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Fluorescent Chemical Sensor for Aromatic Compounds.

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ABSTRACT

Aromatic compounds can present serious medical, environmental, and explosion dangers because they are toxic even at parts per billion concentrations. Measurement of these toxic compounds at trace levels in multi analyte mixtures is still a challenging task and involves the use of expensive laboratory equipment. In this work, the simple sensor is developed which is capable to continuously measure toluene and p-xylene in binary mixtures. The main component of the sensor is fluorescent sensor material consisting of Dibenzoylmethanatoboron difluoride (DBMBF$_2$) fluorophore adsorbed on silica gel surface. The formation of the exciplexes between DBMBF$_2$ and aromatic molecules leads to appearance of new fluorescent band, which can be used for discrimination of these compunds. The analytical model for the chemical sensor operation is proposed. The model reveals ratiometric nature of measurement of proposed sensor. The sensor prototype has been created, calibrated and tested. Selective measurement of toluene and p-xylene in a binary mixture with sensor prototype is demonstrated.

Keywords: fluorescence, sensors, aromatic compounds, Dibenzoylmethanatoboron difluoride, toluene, xylene

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INTRODUCTION

Aromatic compounds are widely used in modern industry, they have many different applications and a great economic and environmental significance. Due to their toxicity even at parts per billion concentrations [1], they can present serious medical and environmental dangers. It is essential to know their concentration in the air, especially in industrial and populated areas. Although various approaches have been tested to develop low-cost sensor device [2-9], measurement of these toxic compounds at trace levels in multi analyte mixtures is still a challenging task. It involves the use of expensive laboratory bound equipment such as gas chromatography [10-15] or selective preconcentration technique [16-18].

The field of optical chemical sensors (OCS) has been a growing research area over the last three decades. Recent developments in this field have been driven by such factors as the availability of low-cost, miniature optoelectronic light sources and detectors, the need for multianalyte sensors (particularly in the area of biosensing). Optochemical sensors for detecting a wide range of analytes involving different sensing principles have been developed and have numerous applications from medical and biochemical to security systems and food-packaging industry [5]. They are used for gas detection and can utilize either direct or reagent mediated methods. Reagent mediated fluorescence detection is one of the most promising optical techniques. Advantages of this method include ultra-high sensitivity, fast response times, and the capability of continuous measurements.

Optical sensors based on fluorescent reagent-mediated principle usually consist of a sensor material and a sensor platform. The sensor material consists of indicator molecules immobilized on polymer or other type of matrix. Only such immobilization results in creation of the sensor material, because properties of the indicator molecule can be changed dramatically by immobilization. The sensor platform is linked intrinsically with physical principle used to read response of the sensor material and a technology used for device manufacturing. The main components of fluorescence read-out platform are light source for fluorescence excitation, filters for separate fluorescence light from excitation light and photodetector.

Dibenzoylmethanatoboron difluoride (DBMBF$_2$) has attracted a great deal of attention due to its specific feature, the ability to participate in quite a strong donor–acceptor interaction with organic electron donors and form charge-transfer complexes in the ground state and exciplexes in the excited state [19-25]. The formation of charge-transfer complexes in ground state and fluorescent exciplexes of DBMBF$_2$ with benzene and other aromatic compounds in various solvents was studied in detail in [20,24]. The potential use of DBMBF$_2$ as a fluorescent molecular sensor for detecting polar organic compounds and aromatic hydrocarbons in both solutions and gaseous phase was shown. [25-27]

The interaction of DBMBF$_2$ with aromatic compounds modifies the fluorescence emission of the fluorophore in two ways: by quenching of the original fluorescence and by the formation of a new exciplex fluorescence band at a longer wavelength. The spectrum of this exciplex fluorescence band is dependent on the molecule involved in the complex with the dye [28]. Maximum of the spectrum shifts bathochromically with increase of ionization potential of aromatic donor. This is a factor that can be used to identify and detect aromatic analytes and for development of devices which can determine analytes in multi-component mixtures.

The aim of this work was to develop a sensor prototype for demonstration of possibility of selective measurement of aromatic compounds with materials based on DBMBF$_2$ dye adsorbed on silica gel in widely industrially used form-factor.

