

## **INVESTIGATIONS OF OPTICAL INTERFEROMETRIC STRUCTURES FOR APPLICATION IN TOXIC GAS SENSORS**

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### 1. INTRODUCTION

The ecological consciousness of the societies has grown in a recent years with progressive industrialization and degradation of the natural environment. Hence the concern about nature preservation and safety has become apparent, and a lawful compulsion of safety in industry, and public places. Many of world known centres of science have focused their attention on developing of effective gas sensors, and on investigations of sensor materials. Since 1990 the optochemical methods of gas detection have become more popular [1]. Their main advantages, comparing to conventional electrical methods, are resistance to electromagnetic interferences, fast response time, functionality in flameable atmospheres. Optochemical sensors, combined with standard optical telecom fibres and integrated optics systems, give an opportunity to create integral optical remote sensing systems.

In optical sensors the detected gas can interact with a sensor layer in many different ways, modifying its optical properties (index of refraction, absorption coefficient, etc...).

The changes of optical properties can be measured in various experimental set-ups.

The most common and mentioned in the literature methods are:

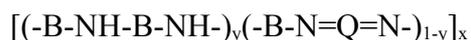
- absorption spectra changes [1],
- reflectance changes measurements[2],
- luminescence intensity variations [3],
- evanescent wave analysis – based methods [4],
- surface plasmon resonance methods (SPR) [5,6],
- interferometric methods [6].

## 2. POLYMERS AS INTERESTING SENSING MATERIALS

In the recent years polymers have been given a great attention in a field of active materials for gas sensor applications. There is a wide opportunity of developing polymer-based gas sensors due to the structure variety of polymers and versatility of chemical and physical interactions between an analyte and a polymer sensor layer [7].

Among conducting polymers, being investigated as materials for a polymer-based gas sensors the one of especially interesting is polyaniline (PANi). The electrical conductivity of polyaniline can be easily modified by its doping by metals, semiconductors or various chemical substances. Also high environmental stability and redox properties of polyaniline, connected with nitrogen atoms in polymer chain, are very interesting for sensor applications. Comparing to the polypyrrole and polythiophene the processing of polianiline is relatively easy due to the high solubility of polyaniline in organic solvents [8].

The structure of the PANi chain, presented in Fig.1, can be expressed by a general formula:



where, B and Q denote the C<sub>6</sub>H<sub>4</sub> ring in benzenoid and quinoid form, y denotes oxidation state and can vary from 0 to 1.

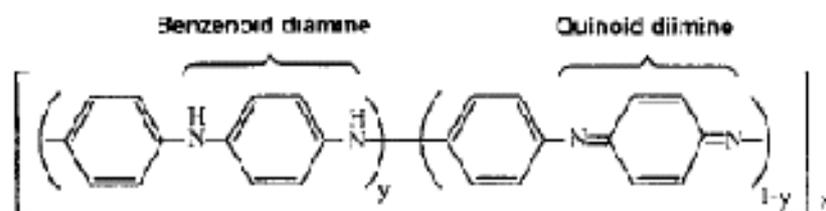


Fig 1 Structure of the polyaniline chain structure (base form) [9]

Polyaniline occurs in many different forms which vary in chemical and physical properties. The intrinsic oxidation state of PANi can have the value from  $y = 0$  for fully oxidized *pernigraniline* (PNA), through 50% oxidized *emeraldine* EM -  $y = 0,5$ , and finally  $y = 1$  for fully reduced (*leucoemeraldine*) (LM,  $y = 1$ ) [8,9].

The most important feature that makes polyaniline so interesting and feasible as a sensor layer for detection of toxic gases is variation of its electrical and optical properties. The variation occurs with protonation and deprotonation process during interaction with gas, which changes the doping state of PANi. The low price of the polymerization substrates and high efficiency of polymerization process is also very significant [10,11,12].

