretical analyses show that the characteristics of plasmon structure reaction in the function of wave length is of a resonance character [3- 5].

For the light incidence angle, when the detector records the minimum of a signal, the biggest resonance energy absorption of electromagnetic wave occurring in the structure for the benefit of surface plasmon wave [3-5] takes place in a given sensor layer. The experiments show that the

angle at which the resonance absorption of electromagnetic wave in a structure occurs changes its value together with the change of phtalocyanine film in a sensor film structure.

Fig. 3 presents signals in a detector with visible plasmon minima for various thickness of lead phthalocyanine in film structures examined in the presence of nitrogen and the mixture of nitrogen and 100 ppm of nitrogen dioxide.
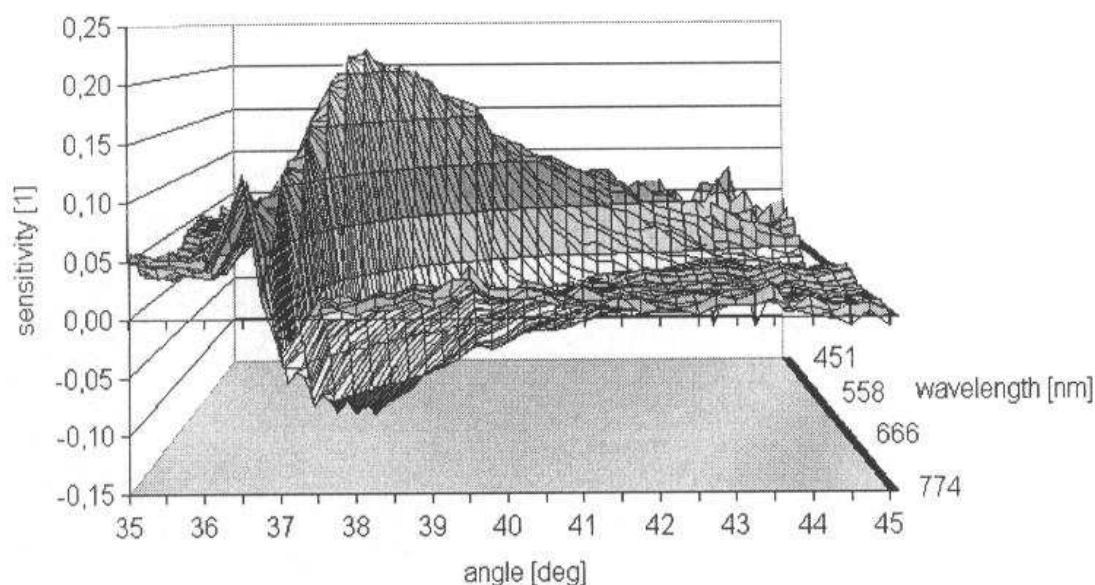

Fig. 3. Sensitivity of a multi-layer structure (sodium and calcium glass + 45 nm Au + 50 nm PbPc) to the exposure of NO_2 of a concentration of 100 ppm .

The characteristics presented show that there is a strong influence of phtalocyanine film thickness on the size and position of plasmon minimum. The characteristics are shifted as a result of the exposure of a layer system to NO_2. The thicker phthalocyanine, the shallower minima of the characteristics – Fig.4. Their changes show that structures with a film of lead phtalocyanine are sensitive to the influence of nitrogen dioxide. For thinner films big intensity sensitivity can be observed , while for thicker films sensitivity resulting form the transfer of plasmon minimum to the higher value of light incidence angle. That offers opportunity to detect sensitivity of a sensor layer NO_2 in two ways. : by the measurement of the changes in signal size and by the measurement of the transfer angle of plasmon minimum. Fig.4 shows that with decreasing thickness of phthalocyanines the minima of recorded signal are observed for the decreasing value of the angle up to a certain boundary value. Further decrease in phthalocyanines thickness results in return

transfer of signal minima. The chapter below describes and analyses sensitivity for some thickness of lead pthalocyaninines.
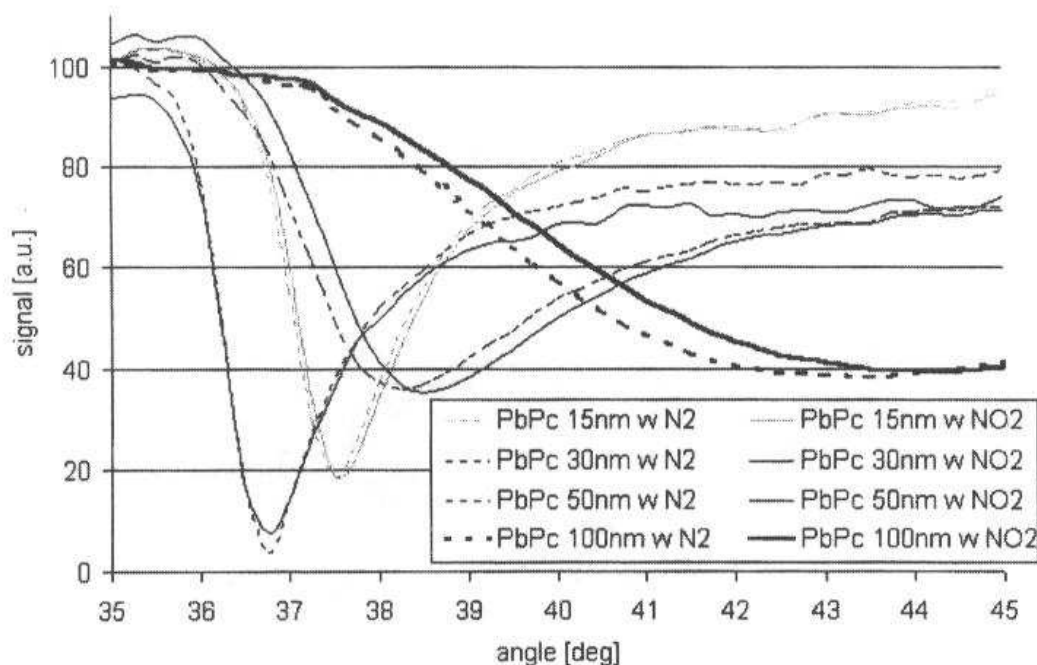