MATERIALS AND METHODS

The design of a sensor and its photography are shown in figure 1. The sensor consists of a cap with a UV-LED (Nichia NSSU123) board, a housing, and a photodiode housing containing a sensor material sample and a board with three photodiodes (Vishay temd7000) and amplifiers. The cap and the housings have been created by SLA method from Accura polymer. Optical filters films (Lee-UV, Lee-121 and Lee-767 filters) were attached directly to the top window of the photodiodes with water-soluble acryl latex glue. To remove photodiode light in visible spectral region Schott UG-1 filter was used. Internal size of sensor was chosen in accordance with city-4 sensor form factor. For signal measurement custom-made board based on Silab

C8051F061 microcontroller has been used. Measurements have been performed in impulse mode to decrease sensor material photodegradation. Impulse duration was 200 µs with period 10 s.

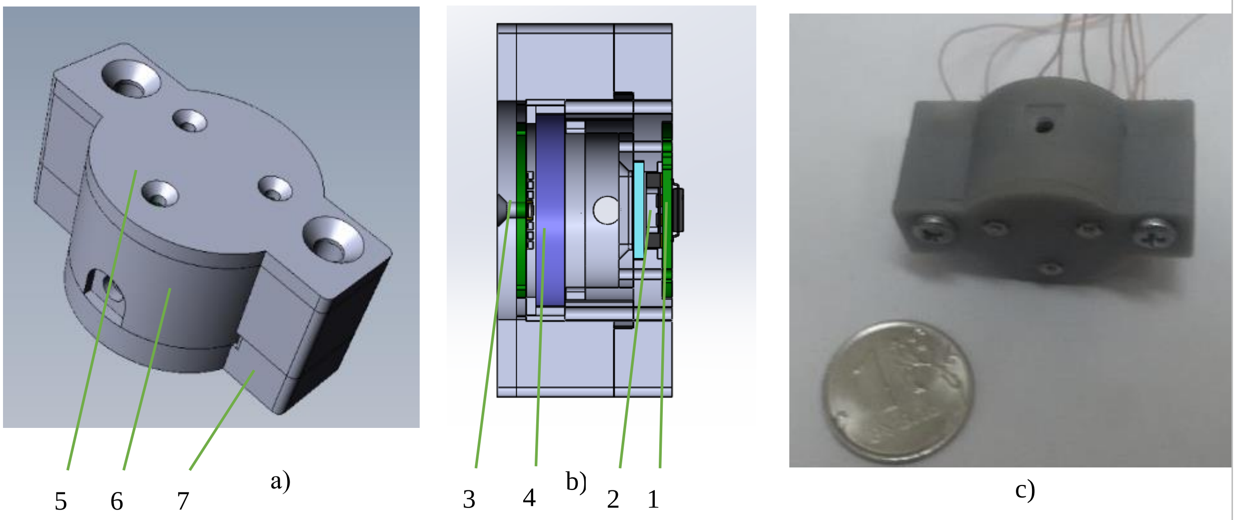

Figure 1 – a) construction of the sensor; b) internal construction of the sensor: 1 - photodiode; 2 – glass with chemosensory material; 3 – UV-led NSSU123; 4 – UV-filter (Schott UG-1); 5 – cap; 6 – housing; 7 –photodiode housing; c) photography of the sensor

The procedures for preparation of the $DBMBF_2$ was described elsewhere[29]. The sensor material consists of microspheres of Kromasil silica gel having an average size 10 µm and average pore diameter of 10 nm. To adsorb fluorophore on microspheres the following procedure was applied. A dye solution in n-hexane with concentration 8.6×10^{-6} mol/L was first prepared. For water removal the microspheres were dried for 24 h at a temperature of 190°C. A 700 mg portion of microspheres was added to 160 mL of fluorophore solution. The resulting mixture was continuously stirring for 24 h at 20°C. After stirring, the mixture was centrifuged at 15,000 g for 1 h and the microspheres were isolated by decantation. The residual solvent was removed by filtration through a nylonfilter. The amount of adsorbed $DBMBF_2$ was determined by spectrophotometric method from the solution after microspheres removal and was 10 mg g^{-1}.To make samples of sensor material on glass a suspension was prepared to have a component ratio of 140 mg of microspheres per 1 mL of 0.7 wt % polyvinylpyrrolidone aqueous solution. Suspension drops of 10 µL volume were drop-casted onto glass cleaned with 2 propanol and dried over 24 h. The fluorescence spectra of the samples in the saturated vapor were recorded with a Shimadzu RF5301 spectrofluorimeter. The sample was placed on the bottom of a quartz cell at an angle of 45° to the beam of excitation light. The cell cap with cotton wool ball wetted with solvent was added to the cell. Spectra were taken at 5 min intervals until equilibrium was established in the cell and the spectra ceased to change.

