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ODOR SENSOR BASED ON THE INFORMATION OF COLOUR

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ABSTRACT
An odor sensor was developed for the detection of volatile organic compounds (VOCs). The responsive elements of the odor sensor used in the study were: seven types of metal-porphyrine; Reichardt's Dye (R-Dye) and six pH indicators. The characteristics of responsive elements of the odor sensor have been described. Under the conditions of hydrophobic polymers, there were various responses for low hydrophobic gases and under the conditions of hydrophilic polymers, there were multi-responses for the gases of high hydrophobe. The present study of the odor sense system with basic function of odor sense confirmed the above description.

Keywords: odor, sensor, VOC, pH, Reichardt, dye, metal, porphyrine.

INTRODUCTION
Under the conditions of lack external odor detection, the development of odor sensor has a great significance to various fields of demands in using and evaluating the odor. In many sensing applications, for miniaturized systems, highly sensitive and of low cost sensor was desired. In addition, it also enables us to understand the relationship between the characteristic of molecular physical chemistry and odor character of matter; in the point of molecular view, to analyze human how to distinguish good smell, comfortable smell and disgusting smell. One of the reasons for the difficulty of odor sense is that the analytic objects with various chemical components and multi-characters. For example, chemical factors decide odor including multi-factors: the types of function groups, the form and size of molecule, dipole distance and solid structure, etc. Besides, it is also difficult to test the substance with high polarity and neutral substance with high hydrophobe at same time.

Currently, the most of responsive elements on the odor sensors from research or market are oxide-semiconductor [1-4], conductive polymer [5-6], crystal vibration [7-10] and etc. However, there is no selectivity to the special odor employing these responsive elements. When the types of odor are detected, it is necessary to employ the combination of multi-arranges or multi-center of multi-sensors of odor. If the ideal sensitivity and repeatability could not be obtained by the odor sensor, in practical stage, the sensor also cannot achieve low cost and miniaturization (mobile). Besides, it cannot be used to measure multiple substances. In order to solve the above problems, the odor sensor based on the colour information has been brought forward in this study.

The objective of the present study was to develop the odor sensor based on colour information. The responsive elements of the odor sensor are mainly discussed in this article. Since most of gases are hydrophobic, dropping on the athwart phase TLC plate which can adsorb these gases, were employed, the responsive cell was made using the compounds of the responsive elements. One of the responsive elements used seven different types of metal-porphyrine [11-15] which coordinate gases to induce colour change. As well as, the Reichardt's Dye (2,6-diphenyl-4-(2,4,6-triphenyl-N-pyridinio)-phenolate, and referred to hereafter as R-Dye) [16-18], which can arose the change of absorb-wavelength based on the polarity change of ambience, was also used. Employing the molecule of Reichardt's Dye (R-Dye), did not aim at a special object, it could response at large kinds of chemical substances. For the molecule contained aromatic electron donor, the molecule which accept electron donor to form complex, was also employed. In addition, six pH indicators were used as the responsive elements. After treating the colour images of these responsive pigments elements, the responsive quantities (for gases) were obtained, then the main components were analysed according to the responsive quantities, these responsive elements whether with the basic functions as the responsive elements of the odor sensors were discussed. The odor sensor was finally evaluated based on the investigation of its responses (reaction) for volatile organic compounds (VOCs).

MATERIALS AND METHODS

The basic experiment
All the reagents were purchased from Aldrich and Tokyo Chemical Industry Co. Ltd. At first, a responsive cell and dropping pigment solution on C18, C2 and Si plates were made. Solvent was eliminated with decompression drying. Secondly, the odor gas was introduced into the responsive cell and the responsive photo was obtained. The last step was images analysis. The images were decomposed to RGB colour components using Scion Image, the level of gray degree in the 10×10 pixel range of each responsive elements were calculated. Evaluation of the response equipped with principal components was analysed.

In this study, only the responsive elements of the odor sensor were discussed. Every test was employed different responsive elements but the basic instruments and operation were the same.

