Sensors and Materials, Vol. 9, No. 4 (1997) 187–196
MYU Tokyo

S & M 0285

Fiber-Optic Evanescent Wave Sensors for Organic Gas Sensing

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(Received October 9, 1995; accepted February 2, 1997)

Key words: organic gas sensing, plastic fiber, evanescent wave, fluorescent dye, dye-doped PMMA surface

We previously proposed an organic gas sensing and recognition system using a plastic optical fiber (POF) sensor array that has six dye/silicone coatings, the absorption intensities of which change with organic gas exposure. In this study, we present a new POF sensor based on evanescent wave fluorescence spectroscopy and describe the design considerations, the preparation method, and the fluorescence response characteristics of the sensor to organic gases. The new evanescent wave fluorescence sensors have higher sensitivities to organic gases than the previous POF sensors based on transmission absorption (or absorbance) spectroscopy. An array of the evanescent wave fluorescence sensors can be used for discrimination of organic gases.

1. Introduction

There is increasing interest in realizing a reliable gas sensor as well as an artificial olfactory sensor. The use of a sensor array combined with pattern recognition techniques is essential for realizing such a sensor with both high sensitivity and selectivity.[1,2] A number of odor or organic gas sensors have been so far proposed and developed.[1,2] The gas sensors having high sensitivity include quartz-crystal microbalance (QCM)[3–5] and surface acoustic wave (SAW)[6] sensors coated with gas-sensitive films, such as lipid membranes, and semiconducting oxide sensors.[1,2,7] Especially QCM sensors have ultra-high sensitivities on the order of nanograms to organic gases. Recently, we have proposed a new odor or organic gas sensing and recognition system using a plastic optical fiber

(POF) sensor array that has six different potential-sensitive dye/silicone coatings, whose transmission absorption intensities change with organic gas exposure.[8] The dyes include NK2367, NK3041, NK1939, rhodamine B, ANS-NH_4 and methylene blue. The most remarkable feature of fiber-optic gas sensor array systems is the great possibility of wide-range distributed sensing or monitoring for environmental applications. A fiber-optic gas sensing system[8] has been applied to distributed sensing and the computer visualization of alcohol vapors.[9,10] However, POF sensors[8–10] have been found to have lower sensitivity to organic gases than the QCM and SAW device sensors. In the course of improving the sensitivity of sensors, we have investigated a new POF sensor based on evanescent wave fluorescence spectroscopy instead of the previous sensors[8–10] based on transmission absorption (or absorbance) spectroscopy. This paper describes the design considerations, the preparation method and the fluorescence responses to organic gases.

2. Materials and Methods

2.1 *Evanescent wave sensor*

A jacketed POF, Super ESCA SH4001, Mitsubishi Rayon Inc., was used. The fiber and jacket diameters were 1.0 mm and 2.2 mm, respectively. After the cladding layer of POF was removed, the surface of the poly (methyl methacrylate) (PMMA) core was treated with a 60 wt% aqueous solution of sulfuric acid. This surface treatment made the surface of the PMMA core hydrophilic and improved the adhesion between the core surface and dyes. The treated core surface was doped with dyes by dip-coating in dye/dichloromethane solutions. An evanescent wave sensor was prepared by joining a dye-doped fiber and an undoped fiber as shown in Fig. 1, whereas a transmission structure had been prepared in previous work.[8] More than twenty dyes including xanthene, cyanine, styryl and coumarin dyes, which have absorption bands in the 450 ~ 600 nm wavelength region and emit argon-laser-induced fluorescence, were investigated in terms of fluorescence spectrum changes with organic gas exposure or their responses to organic gases including alcohol vapors.

2.2 *Absorption spectrum measurement*

A method similar to the previous method[8] was used for multichannel dye absorption spectrum measurements from a six-channel (6-ch) sensor array. For 6-ch spectra measurements, six POF sensor ends were fixed at the monochromator outlet slit. The intensity difference among the six POFs was within 10% as shown in Fig. 2. Furthermore, the intensity difference was reduced by the use of a normalized variable, absorbance $\Delta A = \log (V_0/V)$, in eq. (1) as given below.

$$\Delta A = A - A_0 = \log (V_F/V) - \log (V_F/V_0) = \log (V_0/V) = kC \quad (1)$$

Here, V and V_0 are the input voltages to the A-D converter from a dye-doped sensor in gas and in air, V_F is the input voltage from an undoped sensor in air, C is the gas concentration, and k is a constant.