The dependencies on the analyte concentration in the gas phase was obtained with a setup described elsewhere [30] using permeation tube method. The measurement procedure was following first, clean air at a flow rate of 100 mL min^{-1} was fed to the sensor cell for 1 h; the humidity in the experiments was fixed at a constant level of 30%. After it the flow was set in range 40 – 240 mL min–1 for 20 minutes to obtain concentration of interest. The mixtures were fed to the sensor for 30 min with flow determent by concentration followed by 30 min purging with clean air with same flow. The procedure was repeated for all concentrations.

RESULTS AND DISCUSSION

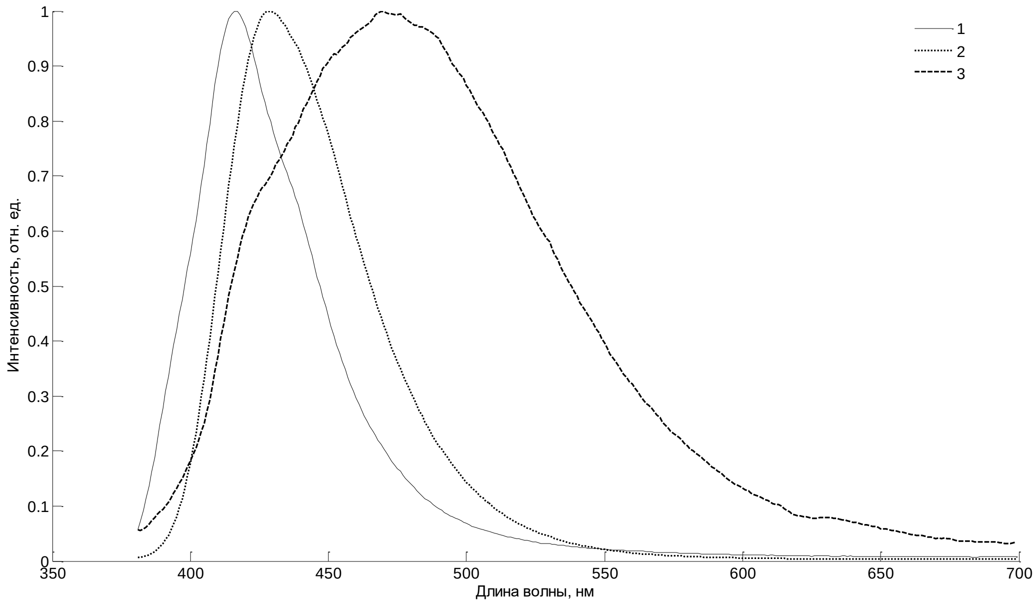

Figure 2. Normalized fluorescence spectra excitation 360 nm: 1) the sensor material 2) the sensor material in the presence of toluene saturated vapor; 3) the sensor material in the presence of p-xylene saturated vapor

Figure 2 depicts the fluorescence and spectra of the sensor material sample in the presence of saturated vapor of toluene and p-xylene upon excitation at 360 nm.