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Pigment elements

The responsive elements used were; seven types of metal-porphyrine, Reichardt's Dye (R-Dye) molecules accepted electron donor to form complexes and six pH indicators. The metal-porphyrine, which arose the color changes due to the gas coordination, was made by the way of the coordination itself and the complexes which the center of molecule contain Zn, Fe, Cu, Mn and Ni were dissolved in chlorobenzene. The concentration of the solution was selected as 1.0×10^{-3} mol/L because it gives the biggest responsive quantity.

The Reichardt's Dye (R-Dye) arises the change of absorb-wavelength based on the polarity change of ambience, was made as 1.0 X 10^{-3} mol/L methanol solution. The molecules which accept electron donor from electric charge transferred complexes: tetracyanoethylene and tetrachloro-1,2-benzoquinone were made as 1.0×10^{-3} mol/L methanol solution. 7,7,8,8-tetracyanoquinodimethane was made as 1.0×10^{-3} mol/L DMF solution. Six pH indicators were used as the responsive elements. Employing the molecule which accepts electron donor was expecting to induce the change of the absorb-wavelength when it approached to the molecule with aromatic electron donor. The color change range of the pH indicators was from pH2 to pH12. The pH indicators were made as their methanol solution.

Fabrication of responsive plates

The responsive plate which the pigment element will be dropped on was made using the following method. Since the components of odor are general hydrophobic, the C18 athwart phase TLC plate (Whatman, KC18 Silica Gel 60, 200mm×50mm×1.7mm), the C2 athwart phase TLC plate (Whatman, KC2 Silica Gel 60, 200mm×50mm×1.7mm) and Silica Gel plate (MERCK,100 TLC plate 50mm×200mm Silica Gel 60), which odor can be absorbed, were employed. 5µl pigment solution was dropped on these plates using minim injector.

During dropping, R-Dye was treated with alkalescence. This is because, R-dye is a general acceptor for different polarity molecules, when it is dropped on the silica gel, silica-alcohol can cause protonation of hydroxybenzene at R-Dye, and thereby the colour of the pigment will disappear. As a result, R-Dye must be treated to eliminate the protonation.

Under the conditions of 50°C and 3mm Hg and after 1h vacuum drying treatment, the solvent in the dropping solution was removed. The dried responsive plate of C18 athwart phase TLC was shown in Figure-1 and the number of pigments was shown in Table-1.

Experimental setup

The experimental setup is shown in Figure-2. Before the experiment, argon gas was flowed to substitute and the responsive plate was dried. The gas flux was controlled using a controller to maintain a fixed flow rate (flow rate during drying or substitution: 2.63 ml/s and during measurement: 2.10 ml/s).

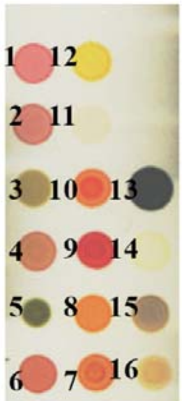

Figure-1. The dried responsive plate of C18 athwart phase TLC.

Table-1. Pigments in the plates.

No.	Pigment
1	5,10,15,20-Tetraphenyl-21H,23H-porphine copper(II)
2	5,10,15,20-Tetraphenyl-21H,23H-porphine
3	5,10,15,20-Tetraphenyl-21H,23H-porphine iron(II) chloride
4	5,10,15,20-Tetraphenyl-21H,23H-porphine zinc(II)
5	5,10,15,20-Tetraphenyl-21H,23H-porphine manganese(II) chloride
6	5,10,15,20-Tetraphenyl-21H,23H-porphine coblalt(II)
7	Thymol Blue (TB)
8	Methyl Orange (MO)
9	Methyl Red (MR)
10	Phenol Red (Ph-R)
11	Phenolphthalein (Ph)
12	Alizarin Yellow (AY)
13	Tetrachloro-1, 2-benzoquinone (TCB)
14	7,7,8,8-Tetracyanoquinodimethane (TCQ)
15	Tetracyanoethylene (TCE)
16	Reichardt's Dye (R-Dye)

The method of obtained response to VOCs was, 5ml of water and 10 ml of VOC in a flask was put into a microwave oven, after heating, the hot samples gas were passed a cooler to be cooled down to room temperature (25±1°C), then the gases were put into the responsive cells.