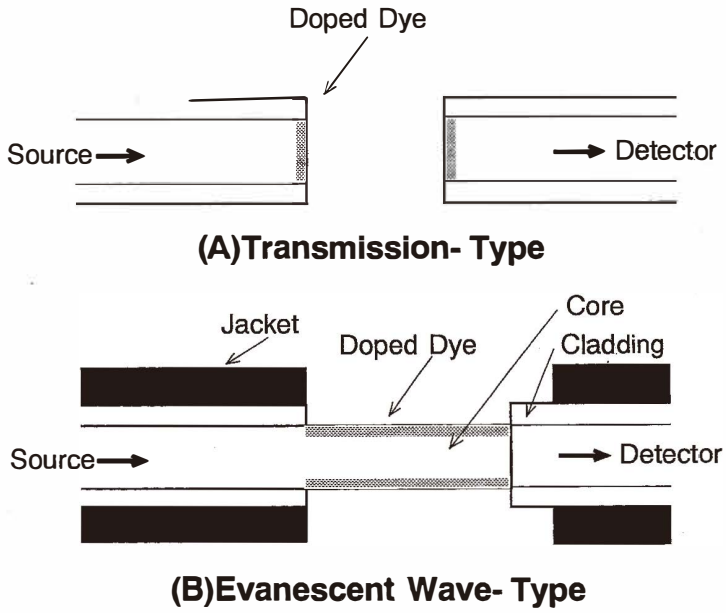

Fig. 1. POF sensor structures.

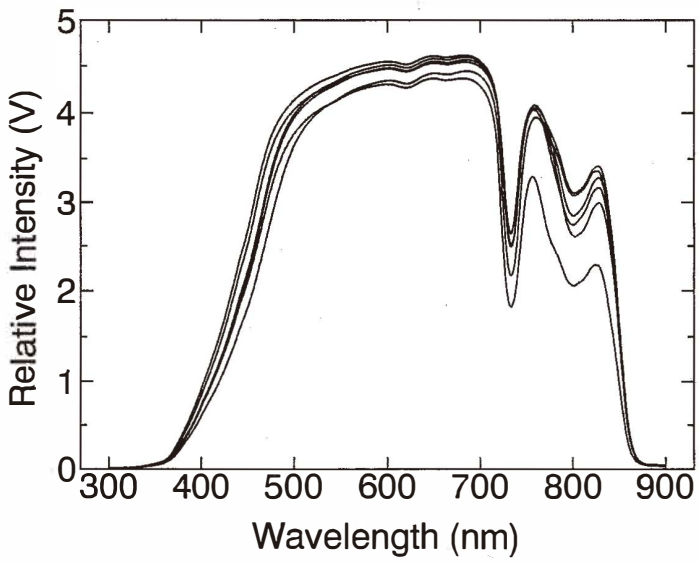

Fig. 2. Intensity differences among six undoped POF sensors.

The absorption changes upon exposure to organic gases and the responses were observed in the same way as in the previous work.[8–9] Light from a halogen lamp passed through a monochromator, entered the six POFs, and reached the corresponding six sensors at the same time. The monochromatic light was absorbed during travel through the dye-doped surface layer and was detected by six photodiodes via six POFs. The sampling time for six sensors was 1.5 min in the 300 ~ 900 nm wavelength range at 1 nm intervals.

2.3 *Measurement of the fluorescence spectrum*

Figure 3 shows the experimental configuration for automatic measurement of six fluorescence spectra from a 6-ch POF sensor array using a polychromator (or a multichannel photodetector) and an optical switch. An argon laser tuned to the 488 nm line was used as a light source to excite the fluorescent dye around the core. The laser beam that was expanded by an objective lens entered the six POFs, reached the six sensors, and then excited the corresponding six dyes. The six laser-induced fluorescence spectra were detected by a polychromator, PMA-10 or PMA-11 (Hamamatsu Inc., 1024 ch in the 300 ~ 800 nm wavelength range). A MOS (metal oxide semiconductor) linear image sensor and a cooled CCD (charge coupled device) linear image sensor were used for PMA-10 and PMA-11, respectively. The sampling time for measuring six spectra in the wavelength range of 300 ~ 800 nm was 1.5 ~ 3.0 s. The same gas-test box as that used in the previous work[8] was used for measuring changes in the fluorescence spectrum upon exposure to gas or the responses to organic gases. Methanol, ethanol, 1-propanol, 2-propanol, diisopropyl ether and n-hexane were used in the recognition or discrimination experiments for organic vapors.