### 3. AMMONIA SENSING SYSTEM – THE SET-UP AND THE PRINCIPLE OF OPERATION

The idea of presented optical ammonia sensor is based on variations of reflected light spectra result from interactions of ammonia with sensing layer. The sensor is the optrode-type fibre-optic sensor. The system monitors the light reflected from the face of the fibre. The sensor head consists of polyaniline and Nafion® layer deposited on the face of the fibre (Fig 2). Nafion® (DuPont product) is a copolymer of tetrafluoroethylene (Teflon®) and perfluoro-3,6-dioxa-4-methyl-7-octenesulfonyl fluoride. Nafion® is highly resistant to chemical attack, but the presence of its exposed sulfonic acid groups confers unusual properties. Sulfonic acid has a very high water-of-hydration, absorbing 13 molecules of water for every sulfonic acid group in the polymer. Consequently, Nafion® absorbs 22% by weight of water [13].

The refraction index of Nafion® was estimated with the Abbe refractometer, and its value was equal to 1.364 (5% solution in mixture of water and lower alifaticalcohole).

In the sensors were used standard telecommunication fibres (from the range of a first telecommunication window - 850nm). As the light sources the white LED or incandescent lamp were used. The lamp ensures high intensity of light in red and near infrared range where strong variations of the reflected spectrum were expected, in effect of ammonia action on sensor structures.

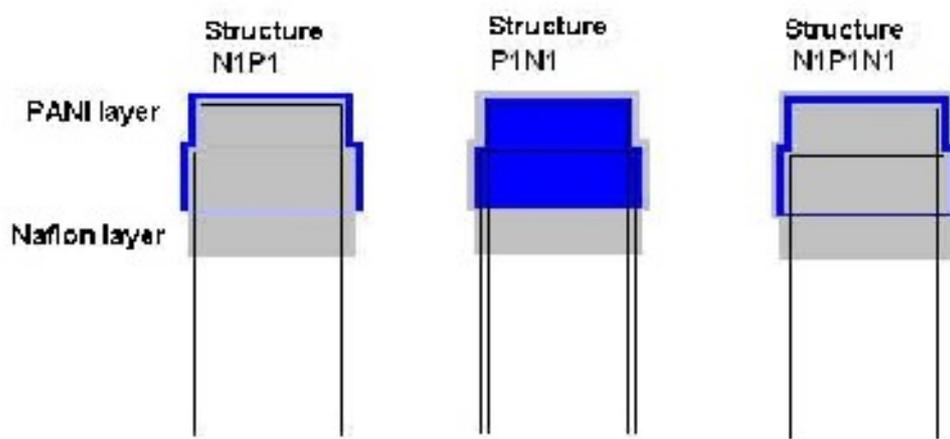


Fig 2 Scheme of the sensor heads

The spectrum analysis is performed by SpectroART-14.1 spectrometer, which spectral range is 380nm – 780nm. (The spectrometer is based on a reflection grating and a CCD array with 256 pixels.) The experimental set-up is presented on Fig 3.

(The connection between the fiber with an investigated sensor and the fibre from the coupler is ensured by a capillary tube connector, with an immersion liquid that provides no reflection at the connector.)