Images obtaining and analysis

The change for the colours of the responsive elements were simply obtained by the way of scanner scanned the images into computer. After the microwave oven heating, the images were scanned every minute.

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The finish time of the response was different for different test samples, which was around 15-25 minutes. Then, gas argon was flowed into the responsive cells; the original image was renewed (120min.). The scanner was 100dpi.

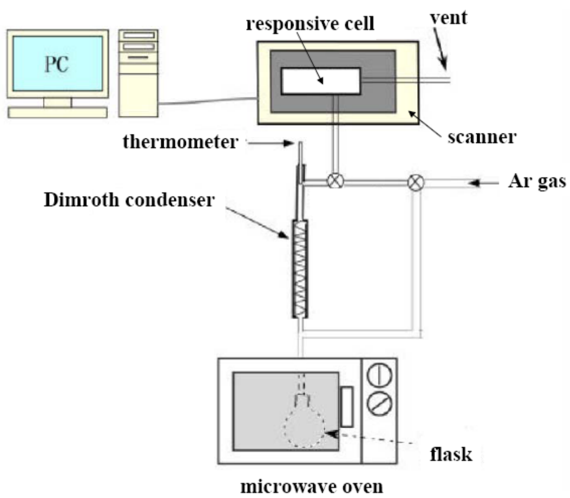

Figure-2. Experimental setup for VOCs.

RESULTS AND DISCUSSION

Influence to VOC response due to different hydrophobe

In order to investigate the chemical characteristic of the responsive elements, the response to VOCs was investigated based on the difference of groups of the VOCs.

From Figure-3 naked-eyes can see the color change of the response to methanol, 5,10,15,20-Tetraphenyl-21H,23H-porphine manganese(II) chloride (TPP-Mn) colour changed from green to red-green, thymol blue (TB), methyl orange(MO), methyl red (MR), phenol red (Ph-R)'s color changed from red to yellow, the color of R-Dye changed from purple to dark-purple.

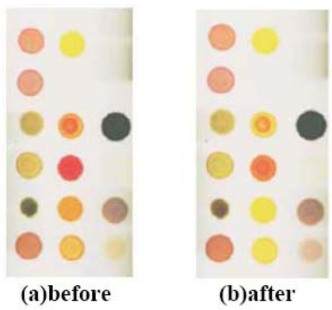

Figure-3. Response to methanol on C18 plate.
The position of each element was the same, see Figure-1.
(a) Original image and (b) responsive image for methanol.

Here, the higher hydrophobe contradictorily phase silica gel plate C18 was selected as the plate of VOC absorbed field, two others silica gel plates: C2 silica gel plate has lower hydrophobe than C18 plate and carbon untreated silica gel plate which only silanol existed were also selected as VOCs absorb fields. The influence to the VOC response due to the different hydrophobe was discussed. Employing pH indicators as responsive elements, the relationship between the pH in adsorb field and the responses was reviewed. According to the results of the experiment, by comparing Figure-3 and Figure-4, the colour change was not only relative to pigment colour change, but it was also relative to the hydrophobe of the basic plate.

The responsive elements of odor sensor have been discussed basically, simple construct of gas sense system received responses, the characteristics of these response elements have been investigated and evaluated.

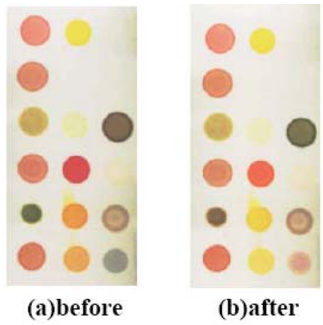

Figure-4. Response to methanol on C2 plate.
The position of each element was the same, see Figure-1.
(a) Original image and (b) responsive image for methanol.