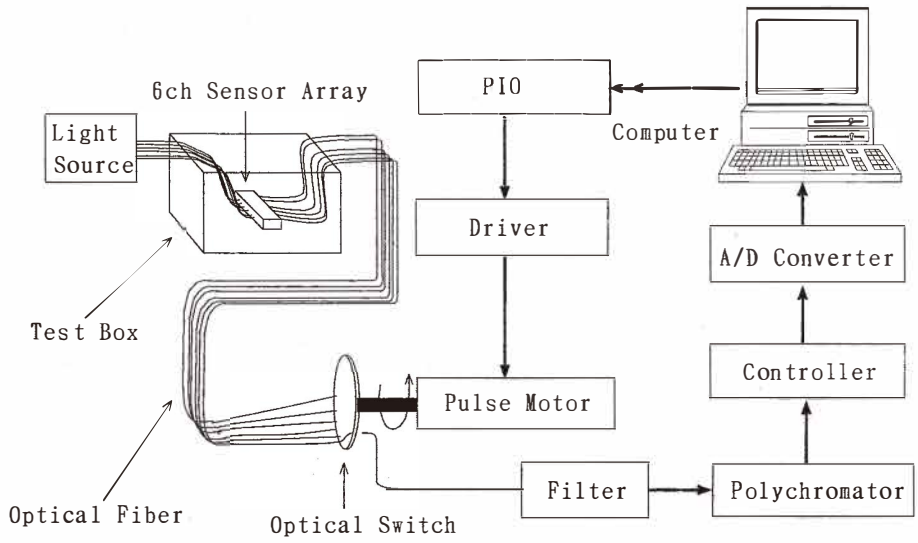

Fig. 3. Dye fluorescence spectrum measurement using a POF sensor array.

3. Results and Discussion

3.1 *Sensor design considerations*

The use of an evanescent wave for a fiber-optic sensor offers many advantages, *e.g.*, mechanical stabilization of dye-doped layers or dye coatings, increased effective path length for optical absorption and excitation (particularly on a multimode optical fiber) and analytical sampling that is restricted to the selective interface.[11] However, few studies have been published on evanescent wave POF sensors.[12] To design evanescent wave POF sensors based on both absorbance spectroscopy and fluorescent spectroscopy, we investigated how to detect effectively the dye in POF sensors, i.e., the relationship between sensor structure and dye detection.

Figure 4 shows the relationship between intensity of a spectum and bending diameter of an undoped POF sensor placed in the gas-test box, which is used for measuring changes in the fluorescence spectrum upon exposure to gases. It is seen that the intensity from a POF sensor increases with bending diameter and becomes a constant value at more than 17 cm of bending. This dependence of spectrum intensity on bending diameter is due to macrobending loss in the POF. From the results in Fig. 4, it is concluded that the POF sensors placed in the gas-test box must be used at a bending diameter of more than 17 cm.

Figure 5 shows changes in dye absorption (550 ~ 560 nm) in spectra from POF sensors doped with rhodamine B in the (0) 8 cm core surface, (1) 8 cm cladding layer, (2) 2 cm core

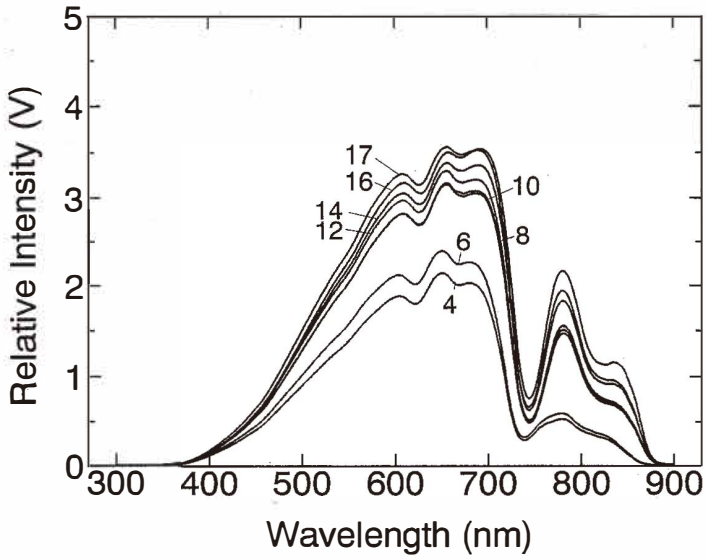

Fig. 4. Relationship between intensity of the spectrum and bending diameter (cm) of an undoped POF sensor placed in a gas-test box.

surface and (3) 2 cm cladding layer. It can be seen that dye doping in the cladding layer results in a low dye absorption intensity, and it is concluded that removal of the cladding layer and subsequent dye doping in the core surface are required to obtain satisfactory dye detection. Figure 6 shows the relationship between absorption intensity of the dye (550 ~ 560 nm) and the core length doped with rhodamine B. Apparently, a doped core length of 1.5 or 2.0 cm is adequate for obtaining satisfactory dye detection.