The following model of the processes occurring in the system can describe the observed spectral changes induced by the vapors of the aromatic compounds. Taking into account the well-known mechanisms of photoinduced electron transfer [31] and the results of the studies on interaction of the $DBMBF_2$ adsorbed on silica gel surface[29] and in solution with aromatic compounds [20, 24] , following scheme of photoprocesses occurring in the system can be proposed. The first step is the diffusion controlled formation of a contact pair between $DBMBF_2$ and aromatic compound. The main difference of the step from the interaction in a solution is in the way of the diffusion process and the formation of the contact pair. The main difference comparing to solution is that the interaction may occur both after the direct arrival of a molecule from the gas phase and by surface diffusion hopping. In the ground state distribution of the probability of finding the aromatic molecule on the distance from $DBMBF_2$ molecule should have a maximum near $DBMBF_2$ due to the high dipole moment of the fluorophore~2 (6.7D [32]). This fact may play a significant role in the exciplex formation kinetics at early stages. The existence of interaction between $DBMBF_2$ and aromatic molecules is also supported by quantum chemical calculations. [27]

Furthermore, the interaction of the contact pair of $DBMBF_2$ with an aromatic can lead to either direct electron transfer or electron transfer involving the formation of an intermediate exciplex and the subsequent formation of an ion pair or radiative or non-radiative decay of exciplex. Exciplex formation is favored by increase of aromatic molecule ionization potential. The processes of electrone transfer compete with exciplex emission and lead to decrease of exciplex fluorescence upon the increase of an ionization potential of aromatic molecule.

When the concentration of aromatic compound vapor over the sample surface is varied, the equilibrium establishes between $DBMBF_2$ and aromatic molecule. A relatively low rate of this process is associated with both the diffusion processes in silica gel and with the rate of establishing a preset concentration in the free volume of the sensor. For the sample of sensor material in equilibrium with the toluene and p-xylene vapors the system of equations presented below can be written:

$$\begin{cases} \dfrac{d[R^*]}{dt} = I_n - k_S[R^*] - \sum\limits_{i=1}^{2}(k_q^i[A_i][R^*] - k_d^i[A_iR^*]) = 0 \\ \dfrac{d[A_1R^*]}{dt} = k_a^1[A_1][R^*] - k_S^1[A_1R^*] - k_d^1[A_1R^*] = 0 \\ \dfrac{d[A_2R^*]}{dt} = k_a^2[A_2][R^*] - k_S^2[A_2R^*] - k_d^2[A_2R^*] = 0 \end{cases} \qquad (1)$$

where [R*] is the concentration of $DBMBF_2$ molecules in the excited state, I_n is the intensity of light absorbed, k_Σ - is the sum of emission rate constant and nonradiative decay rate constant for the excited state of $DBMBF_2$, $[A_1]$ and $[A_2]$ are the surface concentrations, $[A_1R^*]$ and $[A_2R^*]$ are the concentrations of the excited state complex, k^1_d and k^2_d are the dissociation constants of the excited state complexes , k^1_a and k^2_a are the association constant of the excited state complex, k^1_S and k^2_S are the sums of radiative decay rate constant the overall rate constant of all nonradiative decay processes of the excited state complex including electron transfer of the excited state complex, for toluene and p-xylene correspondently.

The expression for the shape of the spectrum depending on the concentration for these two cases is given below.

$$A(\lambda) = \frac{k_f a_0(\lambda)}{k_S + \sum\limits_{i=1}^{2} k_S^i K_i [A_i]} + \sum_{j=1}^{2} \frac{K_j [A_j] k_f^j a_j(\lambda)}{(k_S + \sum\limits_{i=1}^{2} k_S^i K_i [A_i])}, \qquad (2)$$

Where

$$K_i = \frac{k_a^i}{k_a^i + k_S^i},$$

k_f is radiative constant of $DBMBF_2$, $a_0(\lambda)$ is fluorescence spectrum of $DBMBF_2$ normalized on integral the under spectrum, k^1_f and k^2_f is radiative constants of exciplexes, $a_1(\lambda)$ and $a_2(\lambda)$ are fluorescence spectra of $DBMBF_2$ exciplexes normalized on integral under the spectrum with toluene and p-xylene correspondingly.