Fig.4. Signals in a detector in the function of detection angle with visible plasmon minima for lead phthalocyanine of a thickness of a) 15 nm; b) 30 nm; c) 50 nm; d) 100 nm, examined ion nitrogen and the mixture of nitrogen and 100 ppm of NO_2.

2.3. SENSITIVITY TO NO_2 OF SENSOR PHTHALOCYANINE FILMS ON THE BASIS OF GOLD FILM.

Literature [6–12] informs that molecular crystals including metalophthalocyanines, show high sensitivity to oxidizing and reducing gases, including NO_2. Sensitivity of phtalocyanine films also depends on the morphological structure of its surface and the type of the central atom present in the macro-ring [6]. Sensitivity of metal-phthalocyanines to the influence of gases depends on the thickness of a film and mutual proportion of metal-phthalocyaninne molecules to gas molecules.

Fig.5 presents sensitivity characteristics of lead phthalocyanine films in the function of wave length for some chosen thickness. The measurements were taken in the atmosphere of N_2. As shown in Fig. 6, spectral range of sensitivity of phthalocyanine layers for particular thickness of them is the widest for the film about 30 nm thick. That is the optimal thickness of a film considering both recorded high sensitivity of a signal and a wide spectral range, where sensitivity is high.

It can be also observed that decreasing thickness of phhtalocyanine results in the shift of maxima towards the longer waves. That dependence is observed up to thickness of a PbPc film of about 30 nm. For films of smaller thickness the shift of characteristics takes place towards shorter waves.
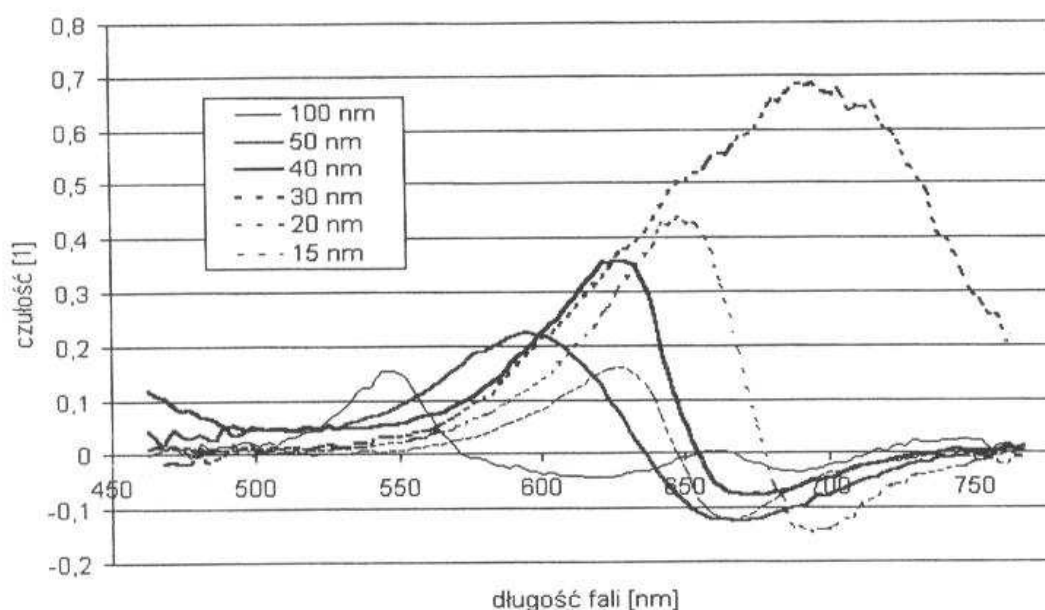

Fig.5. Spectral characteristics of sensitivity of sensor films in the function of wave length for the PbPc films of the following thickness: a) 100 nm; b) 50 nm; c) 30 nm; d) 20 nm; e) 15 nm. The diagrams were made for the light incidence angles, for which sensitivity is maximum.

As Fig. 5 shows, maximum sensitivity of films with phthalocyanine 30 nm thick, takes place in the range of red light. The dependence of the maximum value of sensitivity in the function of the thickness of phthalocyanine film is shown in Fig.6.

The experiments on layers of different phthalocyanine thickness show that the films are very sensitive to the change of light incidence angle. Fig. 7 shows spectral shift of sensitivity characteristics resulting from the change in incidence angle for two thickness of phthalocyanine: 50 nm and 40 nm. The thinner film shows bigger changes of sensitivity value resulting from the change of light incidence angle in a structure. The thinner the layer the more visible the effect.

