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Indoor Air Quality Monitoring via IT Network

Colorimetric Monitoring of Formaldehyde in Indoor Environment Using Image Transmission of Mobile Phone

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Abstract: A simple and rapid monitoring system of indoor air pollution is proposed by integrating a colorimetric detection method of formaldehyde (HCHO) and a function of image transmission of a mobile phone via IT network. The colorimetric detector employs a solid phase colorimetric reagent made from AHMT, ZnO, KIO_4 and agar, and discolors from white to purple when exposed to a certain amount of HCHO gas. Although the color degree responds to the HCHO concentration levels, visual judgment often involves personal bias that leads to uncertainty. In this feasibility study, variation of the acquired photo images expressed in RGB model was investigated by changing a type of mobile phone and conditions of photography. As a result, the calibration of the measured color degree with a color standard reduced the variation of the results and gave a significant color degree when the images were taken under the consistent condition. Since the light source was one of the significant elements for image analysis, the light condition should be decided for practical applications.

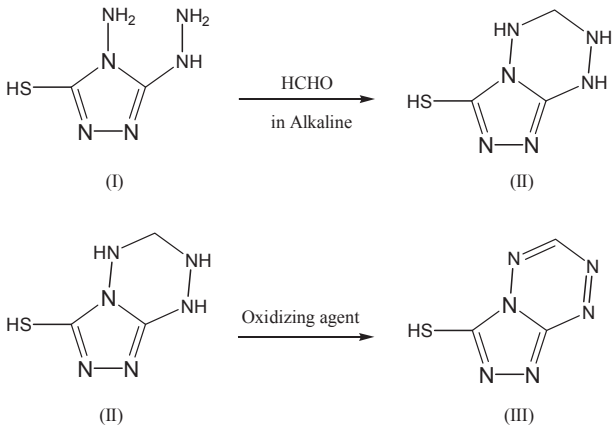
Keywords: formaldehyde, colorimetric detection, mobile phone, image transmission, home testing

1. INTRODUCTION

Indoor air quality in the living environment has been inviting a growing concern as a personal matter. Exposure to formaldehyde (HCHO) in indoor air has been known to cause adverse health effects on human health, particularly in relation to Sick Building Syndrome (SBS), also known as Sick House Syndrome (SHS). Major emission sources of indoor HCHO are plywood, particleboard and adhesives for wall clothes, commonly used in construction and interior finishing. Therefore, information of the indoor air concentration levels and emission rates from the materials is important for the determination of indoor air quality of living environment.

Solid sorbents coated with 2,4-dinitrophenyl hydrazine (DNPH) have been used as trapping media for the determination of HCHO in indoor air both active [1,2]and passive sampling modes[3-4]. The reaction between carbonyls and DNPH is rapid and quantitative in the presence of acid, and the product can be determined by a high performance liquid chromatography (HPLC) with excellent sensitivity. While this DNPH-HPLC system is widely used as a standard methodology, this requires instrumental sampling devices, analytical procedures using chemical substances and analytical equipment such as HPLC, which should be operated by professionals.

A simple detection of HCHO based on visual color change, which can be used by non-expert users, has been attracting a considerable concern for safe living in a house or building. There are several materials for the detection of HCHO using colorimetric reagents[5-6]. Whilst these previous methodsare convenient, they are not visually sensitive to users due to their yellow or brown colors, interference by other air pollutants and so on. Absorption spectrophotometry employing 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole (AHMT) has been commonly used as a standard method for the determination of airborne HCHO dissolved in a trapping solution [7]. The AHMT(I), prepared for the sensitive detection of aldehydes by Dickinson and Jacobsen [8], condenses with the fromyl group of HCHO to form an unstable and oxygen labile intermediate(II) in a sodium hydroxide (NaOH) solution. The intermediate(II) is rapidly oxidized by oxidizing agent (ie. potassium iodate, KIO_4) to a purple 6-mercapto-s-triazolo[4,3-b] -s-tetrazine (III), which has an absorption bands in the visible region with an absorption maximum at 550nm.