Effect of response to vapor tension

Figure-5 shows the illustration of the response of pigment elements to alcohol on C2 plate.

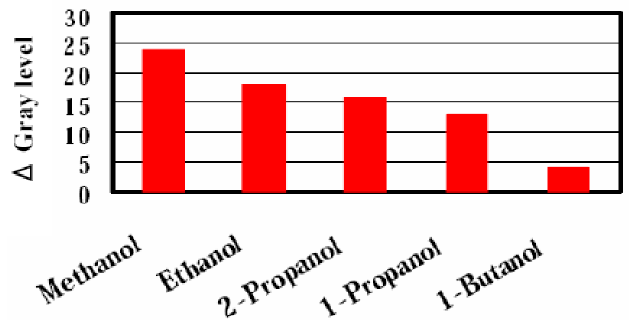

Figure-5. The TPP-Mn to VOC on the C2 plate.

In Figure-6 the boiling point of VOCs with its response showed the relation of a beeline. Although the relation only to alcohol, but the relationship between the boiling point of VOCs and response can be conferred.

Characteristics of each response element

Hereto, the description was based on the response of color change. There was also mechanism of various color change.

R-Dye is a solvatochromic molecule, as soon as the change of ambience such as solvent, it will absorb wavelength of molecule occurred displacement. The R-Dye with the structure of Betaine, was the pigment with zwitterion state and stable existent. The difference of the

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polarity of the solvent molecule and the ambience aroused the excursion of electron cloud of the pigment molecule, thereby caused the change of absorbed wavelength of pigment molecule. Therefore, it could be considered that the responsive elements of odor sensor were effective. There was response to VOCs in common use, even for water, R-Dye was regarded as the responsive element with high validity. But, the inferior of elements was more impetuosity than other pigment elements.

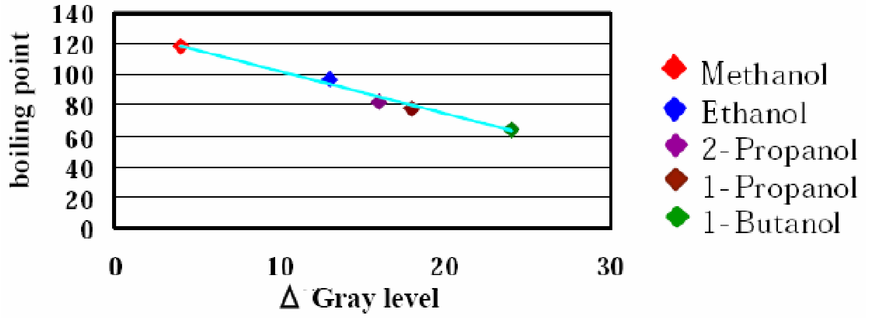

Figure-6. The relation of boiling point and Gray level.

The charge transference complex is the acceptor molecule, when benzene is closed to equal electron donor molecule, there is change for the color of pigment. However, in this experiment, the response for benzene was not found, there was very little response for whole responsive elements. There is some response for the amines, but the reversibility was not viewed. Therefore, the charge transference complex as the responsive element of the odor sensor was not effective.

For metal-porphyrine with six metal co-ordinations, the coordinate bonds were influenced by the gas components of odor, the molecular absorbed wavelength which occurred displacement. Consequently, when various VOCs and the components of odor close up, the colour of the molecule will change. However, as the responsive elements, there were only responses for several VOCs, and few of the form and quantity of responses. Therefore, as the responsive element of odor sensor in common use, it was not so effective.

Besides, six pH indicators nearby the color change range from pH2 to pH 12 were selected. TB has three different ranges for the colour change, blow pH2 was red, pH2-9 was yellow and above pH 9 was purple. MO shows red blow pH4, and yellow above pH 4. MR shows red below pH 5 and yellow above pH5. For Ph-R, it shows yellow below pH 7 and turns red above that. For phenolphthalein (Ph), ith is colourless below pH8 and turns red above pH8. Arizarin yellow (AY) shows yellow below pH10 and red above pH10.

