Visual Color Sensor for Indole Vapors

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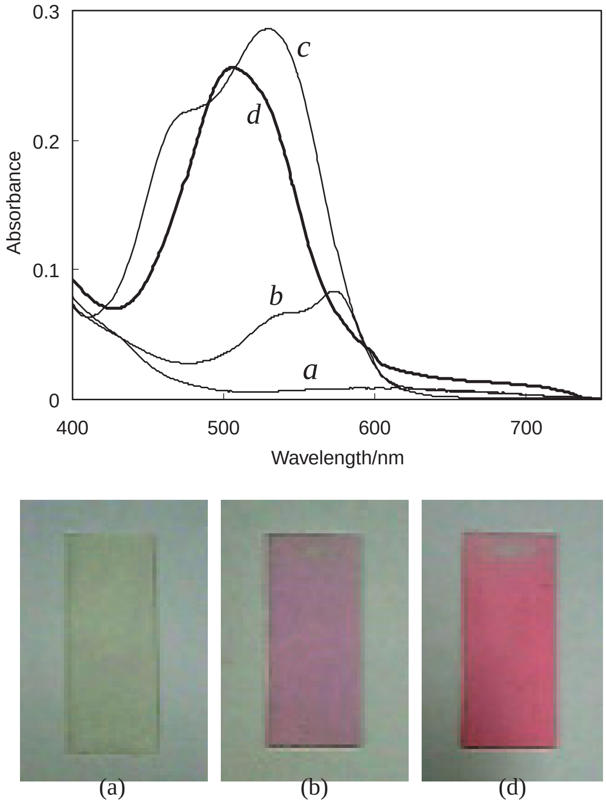
Based on the Ehrlich reaction in solid film, a color sensor has been developed for selective detection of indole and pyrrole vapors in environmental or workplace air. It will be suitable for real-time monitoring since neither pre-treatments of the air sample nor heavy instrumentations are needed.

Sensors for volatile organic compounds (VOCs) have received considerable attention because of its potential use for monitoring environmental or workplace air.[1–5] Among, amine vapors which give off a bad smell can also induce toxicological responses, hence facile detection in air is needed. While various methods for detection of amine vapors, e.g., electrochemical and optical sensing, as well as chromatographic analysis have been used, selective color sensing is of particular interest because of its simple and convenient handling suitable for real-time monitoring. Thus, a chemoselective vapor-sensing array based on metalloporphyrin dyes as a mimic model of mammalian olfactory system has been reported demonstrating analyte-specific detection and vapor dosimetry for a wide range of VOCs,[5] while selective color sensors for neutral analytes in solution have been developed by using reversible chromogenic or fluorogenic reactands.[6] For the detection of biogenic amines, aptamer-based colorimetric selective sensors for cocaine,[7a,7b] adenosine,[7b] and thrombin[7c,7d] have been reported, while highly selective color sensor for catecholamines in blood and urine has been developed by using specific guest–host complexes.[8] This paper is concerned with a simple and selective color sensor for indole and pyrrole vapors, which is visually detectable by naked eyes as well as colorimetrically determinable without heavy instrumentations nor pre-treatments such as condensation or separation of air samples. The color sensor utilizes the Ehrlich reaction[9] in a solid film. The Ehrlich reaction has been used in solution for qualitative (spot-test)[9] as well as quantitative analysis[10] of indoles and pyrroles, but not in the vapor phase. While vapor-phase analysis of indole derivatives has been carried out by using e.g., chromatographic[11] or electrochemical[12] methods, selective and non-instrumental detection of indole vapors has not been reported so far.