Though the AHMT potentially reacts with other aldehydes, it is highly sensitive to HCHO [7]. Applying this AHMT method to the simple detection of gases, there were some problems; the stepwise reaction takes place in a NaOH solution (not preferable for safe handling), the color reagents are added to the HCHO solution (HCHO should be added to the color reagent

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for our purpose), and the reaction media is aqueous (solid phase is preferable). Then, Tsuda and Sekine investigated possible modification of the previous AHMT method and found co-precipitate of Zinc hydroxide, KIO_4 and AHMT could be a solid phase colorimetric reagent for HCHO, which turns purple [9,10].

Based on the technology established, authors propose a simple and rapid home-testing system of indoor air pollution by integrating a colorimetric detection method of HCHO and a function of image transmission of a mobile phone via IT network, in order to realize a ubiquitous point-of-care monitoring system of personal living environment.

2. CONCEPTUAL VIEW

Fig.1 shows a proposed conceptual view of the HCHO detection system via IT network. Firstly, a person, who wants to know the status of HCHO pollution, obtains the colorimetric detector from distributors (as conceptual examples: pharmacy, convenience store, public health centers or so) and exposes the detector to indoor air (for checking air concentrations) or building materials (for exploring the emission source of HCHO).

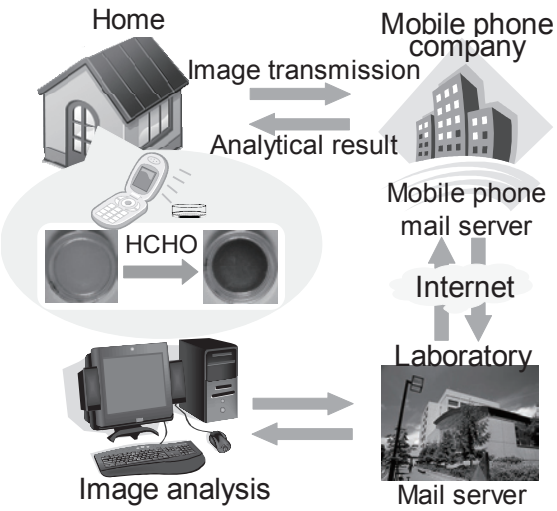


Fig.1 HCHO detection system using IT network.

The colorimetric detector discolors from white to purple when detecting a certain amount of HCHO gas. Although the degree of color change responds to the HCHO concentration levels, a visual judgment, comparing with a color sample printed on a paper, often involves personal bias that leads to uncertainty. Then, in this system, photo images of the discolored detector, taken by the testing resident, are sent to an analytical laboratory using a function of image transmission of a mobile phone by way of internet.

An operator at the laboratory analyses the images to determine the HCHO pollution level and subsequently returns a report by a mailing service. This system is ubiquitous, user friendly and potentially usable in houses, offices, schools and workplaces in the world.

Fig.2 Acquisition and transmission of a digital image of the colored detector using a function of personal mobile phone.

3. EXPERIMENTAL

3.1 Reagents

Reagent grade hydrochloric acid (HCl), NaOH, Zinc oxide (ZnO, purity >99%), potassium iodate (KIO_4), AHMT, HCHO solution and agar powder were obtained from Kanto Chemicals, Tokyo, Japan.

The aqueous solutions of HCl, NaOH and HCHO were titrated to determine their exact concentrations before use. An AHMT solution was prepared by dissolving 0.1g of AHMT in 20mL of 0.2 M HCl under mild heating in a water bath. Powders of 0.15g of KIO_4 were readily dissolved in 20mL of 0.2M NaOH. A warm agar solution was prepared by dissolving 0.7g of agar powder in 20ml of deionized water under mild heating. Dilution series of HCHO solution was prepared by using the titrated stock solution and deionized water.

3.2 Preparation of colorimetric reagent

Powder of ZnO (0.01g) was dissolved into 2ml of 0.2M HCl solution containing AHMT. To the solution, 2mL of KIO_4/0.2M NaOH solution was mildly added. Then, the precipitate of Zinc hydroxide, involving of AHMT and KIO_4, formed in the mixed solution (Colloidal solution). The product was separated by centrifugation (3000rpm, 10min) and subsequently transferred to a glass Petri dish (Pyrex, 30mmφ, 15mm height, a base part of the Petri dish). A warm liquid agar (0.8mL) was immediately mixed to the co-precipitate. The detector was then lidded and cooled in a refrigerator until the agar set enough. The lidded detector was then sealed by a piece of Parafilm^{TM}, enveloped in an aluminum bag and stored in the refrigerator.