Based on the above results, evanescent wave absorbance and fluorescence POF sensors with 2.0 cm dye-doped core lengths were used at a bending diameter of more than 17 cm (or a bending radius of more than 8.5 cm) in the following experiments.

3.2 *Evanescent wave absorbance sensors*

The evanescent wave POF sensors doped with methylene blue and rhodamine B showed large dye absorbance changes when exposed to alcohol vapors, as did the previous transmission absorbance sensors.[9,10] These evanescent wave absorbance sensors may be also used as well as the previous transmisson absorbance sensors as sensor arrays for discriminating organic gases.[8]

Although more than 20 dyes were investigated for their absorbance changes upon exposure to organic gases, only a few dyes, including methylene blue[9] and rhodamine B,[10] show large absorbance changes. This means a limited choice of dyes for discrimination of organic gases. Instead of dyes that show large absorbance changes, we have

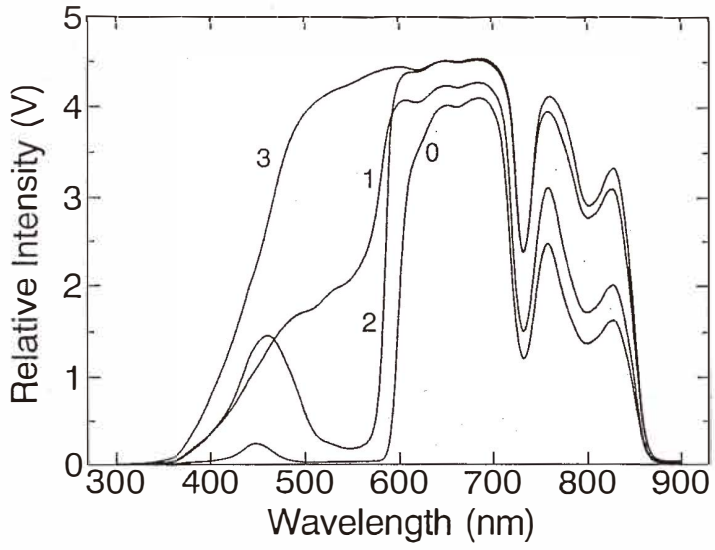

Fig. 5. Dye absorption changes in spectra from POF sensors doped with rhodamine B in (0) 8 cm core surface, (1) 8 cm cladding layer, (2) 2 cm core surface and (3) 2 cm cladding layer.

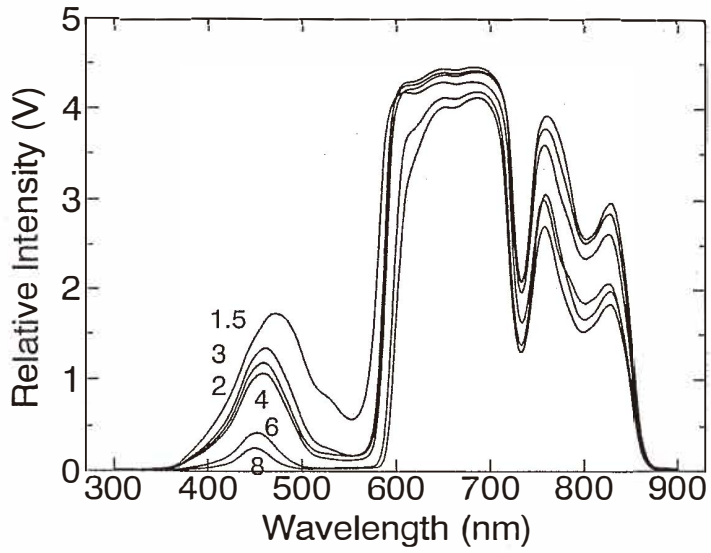

Fig. 6. Relationship between dye absorption intensity and core length (cm) doped with rhodamine B.

surveyed fluorescent dyes that show large fluorescence changes upon exposure to organic gases, as shown in the following sections.