Table 1 sums up research results for sensitivity characteristics of phthalocyanines of various thickness. It presents the review of sensor layers made on the basis of gold and lead phthalocyanine.
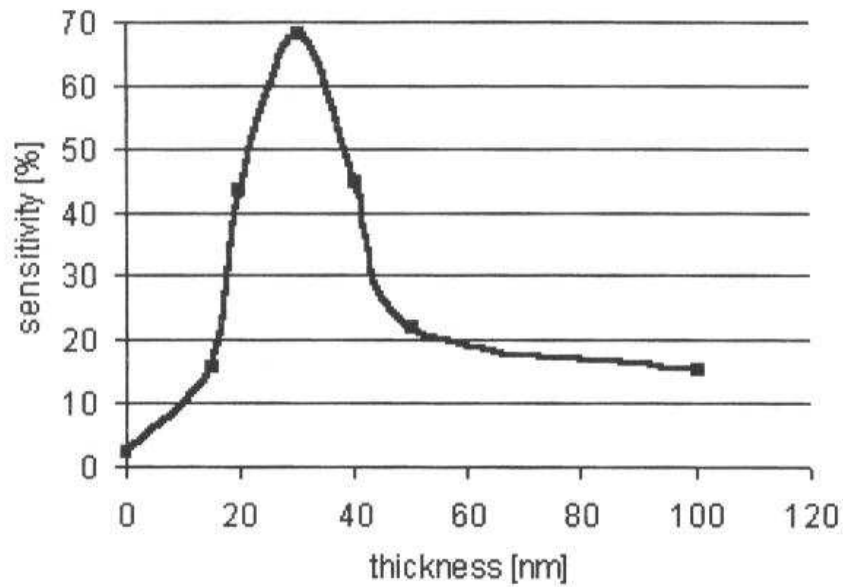
Fig.6. Dependence of lead phthalocyanine sensitivity in the function of its thickness.
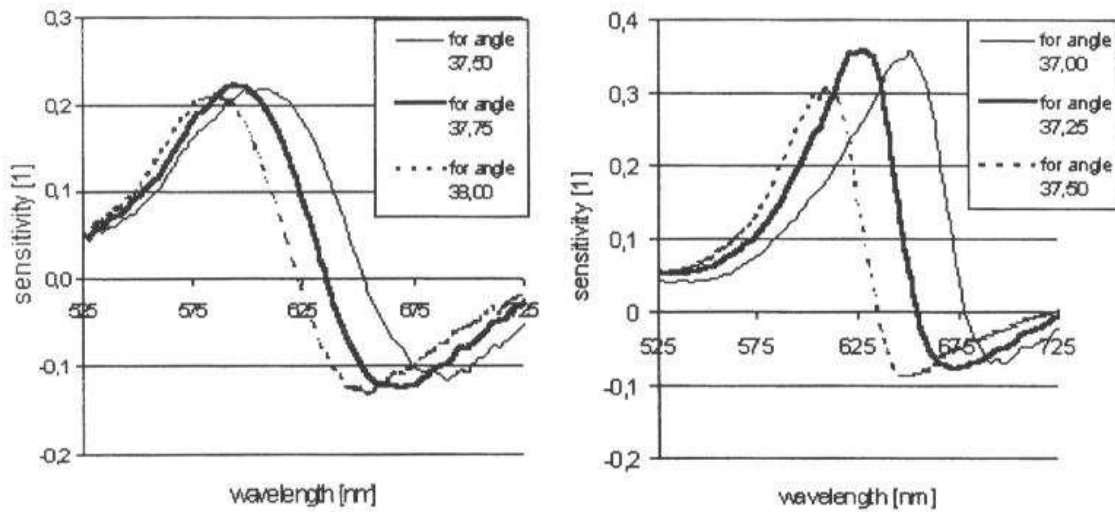

Fig.7. Spectral characteristics of sensor structures sensitivity in the function of wave length for
lead phthalocyanine of thickness : a) 50 nm (on the left); b) 40 nm (on the right).

Table 1 presents a few kinds of sensor layers , their sensitivity and ranges of wave length for their maximum sensitivity. In the last column of the table, the wave length range for which layer sensitivity is equal at least 50 % of maximum sensitivity was enlisted. The length of wave for which sensitivity gains its maximum is given in brackets.

On the basis of conducted research the optimal thickness of phthalocyanine film , when sensitivity is maximum can be defined   (Fig.6). For lead phthalocyanine the value equals about 30nm.

Table 1. Sensitivity of sensor layers on the basis of gold and lead phthalocyanine determined during the exposure of 100 ppm NO_2 for about 0,5 h.

Sensor film	thickness of phthalocyanine film [nm]	max. sensitivity [%]	Angle* [deg]	range of wavelength [nm]
Lead phthalocyjanine				
1. Au+PbPc	100	15,5	41,25	528-560 (549)
2. Au+PbPc	50	22	37,75	558-621 (594)
3. Au+PbPc	40	35,5	37,25	610-660 (627)
4. Au+PbPc	30	68	37,25	615-737 (681)
5. Au+PbPc	20	43,5	37	618-666 (648)
6. Au+ PbPc	15	16	37,25	600-642 (627)
Gold	0	2,5	37	590-620 (600)

* Angle for which sensor layer sensitivity is maximum.