3.3 Absorption spectrometry of the detector

Photo-physical properties of the novel reagent and the reaction product with HCHO were investigated in aqueous phase. To 4 ml of the colloidal solution containing $Zn(OH)_2$, AHMT and KIO_4, 4 mL of HCHO

solution (0 – 2.5μg/ml) was mixed with mild shaking. The absorption spectra of the supernatant was then observed by Shimadzu UV mini 1240 spectrophotometer using deionized distilled water (DIW) as a reference.

3.4 Exposure tests in a closed Petri dish

Colorimetric performance of the detector was firstly assessed by exposure to a vapor of HCHO from a droplet of HCHO solution in a closed Petri dish. The detector (base) was capped with a lid of the Petri dish (Pyrex, 35mmφ, 15mm height) where 0.05mL of HCHO aqueous solution was dropped. Through the open face, HCHO gas generated from the droplet moved toward the colorimetric reagent within a headspace by molecular diffusion and the gas molecules then reacted with the reagent. The closed pair of dishes was then stand for 24hrs and the color change was observed.

To quantify the color change of the detector, the color was converted to a color value of green in a RGB color model. A digital image of the detector was taken by a digital camera positioned at 15 cm above the desk level under constant light. The color value of G was obtained by editing the image in a graphics editor, Adobe Photoshop™. Since purple is complementary color of green, the G value decreases with an increase of color change of the detector. Then, the color response was expressed as color intensity, P defined by equation (1).

$$P = 255 - G \quad (1)$$

3.5 Optimization of response of the detector to vaporized HCHO

Response of the detector was investigated by changing pH of the colloidal solution. Powder of ZnO (0.01g) was dissolved into 2ml of 0.201M HCl solution containing AHMT. To the solutions, 1.8, 1.9, 2.0, 2.1, 2.2 and 2.3mL of KIO_4/0.211M NaOH solution were mildly added respectively. The formed co-precipitates were then separated and prepared for the detectors as described in 3.2. The detectors were subsequently exposed to HCHO vapors in closed Petri dishes and the color responses were observed.

3.6 Interference of other gases

To investigate the interference of other gases, the detector was exposed to vapors of acetaldehyde, acetone, methanol, ethanol, toluene, styrene, benzene, p-xylene, ethylbenzene and limonene, commonly found in indoor air of Japan, respectively. The detector was placed on a Petri dish (Pyrex, 35mmφ, 15mm height) where 0.05mL of liquid of each compound or 100, 500μg/ml of acetaldehyde aqueous solution was dropped. The closed dish was then stand for 24hrs and the color change was observed.

3.7 Exposure to HCHO gas in air

Response of the detector to a known concentration of HCHO in air was investigated using a small chamber (7L) with a constant gas generation system under controlled temperature. The detector was put in a transparent desiccator made of acrylic resin (AsOne, type VS), and HCHO gas was constantly introduced from a gas generator at a flow rate of 10L/h (air exchange rate=1.4 /h). Diluted aqueous solution of HCHO set in an incubator (298K) was used for gas emission source of the generator. Digital images of the detector were automatically taken by the digital camera positioned at 15 cm above the desiccator, and time series of the color intensity was obtained.

Air concentrations of HCHO at inlet were determined by DNPH active sampling - HPLC method. Inlet air was passed through DNPH coated solid cartridge (GL Science, AERO-DNPH) connected with an air pump (Sibata Science, MP-Σ30) at a flow rate of 10L/h for 0.5h. After sampling, the DNPH derivative was eluted by passing 10mL of acetonitrile in 5 min, and determined by HPLC. The HPLC system consists of Hitachi L-2130 pump with Hitachi L-2400 UV-Vis detector. The following condition was used: column, 4.6 mm×150 mm, 5 μm, Inertsil ODS-80A (GL sciences); eluent, acetonitrile : distilled water in the ratio of 1 : 1 (vol/vol) at 1.0 mL/min (isocratic) ; detection, 360 nm; Injection volume, 20 μL; Injection mode, manual. Dilution series of DNPH-carbonyl compounds in acetonitrile solution, 0.01, 0.025, 0.05 and 0.1 μg/mL, were prepared from 16-Aldehydes-DNPH mixture standard solution (10 μg/ml in acetonitrile, Wako Pure Chemical Industries) and used for calibration.