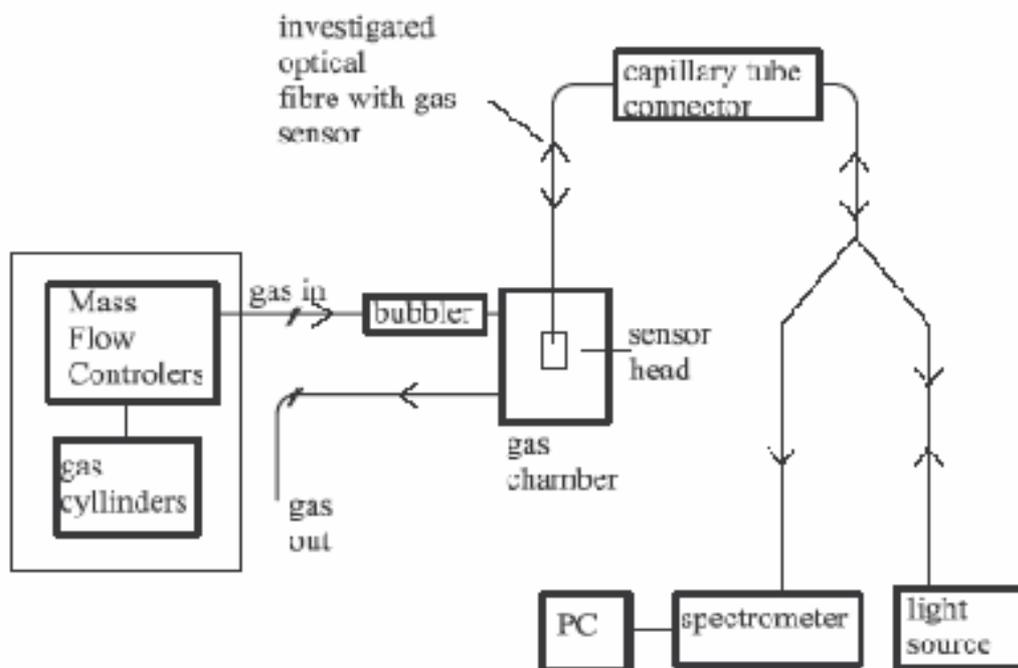


Fig 3 Experimental set-up

#### 4. TECHNOLOGY OF GAS SENSORS

##### 4.1 Synthesis of polyaniline solution

The polyaniline solution has been obtained by the polycondensation oxidizing of aniline in an acidic environment. A solution of 2.25 cm<sup>3</sup> freshly distilled aniline and 1 mole solution of sulphuric acid has been prepared. After dissolution of precipitated aniline sulfate the mixture was cooled in a refrigerator for about 2h at ~5°C temperature.

Simultaneously a solution of oxidizer (5.7g) – ammonium persulfate dissolved in 1 mole solution of sulfuric acid, has been prepared. The oxidier solution has also been cooled for 2h at ~5°C. After cooling, the solutions were mixed together in a beaker for 1h. and next they were left for 24h at room temperature (~18°C). Subsequently the polyaniline was filtered and next it was rinsed with sulfuric acid solution and then it was left to dry (at room temperature). The discussed PANi was doped with camphorosulfonic acid, and deprotonated by mixing with 1 mole solution of ammonia.

Deprotonated PANi (50 mg) was introduced to 5 cm<sup>3</sup> N-metylopirolidone (NMP) and after mixing left for 2-3 days. Then, the solution has been filtered. The filtrate was homogeneous solution of polyaniline in N-metylopirolidon

#### 4.2 Deposition of sensing layer

Polyaniline and Nafion® were deposited on the face of the fibre by immersion of optical fiber in earlier prepared solutions. In the case of PANi, the fibre was immersed in solution of PANi for 30 minutes. Subsequently it was dried in vertical position at 110°C for 24 hours. In order to deposit some PANi sensor layers the heating of the fibre after its immersion have been lasting 1h and next the immerse processes were successive repeated. In a case of Nafion® the immersion lasted only 30s, and the fibre was than dried at 40°C for 24h. The deposition of multilayers of Nafion® involved successive 30s immersion and 20 minutes drying. The described method is simple from the technological point of view. The layer thickness seems to be dependent on viscosity and adhesive force one can assume that the concentration are roughly constant at the constant temperature of deposition, equal to 18°C.

#### 5. INTERACTION OF AMMONIA WITH SENSING LAYER

The protonation reaction with using the *HA* type acid can be expressed by a formula:



where: *PA* and *PAH*<sup>+</sup> denotes the repeating block of a polymer chain before and after protonation.

During the protonation reaction PANi a molecule gains proton, creating energetically more favourable N<sup>+</sup>- H chemical bond. The N<sup>+</sup>- H bonds form positive charge centres. The valence electrons can relocate between those charge centres, increasing the p type conductivity.