2.4. RESEARCH ON THE REGENERATION OF PHTHALOCYANINE FILMS AFTER THE EXPOSURE TO NITROGEN DIOXIDE.

Thorough research on thin layers of lead phthalocyanine from the point of view of their ability to regenerate was carried out. Experiments were conducted on sensor films of phthalocyanine thickness of 50 and 30 nm. Once phthalocyanine had been vacuously placed on a gold film , the samples were heated in vacuum for 1 hour at a temperature of about 100°C to purify phthalocyannine film before the exposure to gas.

The first sample 50 nm thick had been for half an hour to 100 ppm of nitrogen dioxide and then, the structure was placed for about 1 hour in the atmosphere of nitrogen. The structure did not show any signal changes after one –hour stay in the air. The results were identical to those obtained in

the mixture of 100 ppm of NO_2 with nitrogen (Fig.8) . Therefore, further research on the influence of external factors on a given structure was taken up. During further research the film was heated for half an hour at a temperature of 373 K (100°C) and then, once again exposed to 100 ppm of NO_2.
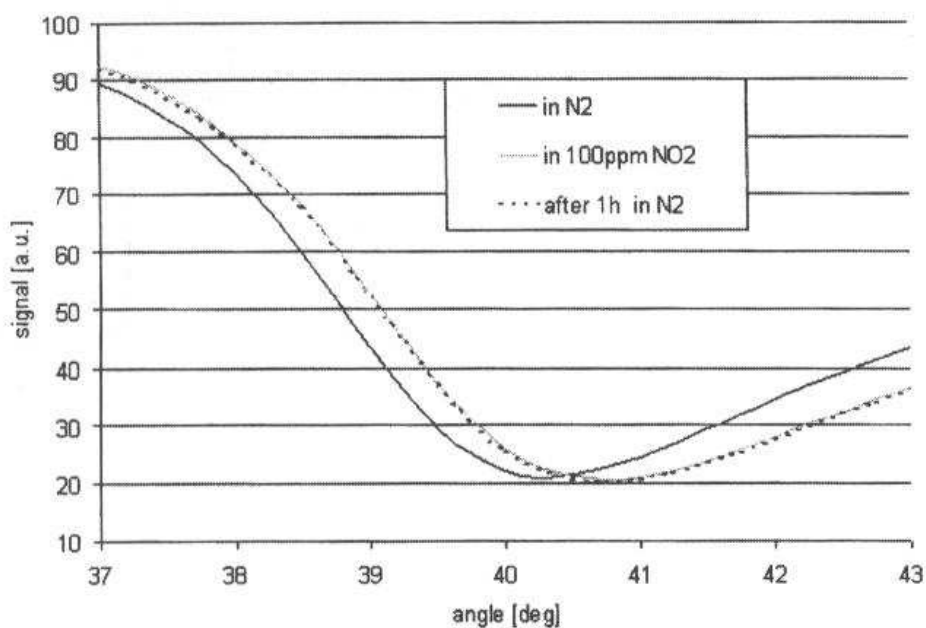

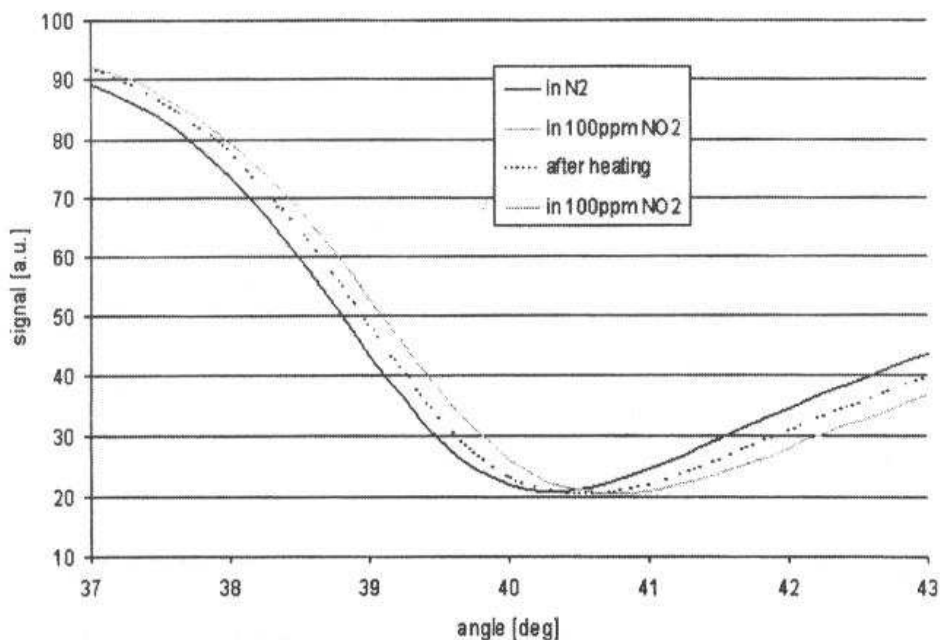Fig.8. Answer of sensor films with 50 nm PbPc lead on gold influenced ppm of NO_2.

Fig.9. Answer of sensor film with 50 nm PbPc lead on gold undergoing regeneration by heating and then, exposed again to 100ppm of NO_2.

Fig. 9 presents signal in a detector after subsequent processes the sensor layer underwent.

