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Passive Emission Colorimetric Sensor (PECS) for Measuring Emission Rates of Formaldehyde based on an Enzymatic Reaction and Reflectance Photometry

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A coin-sized passive emission colorimetric sensor (PECS) based on an enzymatic reaction and a portable reflectance photometry device were developed to determine the emission rates of formaldehyde from building materials and other materials found indoors in only 30 minutes on-site. The color change of the PECS linearly correlated to the concentration of formaldehyde aqueous solutions up to 28 μg/mL. The correlation between the emission rates measured by using the PECS and those measured by using a desiccator method or by using a chamber method was fitted with a linear function and a power function, and the determination coefficients were more than 0.98. The reproducible results indicate that the emission rates could be obtained with the correlation equations from the data measured by using the PECS and the portable reflectance photometry device. Limits of detection (LODs) were 0.051 mg/L for the desiccator method and 3.1 μg/m^2/h for the chamber method. Thus, it was confirmed that the emission rates of formaldehyde from the building materials classified as F four-star ($<$0.3 mg/L (desiccator method) or $<$5.0 μg/m^2/h (chamber method)), based on Japanese Industrial Standards (JIS), could be measured with the PECS. The measurement with PECS was confirmed to be precise (RSD $<$ 10%). Other chemicals emitted from indoor materials, such as methanol, ethanol, acetone, toluene, and xylene, interfered little with the measurement of formaldehyde emission rates by using the PECS.

Introduction

Recently, buildings that are tightly sealed to save energy and new types of building materials have caused air pollution problems inside many houses in Japan. Many people suffer from sick building syndrome (SBS) and from multiple chemical sensitivity (MCS) in such houses. Formaldehyde, which is emitted from adhesives, bleach, fungicides, etc., has been reported to be one of the chemical substances responsible for causing SBS and MCS symptoms, such as eye irritation, respiratory tract irritation, dizziness, fatigue and neurotoxicity (*1–3*). Guideline levels published by the Japanese Ministry of Health, Labour and Welfare (MHLW) and the World Health Organization (WHO) for chronic exposure to formaldehyde in indoor air are 100 μg/m^3 (0.08 ppm), based on the level that has been shown to cause nose and throat irritation in humans (*4, 5*). In Japan, plywood and particleboard have been classified into four categories (F one-star to F four-star) depending on their formaldehyde emission rates, which are measured by using emission chamber or desiccator methods. In Japanese Building Codes, the areas in which these materials can be used in house construction are limited by their classification and by the ventilation capacity of the house (*6*). The guidelines and law have been successful in reducing the mean indoor concentration of formaldehyde in new houses from 0.073 ppm (number of samples, $N = 2815$) in 2000 to 0.026 ppm ($N = 1349$) in 2004 (*7*). Since the law applies only to new houses, older houses and furniture are not affected. Thus, the major emission sources have to be identified and removed from older houses if the formaldehyde concentration is high.

Although it is desirable to remove the major emission sources of formaldehyde, it is difficult to determine which sources significantly affect indoor air quality, because there are several possible sources, such as flooring, doors, closets, desks, beds, etc. An emission chamber method (*8–12*) and a desiccator method (*13*) have been used to measure the emission rates of chemical compounds from building materials. However, it is impossible or impractical to use these methods on-site in actual rooms because the emission sources to be measured must be placed in a desiccator or a chamber. Recently, field and laboratory emission cells (FLEC) (*14–16*), a passive flux sampler (PFS) (*17–19*), and an advanced diffusive sampling emission cell (ADSEC) (*20, 21*) have been proposed and applied to measure the emission rates in the field. Although these methods can be used in both the field and the laboratory, they are unsuitable for multipoint field sampling, because of size, weight, and cost considerations and/or the necessity for technical analysis.