According to [29] concentration at silica gel surface in investigated range can be calculated from concentration in gas phase using Henry isotherm and the result expression is shown below:

$$A(\lambda) = \frac{k_f a_0(\lambda)}{k_S + \sum\limits_{i=1}^{2} k_S^i K_i K_i^{\Gamma} [C_i]} + \sum_{j=1}^{2} \frac{K_j K_j^{\Gamma} [C_i] k_f^j a_j(\lambda)}{k_S + \sum\limits_{i=1}^{2} k_S^i K_i K_i^{\Gamma} [C_i]} \qquad (3)$$

The expression can be written as

$$I(\lambda) = C(k_f a_0(\lambda) + \sum_{j=1}^{2} K_j K_j^{\Gamma} [C_j] k_f^j a_j(\lambda)) \qquad (4)$$

Where

$$C = \frac{I_n}{k_S + \sum\limits_{i=1}^{N} k_q^i [A_i]} \qquad (5)$$

The equation (4) shows that the measurements based on exciplex are ratiometric in nature. This means that ratio of intensity in two spectral channels (on two wavelengths) depends only on analyte concentration and is not influenced by changes in DBMBF$_2$ concentration or fluctuation and drift of excitation source. In actual practice the fluorescence spectrum of the sensor material is obtained as column of values with length L and above equation can be written in matrix form.

$$\begin{bmatrix} I_1 \\ I_2 \\ \dots \\ I_L \end{bmatrix} = \begin{bmatrix} K_0^1 & K_1^1 & K_2^1 \\ K_0^2 & K_1^2 & K_2^2 \\ \dots & \dots & \dots \\ K_0^L & K_1^L & K_2^L \end{bmatrix} \begin{bmatrix} C \\ [C_1]C \\ [C_2]C \\ \end{bmatrix} \qquad (6)$$

This overdetermined equation can be solved with respect to C и [C$_i$]C if rank of the matrix K is no lower than the number of analytes M + 1 = 3. This condition means that spectra a$_i$(λ) of DBMBF2 fluorescence and fluorescence of DBMBF$_2$ exciplexes with toluene and xylene differ enough. If spectra of molecules exciplexes are equal then only linear combination of their concentration can be obtained.

The numerical solution of this equation in sense of least square can be found. The numerical criteria of possibility of the solution is based on $\mu(K)$ a condition number of the matrix K. The solution is possible if an equation show below is fulfilled.

$$\mu(K) < 100, \qquad (7)$$

Calculated for spectra presented on figure 2 $\mu(K)$ = 8. Thus, for selective determination of toluene and p-xylene it is necessary to perform measurements by three different spectral channels. The spectral characteristics of the filters of the photodetector channels used in this study are shown in figure 3.

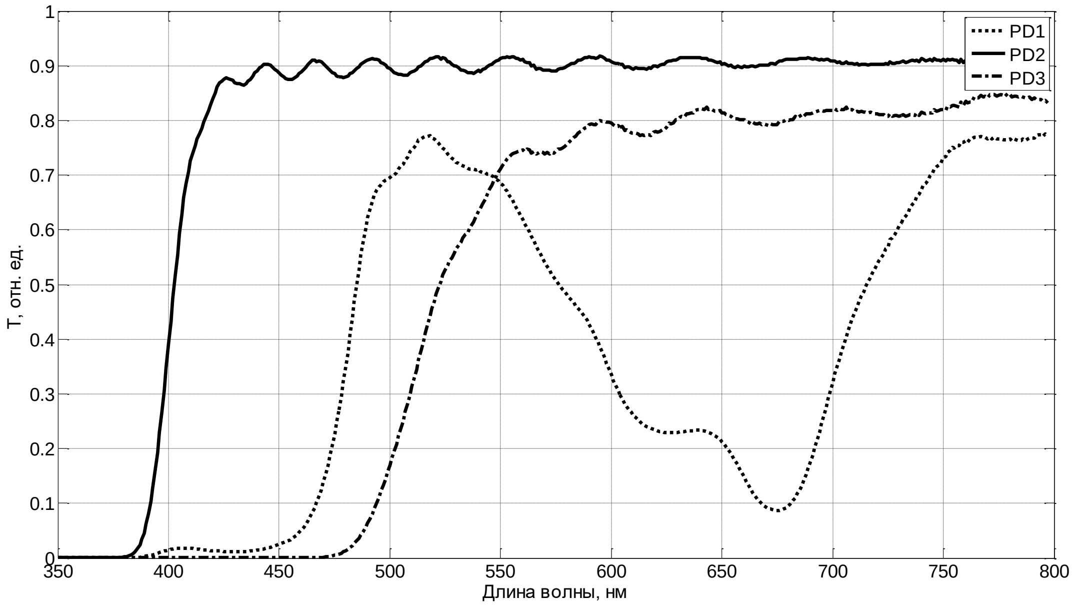

Figure 3. Transmittance spectra of the filters used in the spectral channels

A new spectral matrix K' for spectra obtained with these spectral channels can be calculated according to the following equation.