As a result, the responsive elements employed in this odor sensor, for the same VOC, there were mostly colour changes for them, showing responses. In addition, as the neutral gas with response, was not only the colour changes which occurred as soon as only VOCs gas closed up, the above results caused the responsive mechanism of the pH indicator, the mechanism was described.

The colour changes of pH indicators were determined by the balance of ambience and proton. As well as, the colour change was the result of the proton balance affected. The pH indicator in the silica gel circumstance, under the conditions without the components of VOCs and odor, kept some degree proton balance. But, when the components of VOCs and odor entered the polarity of the silica gel environment occurred changes. The change of microenvironment influenced the proton balance, for pH indicator the changes were shown in the distinct color change; this was the responsive mechanism of pH indicators. Evermore, like VOCs of such amine with stronger alkalinity, was not the change of the silica gel microenvironment, but was that the balance of pH indicators were destroyed, therefore there were various big responses. For neutral VOCs, the change of microenvironment of pH indicators, the differences between VOCs could be seen, and there was the selection of responses.

Since the validity of pH indicator as responsive elements was gained approbatory, well then pH indicator was mixed with three polymers with different chemical characters, and then these mixtures were dropped on the silica plates. Even employing the same pH indicator, when the polymer which would be mixed with the pH indicator, was different, the colour of the pH indicator would be different too. Concerning this, we can see it in Figure-7.

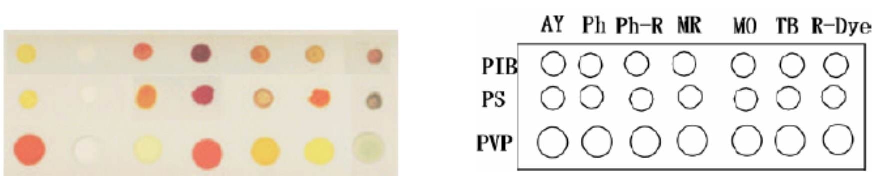

Figure-7. The original graph of responsive plate of pigment/polymer mixed pigment.

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Influence to response due to polymer mixed

For the responsive element mixed polyvinylpyrrolidone K30 (PVP), based on the pH indicator and its colour change range, the pH around the responsive elements should be about 4-5. But the colour change range of pH indicator was not suitable for the polymer like polyisobutylene (PIB) and polymer styrene (PS) with such high hydrophobe. In addition, the chemical character of polymer could be confirmed from the response of water. There was few response of MO to water in PIB and PS such high hydrophobic polymer. Conversely, the response of MO in the hydrophilic PVP polymer could be seen.

The responsive characters were described as follows. According to the order of hydrphobe, cyclohexene, benzene and ethanol were selected as VOCs. As the hydrophobic index, the order of the hydrophobe was decided by the distribution rates, which were evaluated based on the solubility of VOCs in water and octanol. In addition, the difference of the vapor tension of VOCs would influence the concentration of inside the cell; the boiling points of three VOCs (83°C, 80°C and 78°C) were close to each other to make sure the concentration inside the cell is consistent. The three responses of VOC were recorded (Figure 8a, b and c).

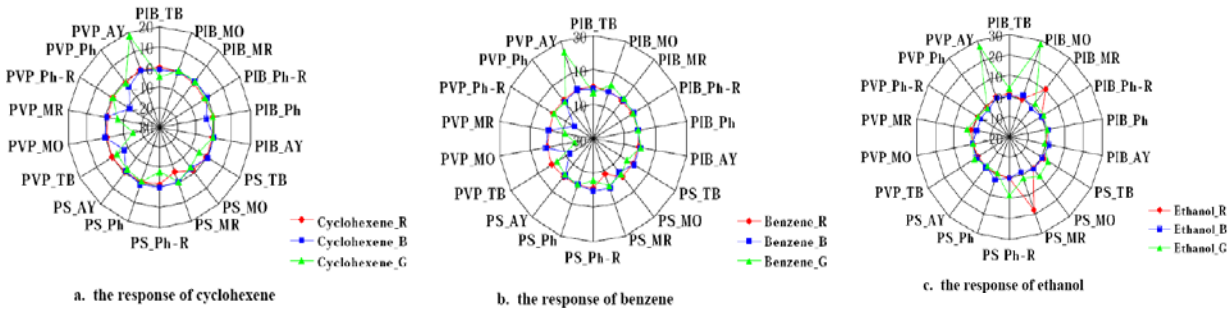

Figure-8. The response of cyclohexene, benzene and ethanol.