In this study, a coin-sized passive emission colorimetric sensor (PECS) and a portable reflectance photometry device were developed to measure the formaldehyde emission rates on-site. Major emission sources of formaldehyde in a residential room could be easily identified with a measurement time of only 30 minutes using the sensor.

New Sensor for Formaldehyde Emission Measurement

Sensor Design and Principle. A photograph and a schematic diagram of the PECS are shown in Figure 1. The sampler consists of a polyethylene terephthalate (PET) body (external diameter = 23 mm, internal diameter = 18 mm, thickness = 3.2 mm, inner depth = 1.6 mm), which has a hole (diameter = 5.0 mm) in the center of the patch side, adhesive for the patch, a water-retaining glass filter, and an enzyme test sheet (5 mm × 5 mm) which turns red in the presence of formaldehyde. To obtain the sensitive and stable enzymatic activity, we selected a water-retaining glass filter (DP-70, Toyo Roshi Kaisha, Ltd., Japan), which can retain an appropriate amount of water and does not contain formaldehyde, from among several kinds of water-retaining glass filters because

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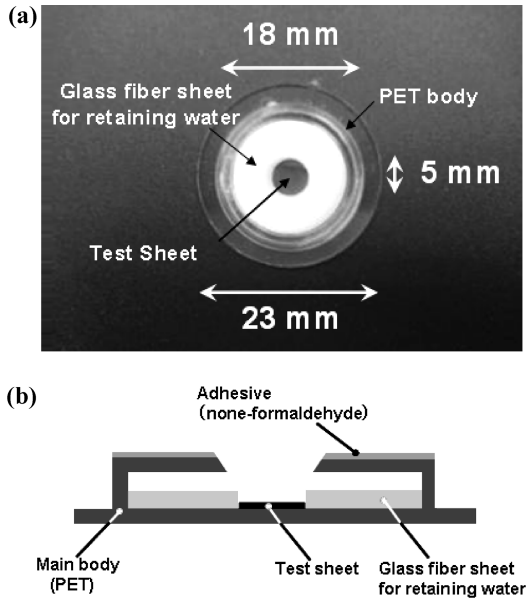

FIGURE 1. Developed detector (PECS): (a) photograph and (b) schematic diagram.

the enzymatic activity is not stable without an appropriate amount of water. The PET and adhesive which do not include and emit formaldehyde were used for the PECS. Formaldehyde dehydrogenase, nicotinamide adenine dinucleotide (NAD^+), 2-(p-iodophenyl)-3-(p-nitrophenyl)-5-phenyltetrazolium chloride (INT), and diaphorase are impregnated in the enzyme test sheet.

At the beginning of the measurement, the PECS is placed on each indoor material to be tested, such as flooring, walls, ceiling, doors, closets, desks, and beds. Formaldehyde emitted from the material diffuses through the hole into the PECS, dissolves in water on the test sheet, and undergoes a two-stage enzymatic reaction on the test sheet, resulting in a red color due to the product formazan (*22, 23*):

$$HCHO_n + {}_nNAD_n^+ + H_2O \xrightarrow{\text{Formaldehyde dehydrogenase}} HCOOH_n + {}_nNADH_n + {}_nH^+ \quad (1)$$

$$NADH_n + {}_nINT_n + {}_nH^+ \underset{\leftarrow}{\xrightarrow{\text{Diaphorase}}} NAD_n + {}_n\underset{[red]}{Forazan} \quad (2)$$

The PECS is highly formaldehyde-selective because of the enzymatic reaction.

It is well-known that passive sampling in indoor and outdoor environments is affected by the geometry. Since the thickness of boundary layer on the passive sampler varies according to the air velocity, the diffusion resistances of passive samplers are designed large enough to ignore the molecular diffusion in the boundary layer. On the other hand, in the measurement of the emission rates by using the PECS, formaldehyde diffuses by molecular diffusion inside the PECS without the effect of the turbulent flow because the inside of the sensor is sealed with sensor and target material. The diffusion length (inner depth of the sensor) can affect the sampling rate of the PECS. Thus, the inner depth of the PECS was decided as 1.6 mm according to the sensitivity of the PECS.