3.8 Exposure to building materials

Response of the detector to HCHO gas emitted from plywood with a known emission flux of HCHO was investigated. The plywood samples, generally used for flooring in a house and presently banned for use due to large emissions of HCHO, were obtained from a stock source. The detector was place on the surface of a piece of plywood at 298K and stand for 48 hrs.

According to JIS A 1901:2003, the emission flux of HCHO from the plywood samples were separately determined using a small chamber (20L) with a constant airflow of 0.167 mL/min (air exchange rate=0.5 /h) under controlled temperature of 298K. Loading factor of the plywood sample was 1.12 m^2/m^3. Air concentrations of HCHO at outlet were determined by DNPH active sampling - HPLC method as described above.

3.9 Image acquisition by mobile phone camera

As a feasibility study, variation of the acquired photo images expressed in RGB model was investigated by changing a type of mobile phone and conditions of photography. To quantify the color change of the detectors exposed to a droplet of HCHO solution for 24hrs, digital images were taken by built-in cameras of mobile phones positioned at 10～20 cm above the desk level under constant lights such as natural sunlight, reflector lamp and fluorescence tube. The color was converted to a color value of green in a RGB color model on a personal computer and converted to color intensity by equation(1).

4. RESULTS AND DISCUSSIONS

4.1 Development of the novel reagent

In the analytical procedure of the original AHMT method, AHMT solution and oxidizing agent was added to the HCHO solution in this order. This order was absolute, because HCHO was easily oxidized by oxidizing agent and did not form the purple compound (III) when HCHO was added to the mixed solution of AHMT and oxidizing agent. To the contrary, the novel reagent consisting of co-precipitation of $Zn(OH)_2$, AHMT and KIO_4 significantly reacted with HCHO to form compound(III) even when the HCHO was added behind. The formation of the compound (III) was firstly confirmed by examining photo-physical properties of the novel reagent and the reaction product with HCHO in aqueous phase.

Fig.3 shows the typical absorption spectra of supernatant of colloidal solutions with and without addition of HCHO. When HCHO was added, the colloidal solution discolored from white to purple with an absorption maximum at 550nm, which showed the significant formation of compound (III).

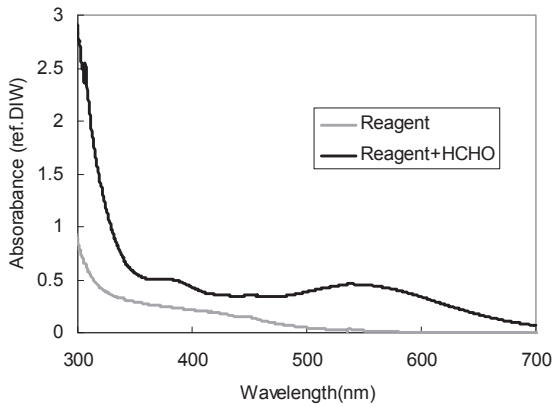


Fig.3 Absorption spectra of supernatant of colloidal solutions of the reagents with and without addition of HCHO (4mL of colloidal solution + 4ml of DIW or 4.5M HCHO(aq)).