A solution containing *p*-dimethylaminobenzaldehyde (DAB) in 5% Nafion® solution (Aldrich Chemicals) was spin-coated on a polyester sheet. The film was air-dried, and cut into pieces of 2.0 × 0.8 cm, as a color sensor (DAB/Nf). Figure 1a illustrates the absorption spectrum of the fresh DAB/Nf film, and Figure 1b the spectrum after exposure to the air containing 14-ppm indole vapor in a 300-mL flask for 30 min, at 21 °C and relative humidity (RH) around 32%. The purple-colored film (b) was further dipped in an aqueous 6% H_2O_2 solution (3 mL) for 10 min, so that the color intensity was extensively increased as shown in Figure 1c. After rinse with pure water and air-dry, the film showed magenta or cherry-pink color as shown in Figure 1d. The color was unchanged at least 2 h at room temperature in air. By this method, vapors of 2-methylindole and 1-methylindole showed much more intense pink color, but 3-methylindole showed nil color reaction. Pyrrole vapors showed similar color reaction to those of indole vapors, but no such color reaction was observed with vapors of pyridine, thiophene, and ketones.

Aliphatic amine vapors gave Schiff bases with faint yellow color while aniline and furan gave bright yellow color, thus easily distinguishable from the pink or magenta color of indole and pyrrole vapors.

For quantitative analysis, on the other hand, colorimetric measurement of the maximum absorbance allows approximate estimation for the concentration of indole vapor. As shown in Figure 2, the maximum absorbance around 510 nm of the colored film changed in response to the indole concentration, though not strictly proportional to the concentration (as shown



(a) (b) (d)

Figure 1. Absorption spectra of DAB/Nf film (a) before exposure, (b) after 30-min exposure to 14-ppm indole vapor in air at 21 °C and HR of 32%, (c) after 10-min immersion in aqueous 6% H_2O_2 solution, and (d) after rinse and air-dry. Real color images of (a), (b), and (d) are shown at the bottom.

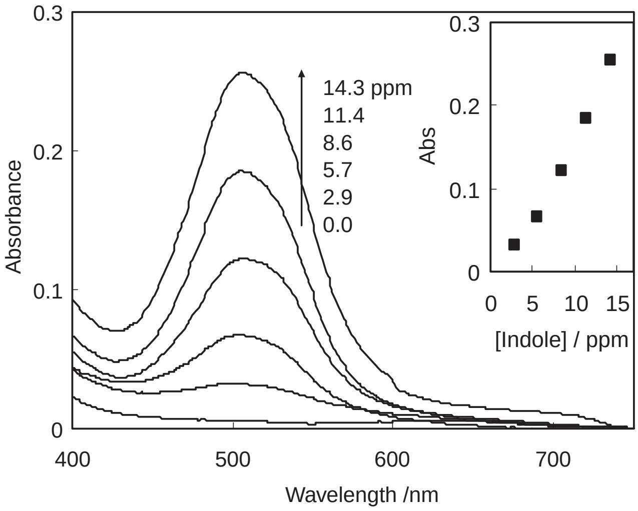


Figure 2. Absorption spectra of the dried DAB/Nf film after exposure to various concentrations of indole vapor followed by treatment with aq. 6% H_2O_2 solution. The inset refers to the plot of absorbance at 510 nm against the concentration of indole vapor.

Figure 3. Color changes of the detector tube after pumping a 100-mL indole-mixed air. Concentration of indole vapor in air was 0.0 (as a blank), 2, 6, and 10 ppm, respectively, from the left.

in the inset). The sensitivity was almost constant at RH above 30%, but significantly decreased at RH below 20%.

For further demonstration, a handy detector tube for environmental or workplace air analysis[1] was prepared. Thus, 5 g of sea sand (20–35 mesh, Wako Chemicals) was mixed in a mixture solution containing DAB (200 mg) in 8-mL methanol and 18 wt % poly(4-styrenesulfonic acid) in 2-mL water. The yellow sand was separated and heated at 50 °C for 30 min, then packed in a glass tube as a detector tube (5-mm diameter and 60-mm length). The detector tube was connected to the gas inlet of a commercial handy pump[1,2] (GASTEC GV-100S). Figure 3 illustrates a color change of the detector tube from yellow to magenta upon pumping a 100-mL air containing 2–10 ppm indole vapor through the tube, while no color change was observed with a blank (air without indole). By this detector tube, the time needed for the air analysis can be shortened to be 2–3 min.

The present color sensor may serve as a simple and selective detection for indole and pyrrole vapors in environmental or workplace air, without pre-treatment of the air sample nor with heavy instruments.

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