Measurement Procedure. The measurement procedure for the formaldehyde emission rate using the PECS was as follows: (i) a drop of pure water was put into the PECS, since the enzymatic reaction requires water; (ii) the PECS was placed with its open face on the material to be tested, such as flooring, walls, ceiling, doors, closets, desks, beds, etc. for 30 min; (iii) the PECS was peeled off of the material; and (iv) the color of the test sheet was determined by visual observation or by using the portable reflectance photometry device.

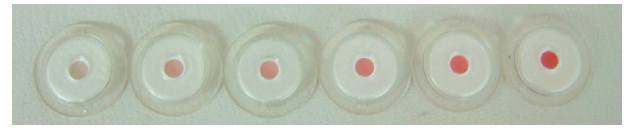

FIGURE 2. Color changes of the PECS for different kinds of particleboard. From the left, the concentrations of formaldehyde from the particleboard obtained by using the desiccator method were 0, 0.08, 0.23, 0.79, 1.42, and 3.06 mg/L.

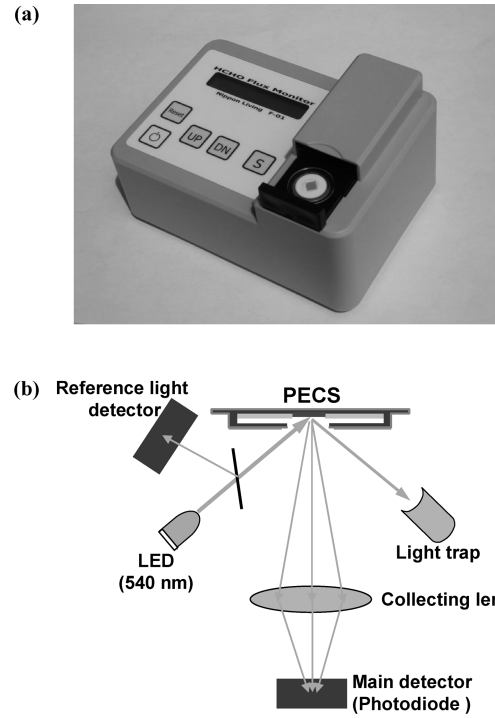

FIGURE 3. Developed reflectance photometry device: (a) photograph and (b) schematic diagram. (i) Test sheet of PECS, which is placed in the instrument, is irradiated by green light from a light emitting diode (LED); (ii) the reflected light is concentrated with a condenser lens; and (iii) the concentrated light intensity is measured as voltage with the photodiode. The reflected light that is not collected with the condenser lens is trapped with a light trap to keep it from reflecting diffusely. Part of the light from the LED is measured with a reference light detector before it irradiates the PECS.

Portable Reflectance Photometry Device. Visual observation can identify at most 5- or 6-points scale of emission rates (Figure 2). In addition, the results of visual observation could differ from one person to another. Precise measurement is difficult via visual observation, especially in the case of low emission rates. Hence, we developed a portable instrument that uses reflectance photometry to easily and precisely measure the color change of the PECS on-site. A photograph and schematic diagram of the device are shown in Figure 3. The measurement procedure is as follows: (i) the test sheet of the PECS, which is placed in the instrument, is irradiated with green light from a light emitting diode (LED); (ii) the reflected light is concentrated with a condenser lens; and (iii) the concentrated light intensity is measured as voltage with a photodiode. The reflected light that is not collected by the condenser lens is trapped with a light trap so that it does not reflect diffusely. As a reference, the intensity of the light from the LED is measured by using a reference light detector before the PECS test sheet is irradiated.