$$K' = S \times K \quad (8)$$

Where S is a matrix consisting of spectral sensitivities of the three channels. Calculated spectra for three-channel detection system are shown in figure 4. A Condition number calculated for the new spectral matrix $\mu(K')$ = 30. Thus, the theoretical consideration of the proposed sensor systems shows that it is capable for selective detection of toluene and p-xylene.

If fluorescence spectra of $DBMBF_2$, and its exciplexes with toluene and p-xylene are known the spectra matrix K' can be constructed from them and inverse or pseudoinverse matrix K'^{-1} can be found and used for concentration measurement. In a real experimental case spectra described above will differ from calculated due to unknown spectral sensitivity of detector and possible parasite light from excitation light source. The fluorescence spectrum of $DBMBF_2$ is always known because it is a default signal in measurement system. The spectra of exciplexes and other parameters of the model can be obtained from a calibration procedure which is based on fitting of dependency of single analyte on concentration according to the model described above (equation 3). The calibration procedure to determine these parameters was developed, an example of results obtained for toluene is shown in figure 5.

Figure 4 depicts dependencies of photodiodes voltages on concentration of toluene. Exposure of the sensor to toluene leads to increase of the voltage in all channels. Upon addition of p-xylene decrease signal in channel 2 and increase voltage in channel 2 and 3 are observed. These results are in a good agreement with prediction from above theoretical estimations of spectra.

The condition number for the spectral matrix consisted of fluorescent spectra of $DBMBF_2$ and its exciplexes with toluene and p-xylene is 140. Limit of detection is about 1 ppm for toluene and 0.5 ppm for p-xylene. Response and relaxation time calculated by 90 % level is about 30 seconds for toluene and 60 seconds for p-xylene.

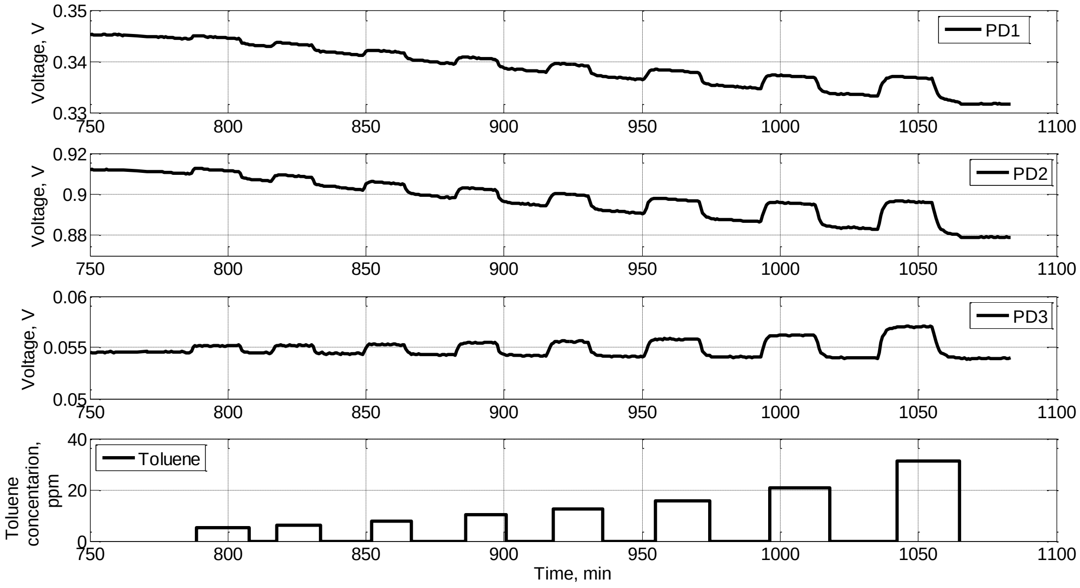

Figure 4. Changes in photodiode voltage during exposition to various concentration of toluene