3.3 *Evanescent wave fluorescence sensors*

Figure 7 shows a typical change in the fluorescence spectrum from a POF sensor exposed to ethanol vapor at varying concentrations. As shown in Fig. 7, the exposure to vapor causes only fluorescence intensity changes, not shifts to other wavelengths. Exposures to methanol, 1-propanol and 2-propanol vapors cause similar changes. A comparison between the fluorescence changes and the absorbance changes for the same dye-doped evanescent wave sensor exposed to the same vapor showed that fluorescence sensors give a much higher S/N ratio than absorbance sensors.

3.4 *Fluorescence responses to organic vapors*

Figures 8 shows the ethanol vapor concentration dependences of normalized fluorescence intensity values F/F_0, which were calculated from the peak values F_0 and F in fluorescence spectra measured in air and in organic gas, including the data in Fig. 7. From a comparison between the previous results[8–10] and Fig. 8, it is apparent that the fluorescence changes occur at a lower alcohol vapor concentration than the absorbance changes. In other words, evanescent wave fluorescence sensors have higher sensitivity to alcohol vapors than the absorbance sensors.[8–10]

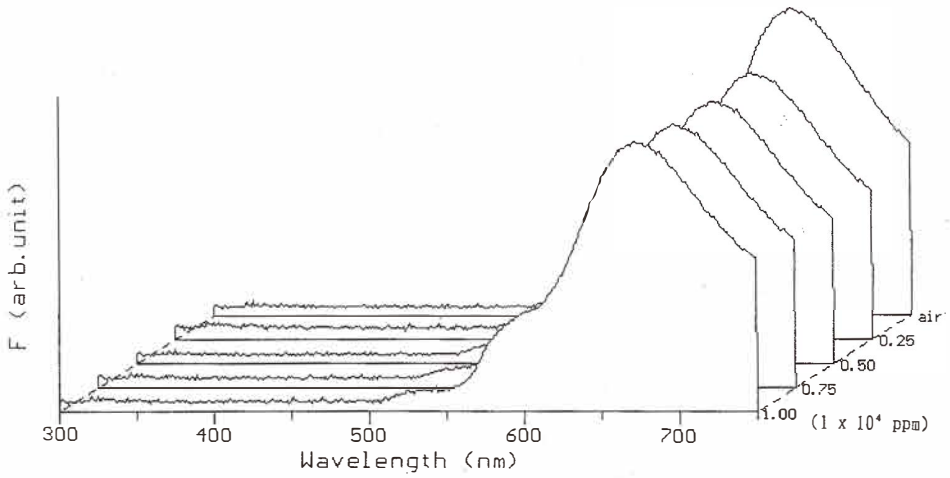

Fig. 7. Typical fluorescence spectrum changes from a POF sensor exposed to various concentrations of ethanol vapor.

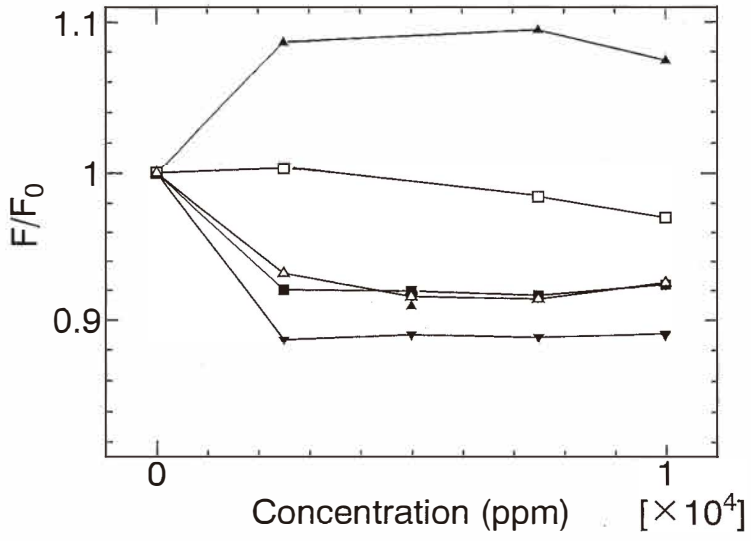

Fig. 8. Dependence of fluorescence intensity changes on vapor concentration from a POF sensor array exposed to ethanol vapor.