After one-hour film recovery in nitrogen at a room temperature , the signal measured does not change its position in practice (Fig.8). The changes are observed after regeneration at a temperature of 100°C. The shift of resonance minimum indicated partial recovery of the layer. Another half an hour exposure to 100 ppm of NO_2 causes that the recorded signal is identical to the one registered during the first exposure to NO_2 (Fig.9).

Fig.10 shows the changes in sensitivity of the same sensor layer that underwent the process of exposure and regeneration described above at a temperature of 100°C and its another exposure to nitrogen dioxide.
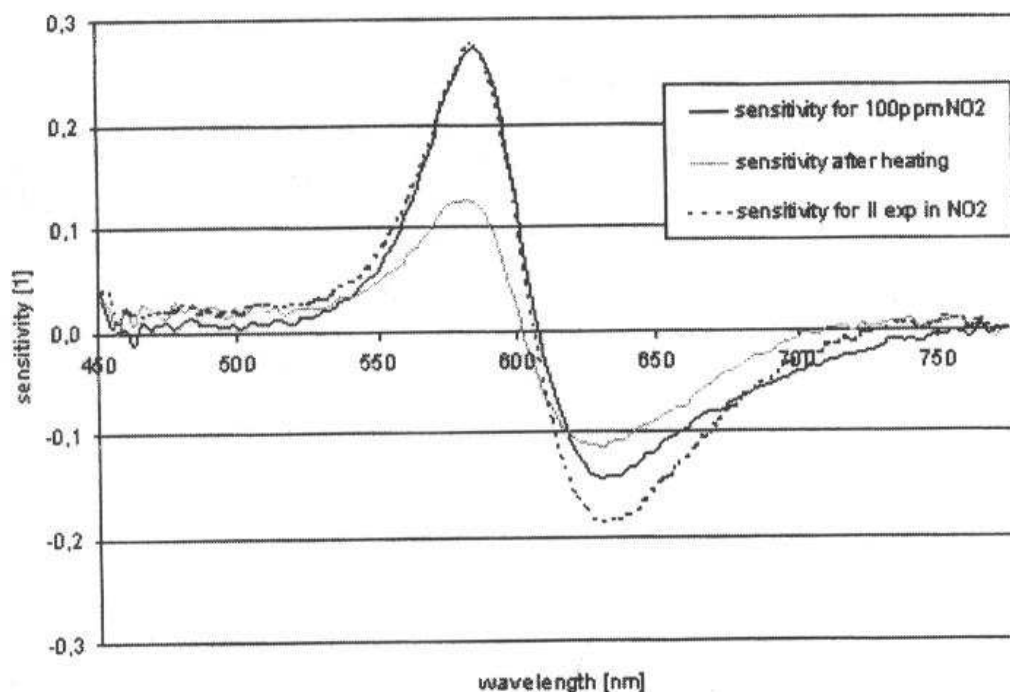

Fig. 10. Sensitivity of sensor layer with 50nm lead phthalocyanine exposed to 100 ppm of NO_2, regeneration at a temperature of 100°C and one more exposure to NO_2.

As shown in Fig. 10, sensor layer of phthalocyanine after heating at a temperature of 100°C shows partial (50 %) detoxication . However, after another exposure to 100 ppm of NO_2, the layer shows the same value of sensitivity as for the first exposure. It can be stated that the sample after heating tends to recover and is still sensitive to nitrogen dioxide. It can be expected that higher temperature or rather longer heating time can result in entire regeneration of an examined film.

During another experiment a sensor layer of phthalocyanine of a thickness equal 30 nm was examined. The sample had been vacuously placed on a film of gold and then, heated for two hours at a temperature of about 100°C in order to purify phthalocyanine film before its exposure to gas.

Fig. 11 presents the reaction of sensor layer exposed to 100 ppm of NO_2, regeneration in nitrogen, the second exposure to NO_2 and heating in vacuum for 1 hour at a temperature of 80°C. The plasmon minima shown in the figure change their position but after having been exposed to NO_2, the curve does not regain its initial position even after heating in vacuum for 1 hour.
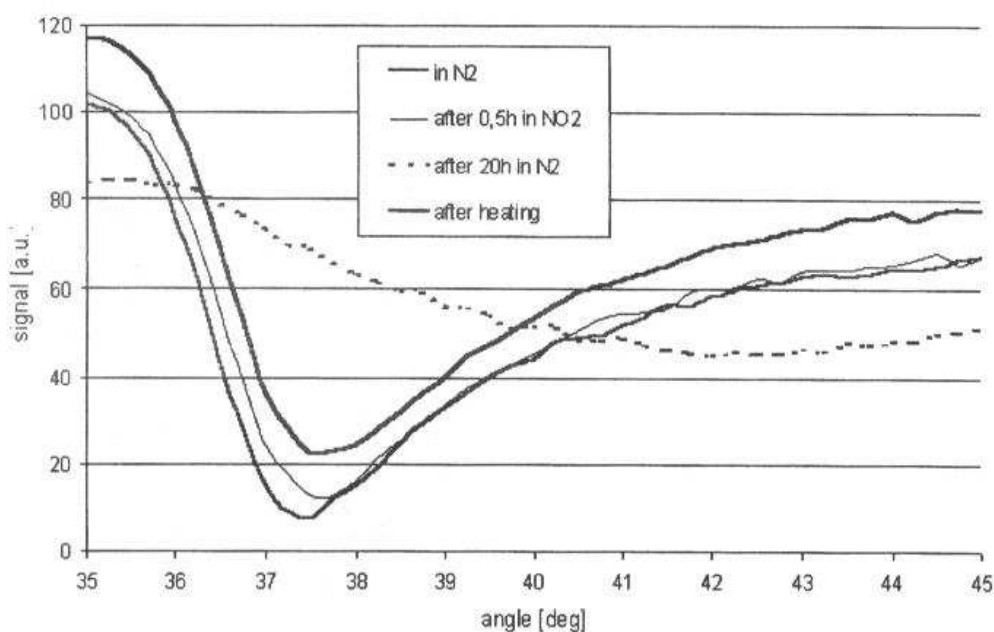