Figure-8a shows the responses of cyclohexene, for hydrophobic polymers, four elements of TB/PIB, TB/PS, MR/PS and Ph-R/PS showed responses; for hydrophilic polymer, five elements of TB/PVP, MO/PVP, MR/PVP, Ph-R/PVP and AY/PVP showed responses. For the responses of benzene, for hydrophobic polymers, five elements of TB/PIB, MO/PIB, TB/PS, MR/PS and Ph-R/PS showed responses; for hydrophilic polymers, five elements of TB/PVP, MO/PVP, MR/PVP, Ph-R/PVP and AY/PVP showed responses.

About the responses of ethanol, for hydrophobic polymers, seven elements of TB/PIB, MO/PIB, MR/PIB, TB/PS, MO/PS, MR/PS and Ph-R/PS showed responses; for hydrophilic polymers, two elements of MR/PVP and AY/PVP showed responses.

These results suggested the following conclusion. Initially, we forecasted that the pH indicators under hydrophobic polymers conditions produced responses for high hydrophobic gases, and on the contrary, the pH indicators under hydrophilic polymers conditions produced responses for low hydrophobic gases produced more responses. However, the results were completely contrary. Under the conditions of hydrophobic polymers, there were various responses for low hydrophobic gases. And under the conditions of hydrophilic polymers, there were multi-responses for the gases of high hydrophobe.

These results related to the mechanism of pH indicators. The color change of pH indicators occurred along with the changes of the surrounding microenvironment. The big change of the microenvironment appeared along with entering different chemical gases in the environment, the change became response to show.

Therefore, in the hydrophobic polymers, the gases with low hydrophobe and different chemical characters were more influenced, in the hydrophilic polymers, the gases with high hydrophobe and different chemical characters were more influenced.

We considered that there was probably a relationship like Figure-9, between the strong or weak of hydrophobe and the numbers of responsive elements (in the hydrophobic polymers).

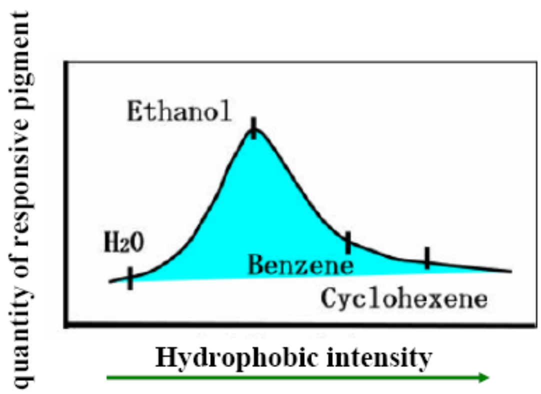

Figure-9. The relationship between the strong or weak of hydrophobe and the number of responsive elements (in the hydrophobic polymers).

In order to make more responsive elements producing responses, the hydrophobe of VOCs need not to be very strong or very weak. Only there was a suitable hydrophobe of VOCs, the surrounding microenvironment of more responsive elements was influenced. Based on these, employing six pH indicators to mix with three polymers of different chemical properties, how influence for the pH indicators to the environmental responses, for responsive elements with responsive characters, the chemical characters of polymers represented more notably, even more, for the responsive elements mixed with polymers, the hydrophobic components of VOCs and odor were also influenced.

From the responses of VOCs point of view, the characteristic of this odor sensor has been described. The responsive identities of function groups for different VOCs were different. In order to visualize for the different responses of functional groups, various variable analytic principal components analysis was employed, whereas, the principal component analysis based on the responses of VOCs could not recognize the functional groups of VOCs, and could only identify the amine with high coordination energy and acidic carboxylic acid.