Figure 5 shows comparison of concentration of analytes in gas mixture and concentration measured with calibrated sensor. Four series of mixtures have been tested. The first series consist of toluene mixtures with concentration in range 2 – 9 ppm, the second is toluene with concentration in range 6 – 40 ppm, the third is p-xylene with concentration in range 8 – 40 ppm, and the fourth series consist of toluene – p-xylene mixtures. Measured concentrations are in a good agreement with concentration in the mixture even in binary mixture. In single analyte mixtures cross sensitivity in given concentration range is not observed.

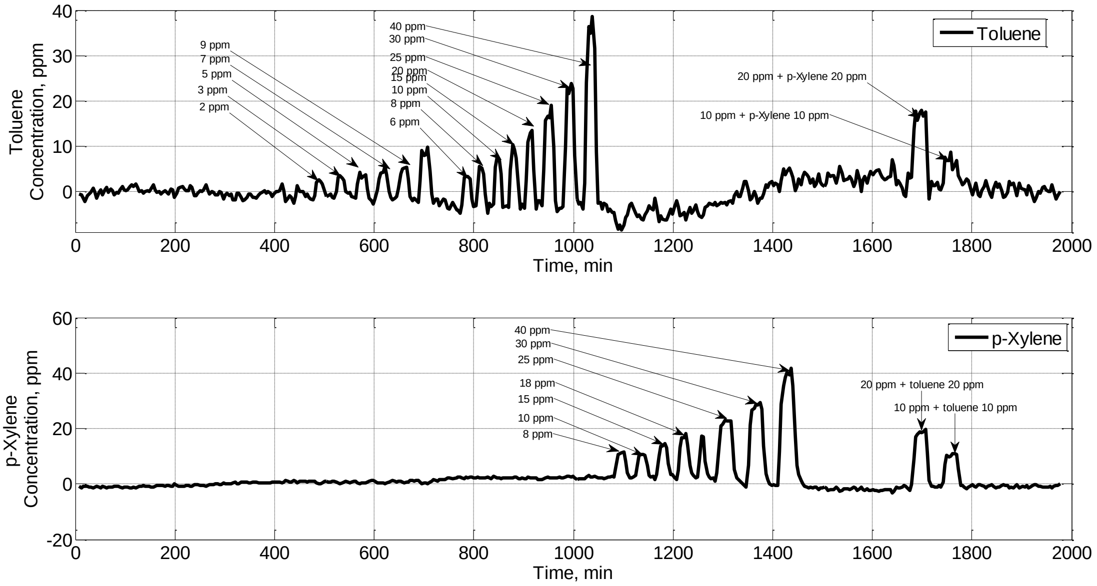

Figure 5. Comparison of concentration in mixture and concentration measured by sensor

CONCLUSIONS

Thus, the physical-chemical analytical model for the chemical sensor based on exciplex formation between $DBMBF_2$ and the aromatic molecules is proposed. The model shows that the sensor material developed is ratiometric in nature and does not depend on changes of fluorophore concentration drift and fluctuation of excitation light intensity. The estimation from the experimentally obtained fluorescence spectra of $DBMBF_2$ and its exciplexes with toluene and p-xylene shows that it is possible to measure these aromatic molecules in binary vapor mixtures selectively. The estimation made for set of spectral filters considered in the study demonstrates that three channels are enough for selective measurement of these aromatic compounds. The sensor prototype with the given set of filters was created. The calibration procedure for such sensor has been proposed and tested. The spectra found by calibration procedure are in good agreement with the estimated spectra. The absences of cross-sensitivity in single analyte mixtures and the measurement of toluene and p-xylene in a binary mixture with sensor prototype are demonstrated. The principle considered in this study can be applied to wide variety of fluorescent sensor systems based on complex formation in excited state accompanied with spectral changes.

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