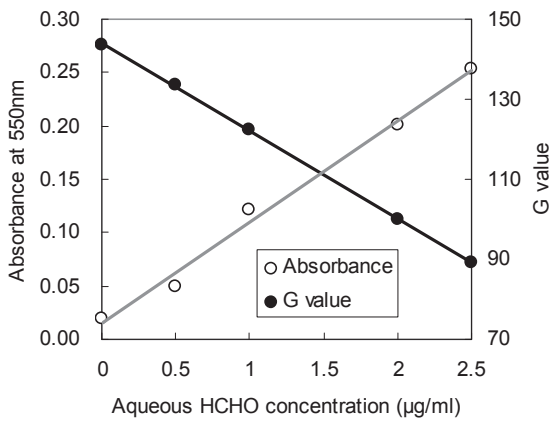


Fig.4 Plots of absorbance at 550nm and G value against the concentrations of HCHO aqueous solutions added to the colloidal solution.

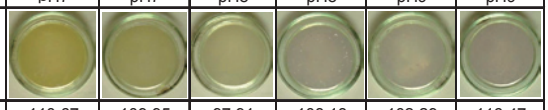
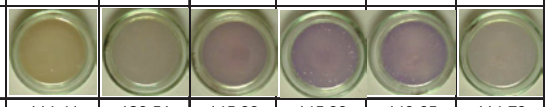
The absorbance increased with an increase in concentrations of aqueous HCHO solutions, whilst G value decreased correspondingly (Fig.4). This means the formation of compound (III) corresponds to the moles of HCHO added to the system and the G value measured by the conventional image analysis could be a good indicator for the color change. Then, the color change was expressed in color intensity, *P* defined by equation (1).

The co-precipitate was then separated from the supernatant and developed on the Petri dish. The product was however sensitive to dryness probably due to aerial oxidation of AHMT. Therefore, agar was mixed to the co-precipitate to keep moisture. The final product was a white gel, which clearly turns purple when exposed to HCHO vapor. However, the color intensity was found to change with pH of the colloidal solutions. Then, the preparation method was optimized as follows.

4.2 Optimization of response of the detector

The detectors were prepared by changing the acidity or basicity of the colloidal solution from pH 7 to pH 9. Table 1 shows the color changes of detectors exposed to HCHO vapor from a droplet of 50μL of 100μg/mL of HCHO solution for 24hours. The higher color intensities were found in the samples prepared by using 2.0 – 2.2 mL of KIO_4/NaOH solution, corresponding to 0.87 – 0.95 of molar ratios of HCl and NaOH. Since the detector was very sensitive to mixing rate of AHMT and KIO_4 solutions, solvents (HCl and NaOH solutions) were strictly titrated before use and the volume of both AHMT and KIO_4 solutions were controlled considering the molar ratio of HCl and NaOH to be 0.87 – 0.95 in the colloidal solution. Under this condition, the pH of the solutions was approximately eight. This is preferable for safe handling.

Table 1 Dependence of mixing ratios as well as pH on the color change of detectors exposed to HCHO gas.

t (h)	Amount of KIO_4 soln. added to 2ml of AHMT soln.(mL) 〔 〕: [HCl]/[NaOH]					
	1.8	1.9	2.0	2.1	2.2	2.3
	〔1.06〕	〔1.00〕	〔0.953〕	〔0.907〕	〔0.866〕	〔0.828〕
	pH7	pH7	pH8	pH8	pH9	pH9
0						
P	110.67	109.95	97.91	108.13	102.29	116.47
24						
P	114.41	126.51	145.33	145.33	140.65	114.78
P_{24}/P_0	1.03	1.15	1.48	1.34	1.38	0.99

Reproducibility of the detector response was assessed by simultaneous exposure of five detectors to HCHO vapors from a droplet of 50 μL of 100 μg/mL of HCHO solution for 24hours. Relative standard deviations of color intensities were 0.72 % at pre-exposure and 1.4 % at 24h. Based on the excellent color change and

reproducibility, we then tested the detector in a small chamber under constant HCHO concentrations.

No interference was found for the color change of the detector when exposed to vapors of acetone, methanol, ethanol, toluene, styrene, benzene, *p*-xylene, ethylbenzene and limonene. Acetaldehyde gave a significant color change of the detector, because it potentially reacts with AHMT. However, it required 5-fold aqueous concentration of acetaldehyde than that of HCHO, when the color intensity became equal to that by HCHO. This means acetaldehyde in actual living environments may not have severe influence on the colorimetric detection of HCHO.