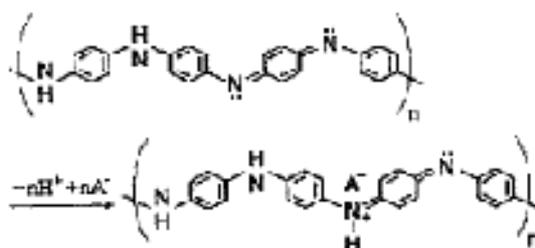
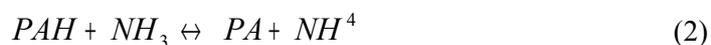


Fig 4 Scheme of protanation of PANi. The repeating block of PANi chain, before (emeraldine base) (top), and after the protation [11]

In contact with a reduction gas ( $\text{NH}_3$ ,  $\text{H}_2\text{S}$ ) the protonated form of PANi is susceptible to the redox reaction.

The interaction of PANi (the protonated emeraldine salt ES) with ammonia can be described by a formula:



In the presence of ammonia the reaction proceeds mainly towards the right side: the  $\text{NH}_3$  molecules reach the surface of PANi, react with the NH groups of the polymer chain, and gain their protons forming the energetically more favourable ammonium  $\text{NH}_4^+$ , which stay near the acid radicals  $A^-$ . Above reaction describes the deprotonation of PANi to the emeraldine base form (EB).

In air, without constant flow of ammonia, the reaction (2) starts to go towards the left side. The ammonium  $\text{NH}_4^+$  decomposes into ammonia  $\text{NH}_3$  (which volatilizes) and proton, which absorbed by PANi, recovers the initial state of doping – of ES. Hence the reversibility and regeneration of the sensor is achieved [11,14].

## 6. INVESTIGATION OF SENSING STRUCTURES

### 6.1 Measurement course

The sensor response to ammonia concentration changing from 78ppm to 5000ppm was measured. The sensor was exposed to ammonia/synthetic air mixture in a 200s cycles. Each mixture cycle was followed by pure synthetic air cycle, providing the regeneration of the sensor (by protonation of PANi). The additional dynamic regeneration was ensured by Nafion®.

### 6.2 Optimal structures

Many sensor structures of different thickness and combination of polyaniline and Nafion® layers were fabricated and investigated. The optimal solution seems to be structures with small number of PANi layers (up to two). In the structures with a greater amount of PANi layers the strong attenuation of the reflection light was observed and the output signal was weak. Simultaneously the  $\text{NH}_3$  molecules can not be able to penetrate the sensing layer deep enough to reach the lower layers. Hence the multilayer structures seems to be useless in that case.

### 6.3 The interferometer structures

The optical fiber sensor structure of the type: glass-PANi-Nafion®-air is presented in Fig.5. The reflection of light are realized on the boundaries: PANi-glass, PANi-Nafion® and Nafion® -air. For the gas sensor application the essential are the reflection at boundary PANi-glass and PANi-Nafion®. Those two reflection mirrors have been forming the resonant cavity. The two reflected beams interfere together. The interference image can be observed in reflected light that reaches the CCD array of the spectrometer. The optical properties of the cavity and the mirror are altered by the action of  $\text{NH}_3$  which determine the position of interference fringes.