Fig. 11. Reaction of sensor layer with 30 nm of lead phthalocyanine exposed to 100 ppm of NO_2 , regeneration to nitrogen and heating.

Fig. 12 shows layer sensitivity at particular stages of the experiment. As observed in Fig. 11 and 12, the sensor layer examined exposed to NO_2 for the first time does not recover at a room temperature. The layer left for 20 hours in the atmosphere of nitrogen changes the picture of signal in a detector, which is clearly visible in; both figures. Next, the layer heated in vacuum shows partial regeneration. That recovery does not, however, take place to such a degree as it was in the case of the layer presented in Fig.9 and 11. It is probably cased by long-term stay of NO_2 molecules on the surface of phthalocyanine, where the molecules of nitrogen dioxide had been absorbed to phthalocyanine volume in the process of diffusion [8]. Thus, the structure of phthalocyanine was changed [8,9] and heating in vacuum only purified the surface of phthalocyanine film from the NO_2 molecules. As a result , after the second exposure to nitrogen

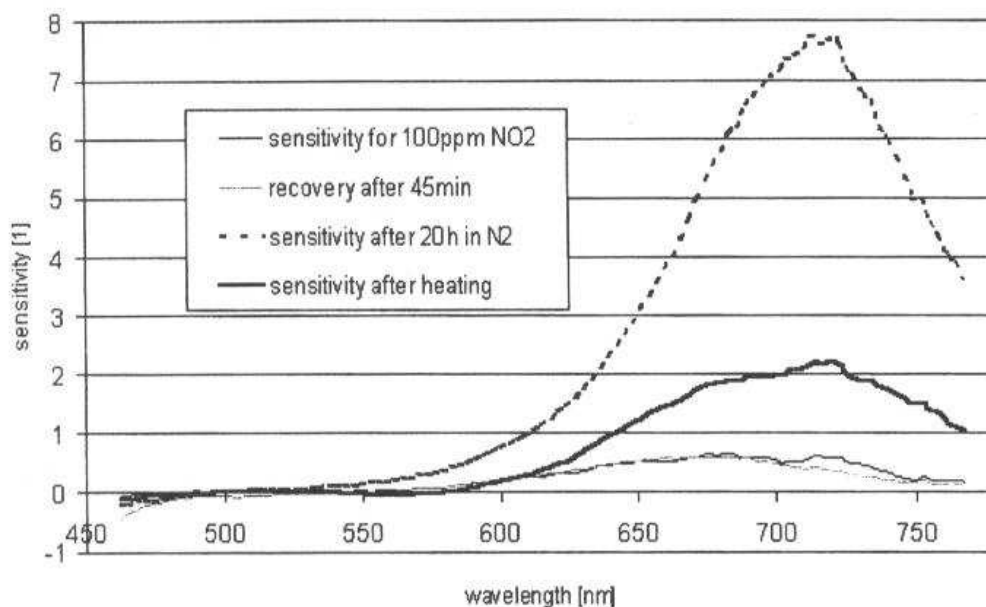dioxide, the phthalocyanine layer did not entirely recovered once it had been heated in vacuum – Fig.12.

Fig.12. Sensitivity of sensor layer with 30 nm of lead phthalocyanine exposed to 100 ppm of NO_2, exposed to nitrogen and heated.

In the reaction between phthalocyanine with the oxidizing gas (e.g. NO_2) the charge is shifted between gas molecules and phthalocyanine molecule [6]. During the reaction between phthalocyanine and gas such as NO_2 in the gas adsorption process ,additional carriers are produced on the surface resulting form the oxidation of the system of phthalocyanine ring by nitrogen dioxide [6,7]. In this way, resulting from the reaction between NO_2 and phthalocyanine electrical and optical parameters of sensor surface are changed. The author [9] suggest the following explanation to the mechanism of phthalocyanine reaction to NO_2, basing on spectrometric tests in the infrared. On the surface of phthalocyanine a quick adsorption of NO_2 in the first few monolayers takes place as well as a slow diffusion in the material volume [6,9]. The process occurring on the surface of phthalocyanine during the exposure to NO_2 will be described in chapter 3 of this paper.

2.5. EXAMINATION OF LEAD PHTHALOCYANINE OBTAINED IN FLASH EVAPORATION ON THE BASE WITH A GOLD FILM OF A TEMPERATURE 170°C.

In the process of flash evaporation 45 nm of gold was placed on a base and then, a few various thickness of lead phthalocyanine in the range from about 40 to ca. 90 nm.