The principle of reflectance photometry is as follows. According to the Lambert−Beer law, absorbance, which is correlated to color, is equal to the logarithmic ratio of the incident light intensity and the transmitted light intensity. Since the test sheet in the PECS is not clear, the reflected light intensity can be substituted for the transmitted light intensity when the test sheet is irradiated. Hence, the color of the test sheet in the PECS can be obtained by using the following equation:

$$C \propto A = \log\frac{I_o}{I} = \log\frac{V_o}{V} \quad (3)$$

where C is red color density of the test sheet, A is absorbance of green light from the LED, I_o is the incident light intensity, I is the reflected light intensity, V_o is the response voltage of blank measurement, and V is the response voltage of sample measurement. In a preliminary experiment, three different LEDs (blue, 475 nm; green, 540 nm; and red, 620 nm) were tested, and the green LED was found to produce a higher response and better repeatability for measuring the color of the test sheet (*24*). Hence, the green LED (540 nm) was used in the portable reflectance photometry device in this study. In addition, the diameter of the beam from LED was narrowed and the edge of the hole on the sensor was cut at a slant to improve the precision.

Materials and Methods

Concentration of the Formaldehyde Aqueous Solution vs Color of PECS. To check the correlation between the amount of formaldehyde on the test sheet and the color of the test sheet in the PECS, the color response of the PECS to formaldehyde aqueous solutions of known concentrations was measured by using the reflectance photometry device. Formaldehyde aqueous solutions (40 μL) with concentrations of 0, 0.4, 0.8, 1.0, 3.0, 5.0, 7.0, 9.0, 11, 13, 15, 17, 19, 22, 24, 26, 28, 30, 35, 40, 45, and 50 μg/mL, were each dropped into a different PECS. The PECSs were then capped with aluminum lids for 30 min at 20 °C, and the voltage responses to the PECS colors were measured using the reflectance photometry device. Seven PECS samples for each concentration were tested on four instruments (616 measurements in total).

Comparison with the Desiccator Method and the Chamber Method. To confirm the emission rates measured by using the PECS, they were compared with the emission rates measured by using the desiccator and the chamber methods.

A glass desiccator (017370-240; Sibata Scientific Technology Ltd., Japan) was used to measure the emission rates in the desiccator method according to Japanese Industrial Standard JIS-A 1460 (*13*). Twelve pieces of particleboard (15 cm × 5 cm) and distilled water (300 mL) in a beaker were sealed in the desiccator, and they were left at 20 ± 1 °C for 24 h. Formaldehyde emitted from the particleboard was absorbed into the distilled water. This absorbed formaldehyde in the water was reacted with acetylacetone (5 mL) in the presence of ammonium chloride, and the concentration was measured on a spectrophotometer. The PECSs were placed on both sides of each piece of particleboard in the desiccator for 30 min at 20 °C, immediately after the desiccator test, and the response voltage was measured by using the reflectance photometry device. Twenty-one kinds of commercially available particleboard (12 test pieces for each kind) were used in this test.

The chamber experiment was conducted in a 20 L chamber (ADPAC-A2; ADTEC Co., Japan) according to Japanese Industrial Standard JIS A1901 (*11*). The flow rate, temperature, and relative humidity of the fresh air introduced into the chamber were 167 mL/min, 28 °C, and 50%, respectively. Two pieces of particleboard (14.7 cm × 14.7 cm) were used in the test. Sampling duration was 30 min in the chamber test. In this case, it was necessary to keep the same emission rate stable during the chamber test and PECS measurement. Thus, the chamber test was continued several days until the emission rates of two consecutive measurements showed same results. PECS experiments were conducted at 10 points on each piece of particleboard in the chamber for 30 min at 28 °C immediately after the chamber test. Ten kinds of commercially available particleboard were used in the test.