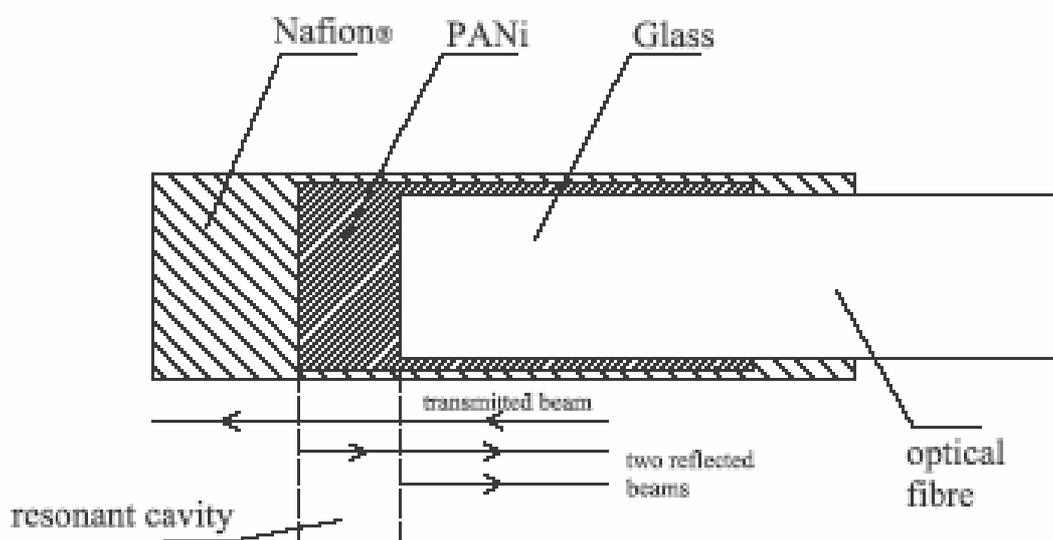


Fig 5 Sensors' head in the case of interferometer structure (the scale in not maintained)

For the analyse of the presented above interferometric structure the numerical system has been elaborated. The numerical system gives the possibility to analyse the sensing structure for arbitrary many layers for their various optical and geometrical parameters. In finally simulation the complex index of refraction of Nafion® ( $n_N = 1,364 + 0j$ ) and PANi ( $n_P = 1,9 + 0,06j$ ) were assumed. Fixing the thickness of layers one can observe that the thickness of Nafion® layer do not influence the interference image. Which means that the cavity is formed by PANi-glass and PANi-Nafion® boundaries. It is very probably because the contrast of the refraction indices between PANi-glass and PANi-Nafion® are bigger than between Nafion®-air. The size of the cavity (the thickness of PANi layer) can be estimated by

matching the measured and simulated image. From the estimation influences that the thickness of PANi layer is about 690 nm.

The most optimal structure, in respect of sensor properties, is a structure with two layers (deposited in two processes) of PANi and one layer of Nafion® at the top. (For us, the experimental structure of this kind was sign as P2N1. The thickness of PANi layers (estimated by our program) was about 690nm.

The example of the spectrum characteristic of light reflected for this sensor is presented in Fig 6.