CONCLUSION

In this study, we have done the responses for VOCs and experimental samples. Although the Principal component analysis could not recognize the functional groups of VOCs, the characteristic of responsive elements of the odor sensor has been described, as the odor sensor should differentiate the components of odor, colligating these responses. Under the conditions of hydrophobic polymers, there were various responses for low hydrophobic gases. And under the conditions of hydrophilic polymers, there were multi-responses for the gases of high hydrophobe. According to above description, the fact of this odor sense system with the basic function of odor sense could be confirmed. Since this research was mostly done on the evaluation of the construction of odor sensor, based on the colour information of responsive elements of odor sense, the validity as the odor sensor was cognizance. For the future, we expect the responsive elements in this article will be employed on the construction of odor sensor.

REFERENCES

[1] J.P. Viricelle, A. Pauly, L. Mazet, J. Brunet, M. Bouvet, C. Varenne and C. Pijolat. Materials Science and Engineering: C, Vol. 26.

[2] V.S. Vaishnav, P.D. Patel and N.G. Patel. 2005. Thin Solid Films. Vol. 490(1): 94-100.

[3] A. K. Srivastava. 2003. Sensors and Actuators B: Chemical. Vol. 96(1-2): 24-37.

[4] N. G. Patel, P. D. Patel and V. S. Vaishnav. 2003. Sensors and Actuators B: Chemical. Vol. 96(1-2): 180-189.

[5] Marek Kozłowski and Stanisław Frąckowiak. 2005. Sensors and Actuators B: Chemical. Vol. 109(1, 24): 141-145.

[6] W. Vonau, J. Gabel and H. Jahn. 2005. Electrochimica Acta. Vol. 50(25-26): 4981-4987.

[7] A.K.M. Shafiqul Islam, Z. Ismail, M.N. Ahmad, B. Saad, A.R. Othman, A.Y.Md. Shakaff, A. Daud and Z. Ishak. 2005. Sensors and Actuators B: Chemical. Vol. 109(2): 238-243.

[8] Abdolreza Mirmohseni and Ali Oladegaragoze. 2004. Sensors and Actuators B: Chemical. Vol. 102(2): 261-270.

[9] T. V. Basova, C. Taşaltin, A. G. Gürek, M. A. Ebeoğlu, Z. Z. Öztürk and V. Ahsen. 2003. Sensors and Actuators B: Chemical. Vol. 96(1-2): 70-75.

[10] Robi Polikar, Ruth Shinar, Lalita Udpa and Marc D. Porter. 2001. Sensors and Actuators B: Chemical. Vol. 80(3): 243-254.

[11] Kenneth S. Suslick, Neal A. Rakow and Avijit Sen. 2004. Tetrahedron. Vol. 60(49): 11133-11138.

[12] N.A. Rakow and K.S. Suslick. 2000. Nature 406. p. 710.

[13] N.A. Rakow and K.S. Suslick In: J.R. Stetter and W.R. Pensrose. 2001. Artificial Chemical Sensing: Olfaction and the Electronic Nose. Electrochem. Soc., Pennington, NJ.

[14] Suslick, K. S.; Rakow, N. A. U.S. Patent 6,368,558, Apr 9, 2002.

[15] Suslick, K. S.; Rakow, N. A.; Sen, A. U.S. Patent 6,495,102 B1, Dec 17, 2002.

[16] S. Fiorilli, B. Onida, D. Macquarrie and E. Garrone. 2004. Sensors and Actuators B: Chemical. Vol. 100(1-2): 103-106.

[17] Peter Blum, Gerhard J. Mohr, Karsten Matern, Johannes Reichert and Ursula E. 2001. Spichiger-Keller Analytica Chimica Acta. Vol. 432(2): 269-275.

[18] Marek Kosmulski. 1999. Colloids and Surfaces A: Physicochemical and Engineering Aspects. Vol. 159(2-3): 277-281.