4.3 Exposure to gaseous HCHO in air

Response of the detector to a known concentration of HCHO in air was investigated using a small chamber (7L) with a constant gas generation system under controlled temperature. Fig.5 shows typical time courses of color intensity of the detectors exposed to 0 (blank), 0.13 and 0.85 mg/m^3 of HCHO gases at 298K. The colors increased with time and approached to plateau depending on the HCHO concentrations: higher initial reaction rate with high color intensity level for higher HCHO concentration, lower initial reaction rate with low color intensity for lower HCHO concentration. Therefore, the intensity at certain elapsed time, for example 24hrs, corresponds to the HCHO concentration in air, as can be seen in Fig.6.

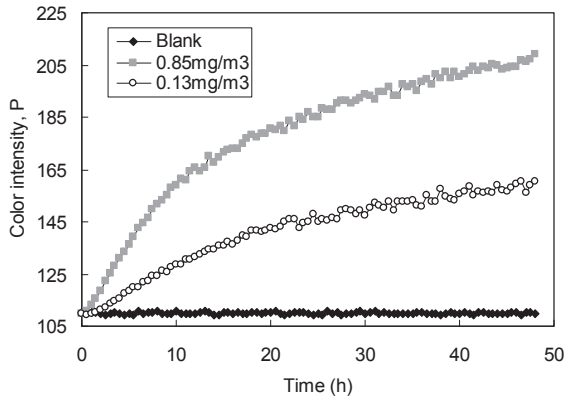


Fig.5 Typical time courses of color intensity of the detectors exposed to HCHO in air at 298K.

To analyze this property in detail, we applied Langmuir - Hinshelwood (L-H) kinetic model, which is shown to provide a quantitative kinetic treatment of many solid-gas phase reactions. The reaction rate, *r* (/h) of a unimolecular surface reaction will obey the following equations:

$$r = \frac{kKC}{1 + KC} \qquad (2)$$

where *k* is the surface rate constant (/h), *K* is the apparent adsorption coefficient (m^3/mg), *C* is the equilibrium air concentration of HCHO (mg/m^3) (in this case, constant air concentration in the small chamber). By fitting the time course data to the linear form of equation (2), we obtained 9.2 /h of *k* and 1.6 m^3/mg of *K* for HCHO at 298K.

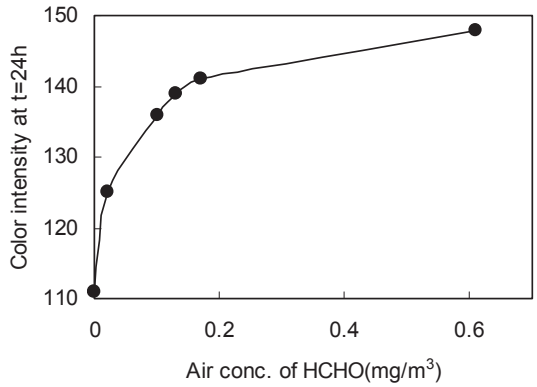


Fig.6 Color intensities at 24 hrs of the detectors exposed to each air concentration of HCHO in the small chamber controlled at 298K.

4.4 Exposure to building materials

The detector also responded to the HCHO gas emitted from plywood. Fig.7 shows linear relationship between color intensity of the detector and emission flux of the plywood samples as a function of the elapsed time (0, 24 and 48hrs) with significant correlations. This results show excellent linearity of the technique and suggest that reasonable accuracy can be expected after establishing the calibration under given measurement conditions.

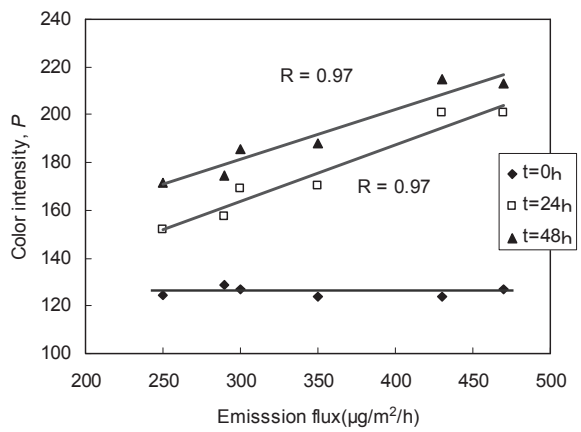


Fig.7 Relationship between color intensity of the detector and emission flux of the plywood samples as a function of the elapsed time (0, 24 and 48hrs) at 298K.