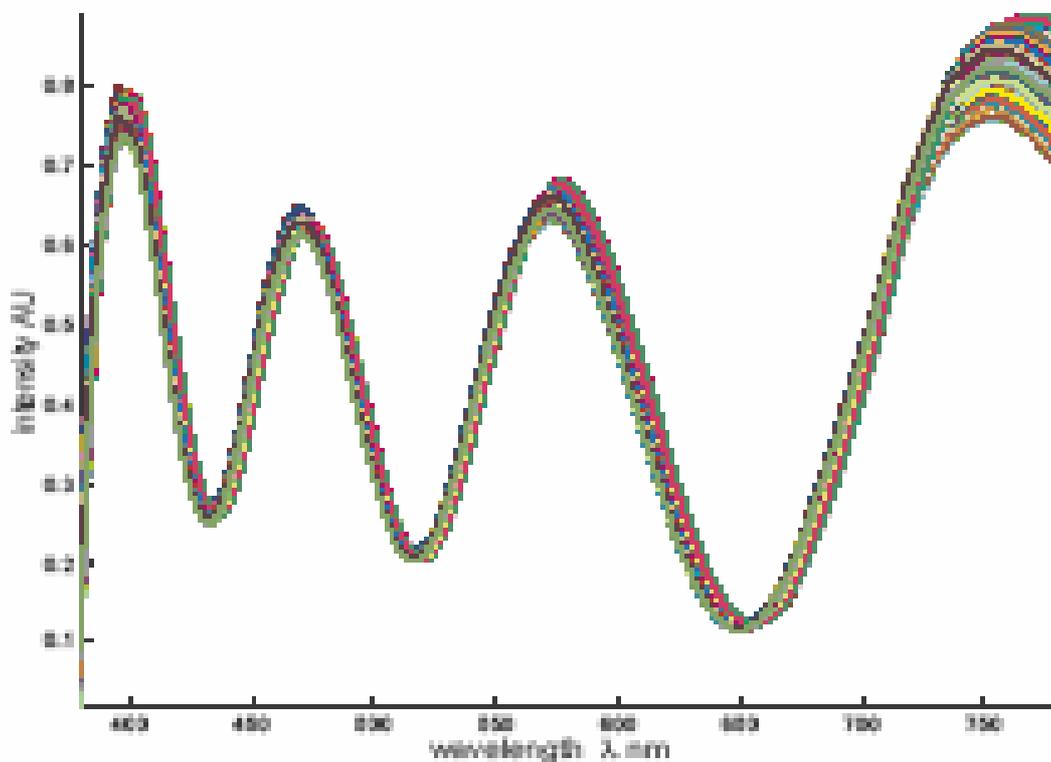


Fig 6 Reflected light relative intensity changes for P2N1 structure.  
The subsequent curves represents the spectrum in following time

The sensor response for the changes of ammonia concentration can be obtained from analysis of the position of the fringe maximum (Fig 7). Figure 7 presents also, the regeneration of the sensor properties after the ammonia flow suppression. The regeneration is caused partly by the presence of Nafion® in the sensor structure.

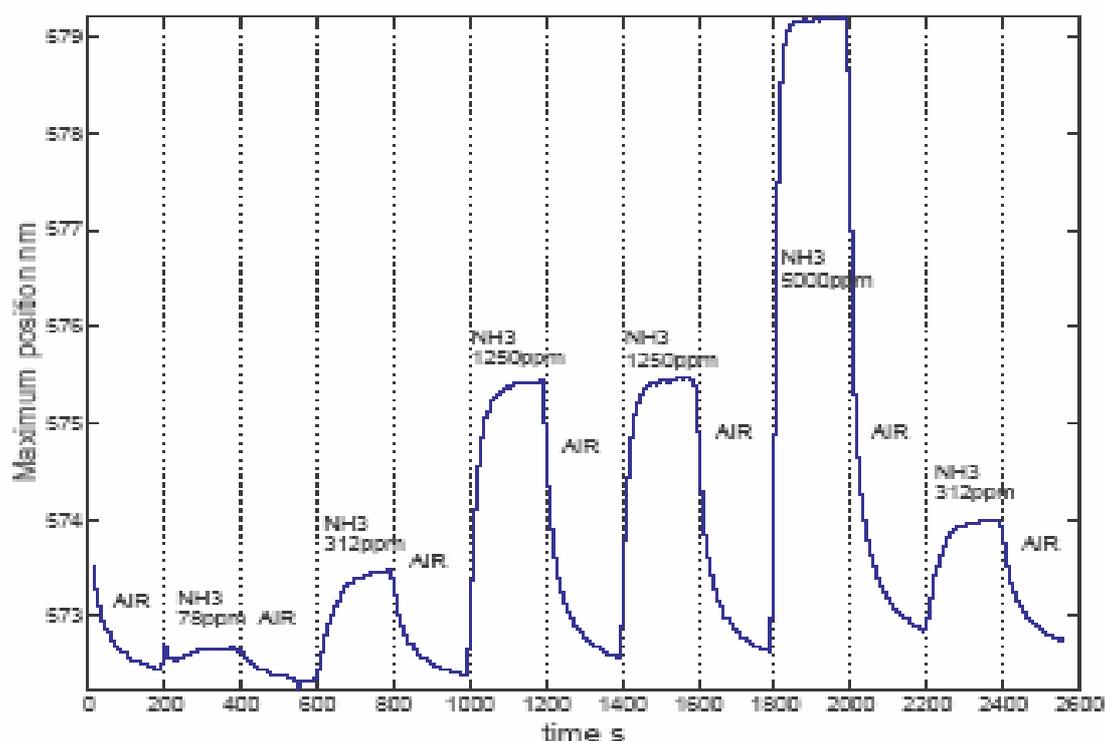


Fig 7 Maximum position variations at 540nm-600nm for P2N1 structure, in response to ammonia concentration changes

The property of the sensor are presented in Fig.8. The characteristics shows a rapid response of the sensor after the ammonia flow starts. The slow drift in the direction of higher values of frequency after stopping of gas flow is observed, too. The drift results from competitive processes of adsorption and desorption of analyte in the sensor layer. Both mechanism were considered in [15]. A small drift of a whole curve and the lack of total regeneration - returning the maximum to the initial position (572nm) seems to be caused by too short step of a single time period (200s) in the gas cycles. The longer time step should provide a better regeneration. (This problem will be investigated in a next researches.)