Fig. 13 presents signals in a detector in the function of detection angle with visible plasmon minima. The increase in the film thickness results in the shift of plasmon minimum towards bigger angles and causes that the minimum becomes shallower. Fig. 14 shows sensitivity of the described films in the function of wavelength. The biggest sensitivity is shown by the film of the smallest thickness and it equals ca. 61 % for the wave length 594 nm.
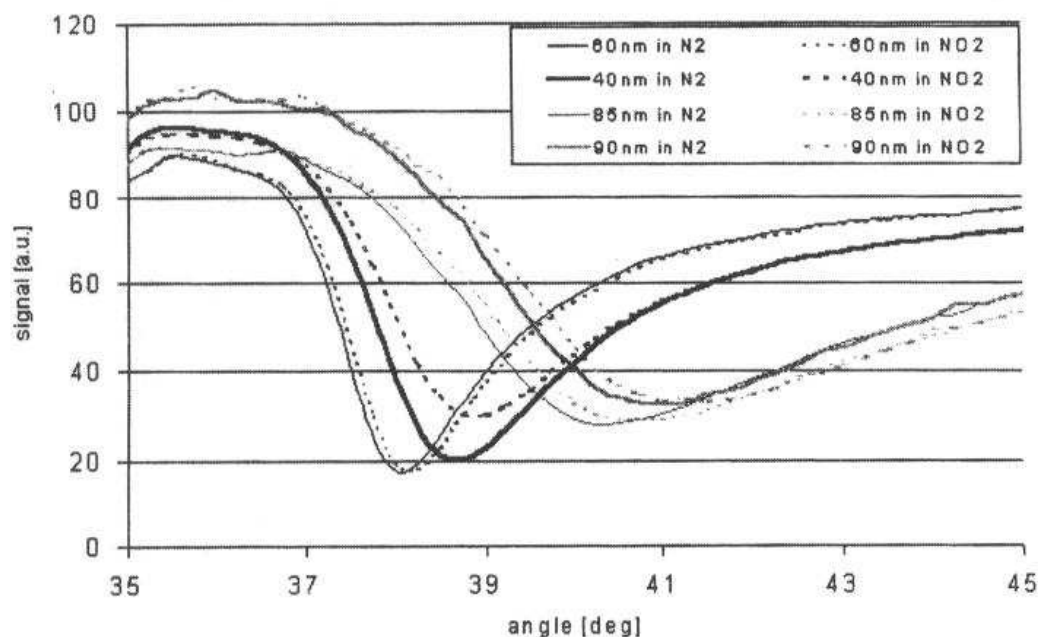

Fig.13. Signals in a detector in the function of detection angle with visible plasmon minima for lead phthalocyanine of the following thickness : a) 40 nm; b) 60 nm; c) 85 nm; d) 90 nm examined in nitrogen and the mixture of nitrogen and 100 ppm of NO_2.

The range of wave length for which film sensitivity is significant (about 50 % of maximum sensitivity) , is similar for all the films and within the range 570 to 612 nm.

During the next experiment optical parameters of phthalocyanine film in its exposure to NO_2 were tested and then, its ability to regenerate while being heated.