4.5 Images taken by mobile phone camera

Variation of the acquired photo images expressed in RGB model was investigated by changing a type of mobile phone (*n*=10) and conditions of photography.

Fig.8 shows measured color degrees of the discolored detectors exposed to different concentration levels of HCHO (No.1 and 2), obtained by 10 types of mobile phones (A - J) positioned at 15cm above desk under indoor fluorescence tube light. Variations in color degrees as received were found especially in lower

HCHO concentration level (No.2). However, calibration of the measured color degree with a color standard, which is located near the detector at photography, successfully reduced the variation of the results within 6% of coefficient of variation (CV).

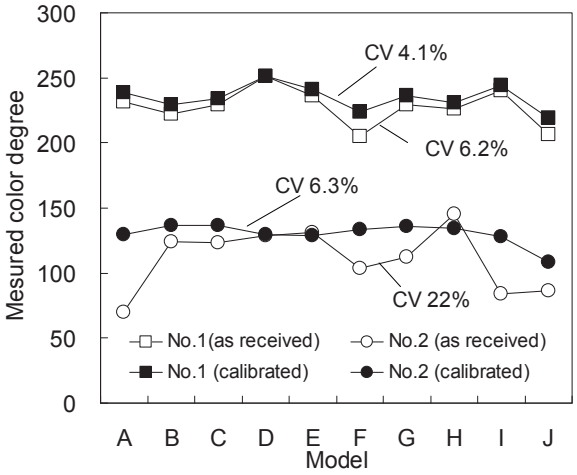


Fig.8 Variations of measured color degree of discolored detectors exposed to HCHO gases by ten models of mobile phone. Concentrations of aqueous HCHO, No.1: 2mg/mL, No.2: 0.05mg/mL.

The distance between a camera of mobile phone and discolored detector was not significant element for the measurement in the range of 10～20 cm above the desk level, when the focus was properly adjusted.

However, the lighting source influenced on the measured color degrees as shown in Fig.9. The photos of the discolored detectors were taken by 10 cameras of mobile phones under natural sunlight, reflector lamp and fluorescence tube. The difference in color degrees was apparent when the photos were taken under natural sunlight. Since the light source was one of the significant elements for image analysis, the light condition should be decided for practical applications.

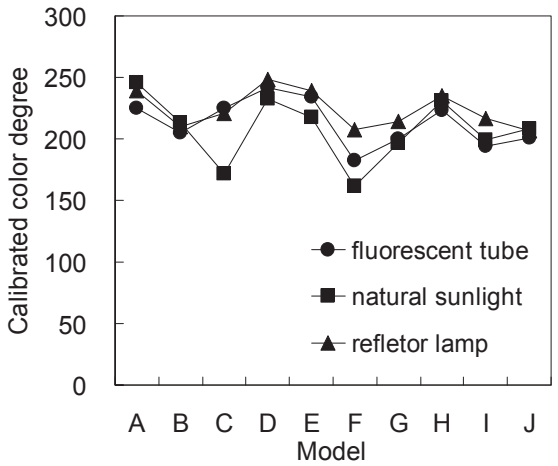


Fig.9 Influence of the lighting source on the measured color degree under the lights indoor. Detector was exposed to HCHO gases from 2mg/mL HCHO aqueous solution.

5. IN LIE OF CONCLUSION

A simple and rapid monitoring system of indoor air pollution was proposed by integrating a colorimetric detection method of HCHO and a function of image transmission of a mobile phone via IT network. The colorimetric detector employing AHMT significantly discolored from white to purple when exposed to a certain amount of HCHO gas in indoor air or emitted from building materials. The calibration of the measured color degree with a color standard gave significant results, even when the images were taken by built-in camera of different types of mobile phone under constant light. The system, when established, will be a member of Point-of-Care home testing for realizing healthy indoor environment.

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