#### 6.4 Other Sensing Structures

In the Fig.8 are presented the results of investigations of the structure which consists only of two polianiline layers (P2) (without Nafion®) deposited on the top of the optical fiber. Fig.9 presents the results of investigations of the structure: two layers of Nafion® and polianiline (N2P1). The sensor responses are obtained from the analysis of the changes of the reflected light intensity at a given wavelength (730nm).

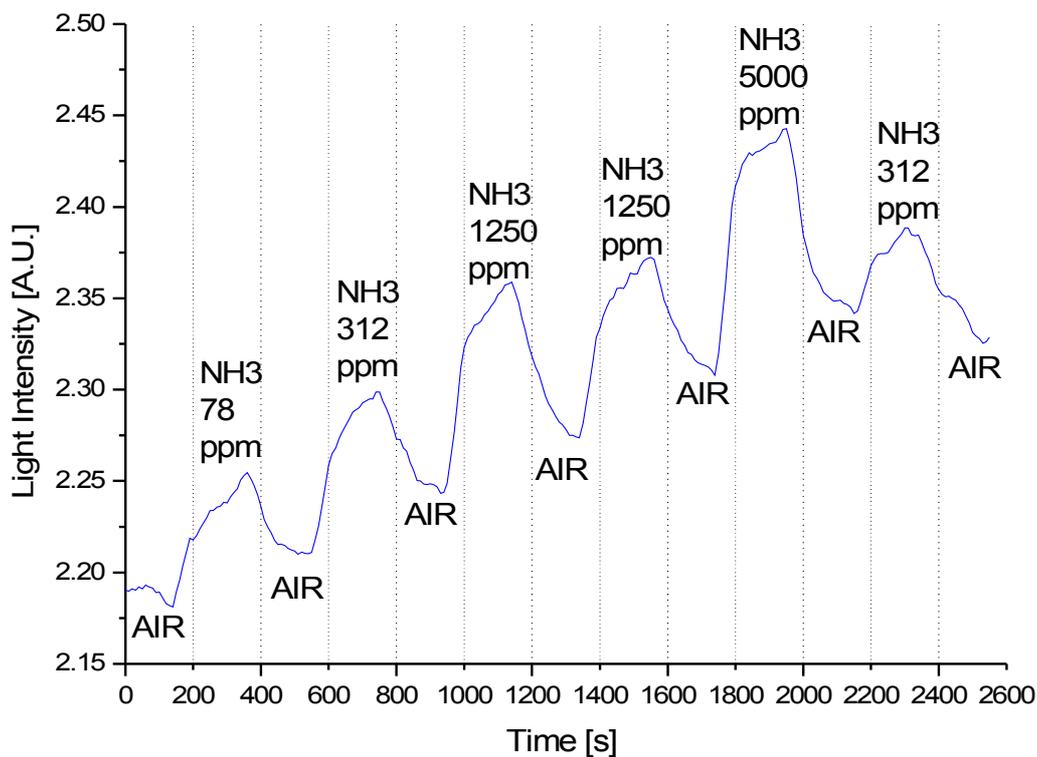


Fig 8 Reflected light relative intensity change for P2 sample, at 730 nm

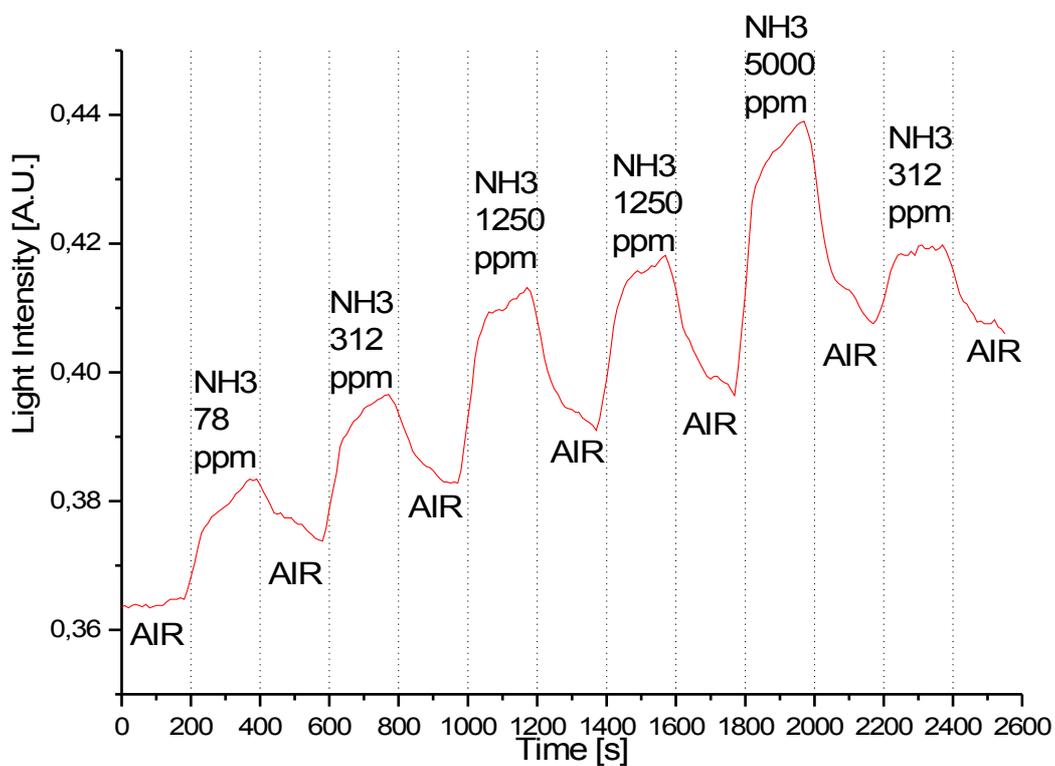


Fig 9 Reflected light relative intensity change for N2P1 sample, at 730 nm

The character of the regeneration of the sensor depends on the presence of Nafion® in the sensing structure. The relative sensitivity on the ammonia action is higher for the structure with Nafion®. It is conformed to the theoretical conclusions [11].

The measurements showed that the “sandwich” structures (Nafion®-PANi- Nafion®) are too thick. The signal reflected from such a structure is strongly attenuated. Also the protonation of polyaniline is very fast, because Nafion® layers are at both sides of polianiline. Hence sensor can not respond to ammonia because it is immediately regenerated.

The preliminary investigations shown that the elaborated sensor structures are not sensitive to NO<sub>2</sub> action. The interferometer structure P1N1 was immune to NO<sub>2</sub> up to thousands of ppm concentrations. It gives an opportunity of construction the selective NH<sub>3</sub> sensor.

## 7. CONCLUSION

Presented the optical polyaniline-based sensor can be an interesting solution for ammonia sensing in some specific conditions. The facility of fabrication and simplicity of operation makes it challenging and interesting in a group of gas sensors. Although the final product needs further investigations, the obtained results are very interesting. The researches done so far were carried out to find the most appropriate structure in respect of number and configuration of polyaniline and Nafion® layers. Further investigations of this structures will allow to determine the influence of other toxic gases, the influence of temperature, moisture or pressure on sensor properties. Also the relationship between the concentration of ammonia and observed spectral shift will be in the interest of following researches.

The characteristic feature of described experiments is the fact of carrying out the measurements in the atmosphere of synthetic air. Such a method imitates a natural work conditions of natural environment sensors. Presented in literature investigations [11,12,14,15] are realized in the atmosphere of pure nitrogen. In our opinion on their base of such investigations will be difficult to predict the behaviours of sensing structures in the natural environment.

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