Fig. 15 presents the reaction of sensor layer of a thickness equal 50 nm PbPc exposed to 100 ppm NO_2, nitrogen and then heated. The layer reaction during the exposure to nitrogen dioxide stabilizes after about 25 minutes indicating sensitivity of 40 % signal change. After a long stay in the atmosphere of nitrogen (more than 20 hrs) , phthalocyaline shows the change of reaction signal. The sensor layer was not purified from nitrogen dioxide molecules after the exposition to NO_2. The fact triggered off the diffusion of NO_2 molecules to the volume of phthalocyanine, which could change its structure and the signal picture in the sensor layer.
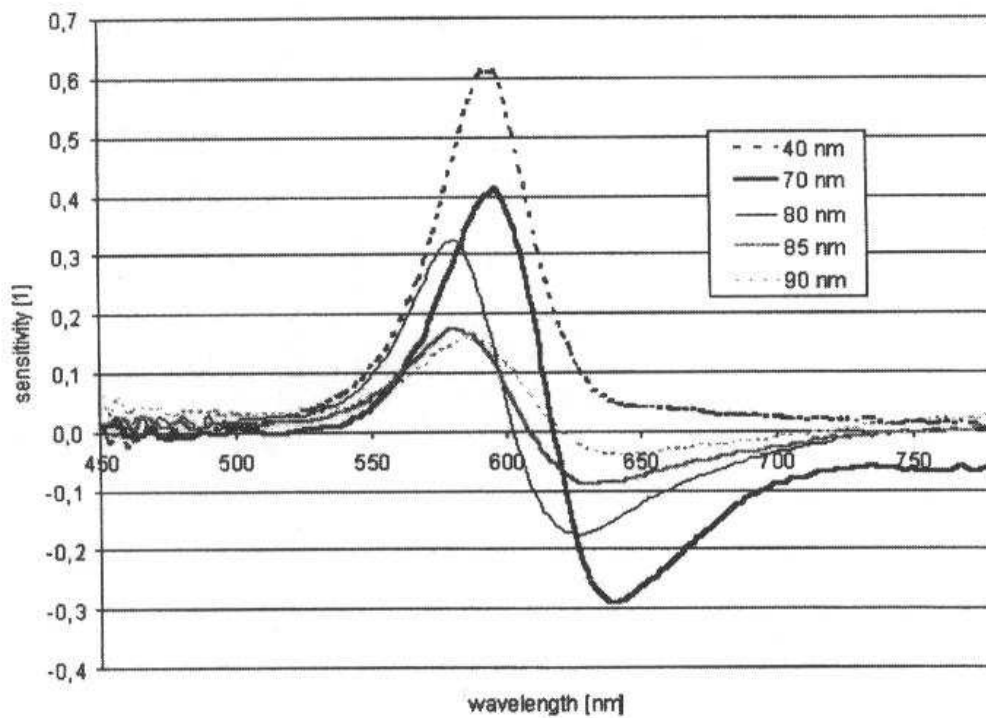
Fig.14. Spectral sensitivity characteristics for sensor layers in the function of wave length for the PbPc films of the following thickness : a) 40 nm; b) 80 nm; c) 85 nm; d) 90 nm. The diagrams were made for those angles of the maximum value of sensitivity.
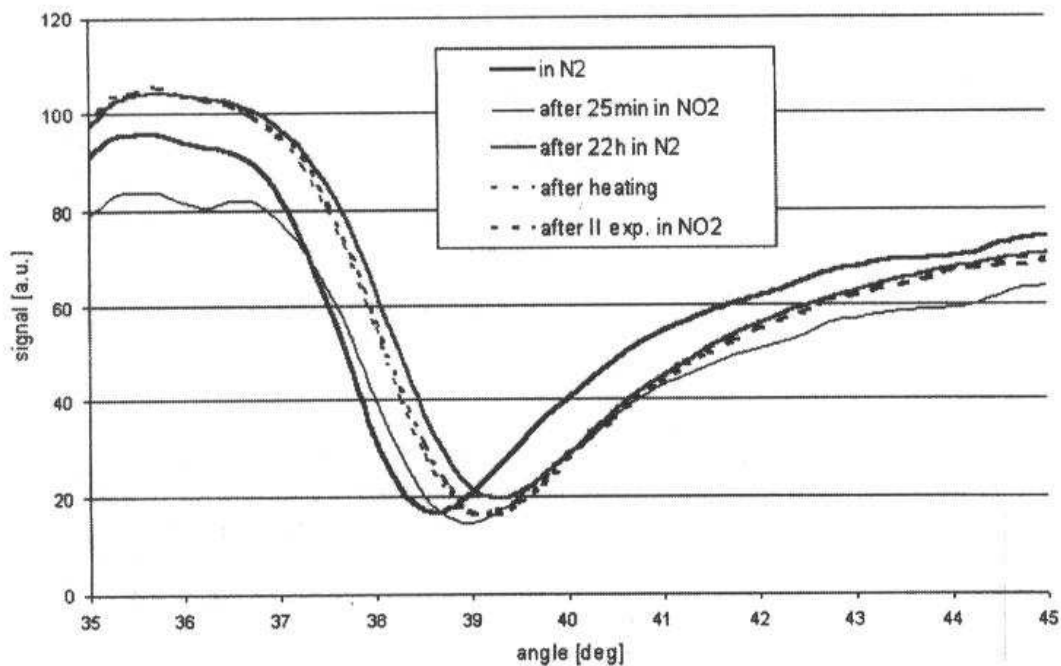

Fig.15. Reaction of sensor layer with a 70 nm PbPc layer exposed to 100 ppm of NO_2 , regeneration in nitrogen and heated.

Next, the layer underwent heating process , where it showed minor recovery abilities. After heating process it does not show almost any sensitivity to 100 ppm of NO_2 during half an hour exposure to that gas.

3. DISCUSSION AND CONCLUSION.

Considering experiments on mainly thin lead phthalocyanine films a strong relation between film thickness and sensitivity can be noticed. Spectral characteristics of the examined films prove wide opportunities to make of specific properties pf phthalocyanines. Dynamic change of wave length range , where phthalocyanine layer is sensitive to NO_2 together with the change of its thickness allows to match the properties of the layers according to the needs. It is worth noting that most optimal parameters of lead phthalocyanine reach the thickness of 30 nm with sensitivity of ca. 95 %. Maximum sensitivity takes place in the range of the red . Phthalocyanine films placed on a base of an increased temperature (170°C) show small changes in the spectral range of sensitivity alongside the change in thickness. Probably the optimal film thickness can be defined for all phthalocyanines.

Research on film regeneration significantly confirm the nature of reactions between oxidizing gas and phthalocyanine. For the concentrations of 100 ppm of NO_2 all the changes in visible and NIR spectrum are almost reversible [9]. Therefore such concentrations of nitrogen dioxide were used in the experiments. Peculiar and various properties of phthalocyanines result from the structure of a macro-ring of phthalocyanine molecule [9]. The efficiency of surface charge transfer depends on the potential of donor ionization, acceptor electron affinity and polarization energy resulting form the transfer of anion and positive ion charge transfer (i.e. their energy reaction with a polarized local surrounding). [9]. Gas molecules absorbed on the surface of a solid body have less polarized surrounding than those bound in gaps and consequently, they can be easily transferred. It gives a fast solid body answer to the influence of NO_2. Gas molecules bound in gaps give a free irrevocable surface answer [9] .

On the basis of research results presented in Fig. 11 and 13 it can be concluded that in the examined films of metal-phthalocyanines takes place diffusion of NO_2 to the film volume and even heating at a temperature ca. 100°C does not remove NO_2 from the volume of metal-phthalocyanine.

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