Fluorescent dyes with high fluorescence intensities and large fluorescence changes were selected for sensor array fabrication, which enabled pattern recognition or discrimination of organic gases. Figure 9 shows fluorescence spectra from a POF sensor array consisting of five evanescent wave sensors. Figure 10 shows the response patterns to organic gases at 1×10^4 ppm calculated from the gas concentration dependence data of F/F_0 including Fig. 8. Each of the six organic gases shows a different response pattern. Accordingly, this sensor array can be used for pattern recognition or discrimination of methanol, ethanol, 1-propanol, 2-propanol, diisopropyl ether and n-hexane.

A comparison between the results in Figs. 7 and 8 and QCM sensor results[2-5] indicates that even the evanescent wave fluorescence sensors have lower sensitivities than QCM sensors, which have high sensitivity of 10 ~ 50 ppm. A more detailed investigation is required on the fluorescent dyes and how to immobilize the dye molecules on the POF core surface for further enhancement of sensitivity.

Acknowledgment

The author thanks Shiho Taniguchi and Masao Takiwaki for their support in the experimental work.

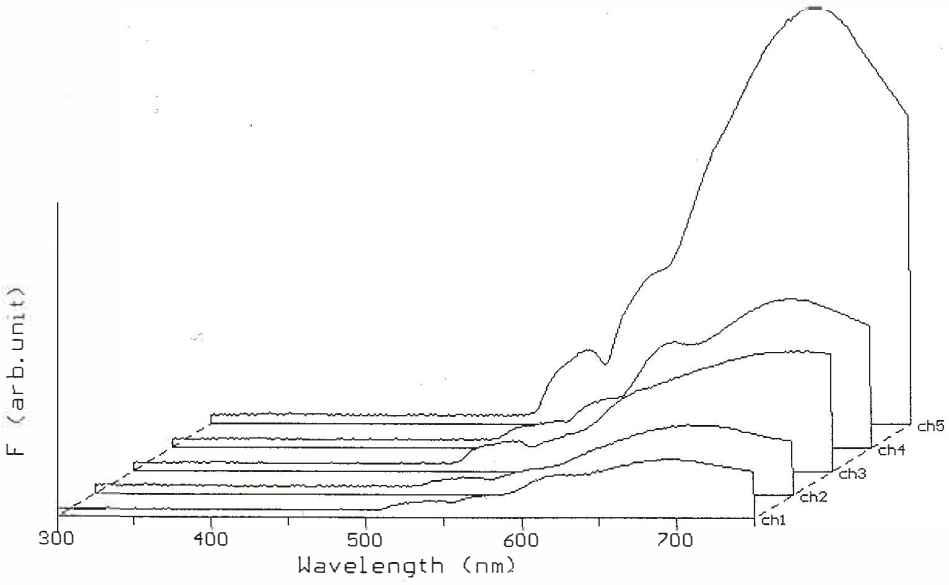

Fig. 9. Fluorescence spectra from a POF sensor array.

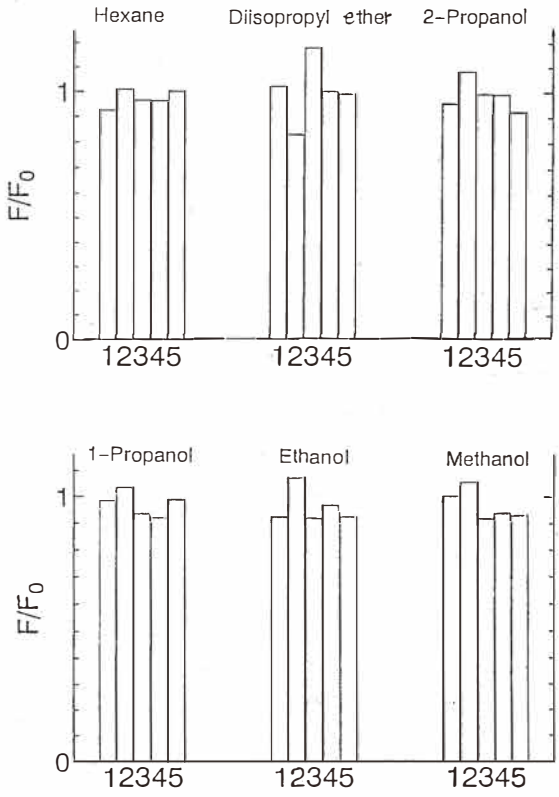

Fig. 10. Response patterns of a sensor array to six organic gases.

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