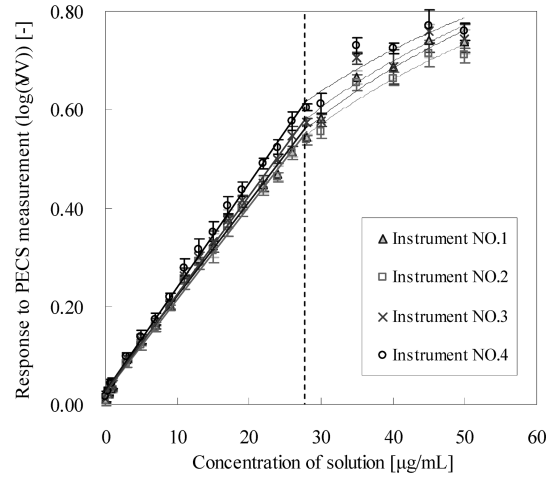

FIGURE 4. Correlation between the concentration of formaldehyde aqueous solution and response of reflectance photometry to the PECS color (N = 7) measured by four instruments (Nos. 1−4).

Limit of Detection. To investigate the limit of detection (LOD), the standard deviation of the responses of PECS blank samples was examined. A drop of pure water was put into each PECS, they were capped with aluminum lids for 30 min, and they were then examined by using reflectance photometry. The LOD was defined as three times the standard deviation (3σ) of the mean value found in the blank samples.

Interference of Other Indoor Chemicals. Some chemicals emitted from indoor emission materials might inhibit the enzymatic activity. Thus, to estimate the interferences of chemicals emitted from indoor materials such as furniture and building materials, the color changes of the PECS due to formaldehyde were measured in the presence of methanol, ethanol, acetone, toluene, and xylene which are often contained in paint and adhesives as a solvent. Although ozone, which is one of the strongest oxidants, could interfere in the enzymatic reaction, the interference by ozone was not evaluated because little ozone is emitted from building materials and furniture. Twenty microliters of a methanol aqueous solution, an ethanol aqueous solution, or an acetone aqueous solution (20, 200, 2000, and 10 000 μg/mL) and 20 μL of a formaldehyde aqueous solution (10, 20, and 40 μg/mL) were dropped into the PECS, giving final formaldehyde concentrations of 5, 10, and 20 μg/mL, respectively. For toluene and xylene, 20 μL of a saturated aqueous solution (515 and 142−185 μg/mL, respectively *25, 26*) and 20 μL of a formaldehyde aqueous solution (10, 20, 40 μg/mL) were dropped into the PECS, giving final formaldehyde concentrations of 5, 10, and 20 μg/mL, respectively. The PECSs were capped with an aluminum seal for 30 min, and the color change was measured.

Results and Discussion

Concentration of the Formaldehyde Aqueous Solution vs Color of PECS. Results are shown in Figure 4. The response of the reflectance photometry, which corresponds to the color of the PECS, linearly correlated with the concentration of the

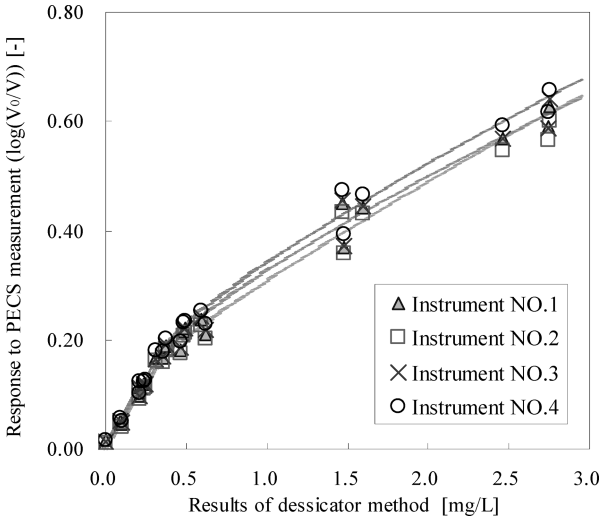

FIGURE 5. Emission from particleboard obtained by using the desiccator method vs the PECS response of four reflectance photometry instruments (Nos. 1−4).

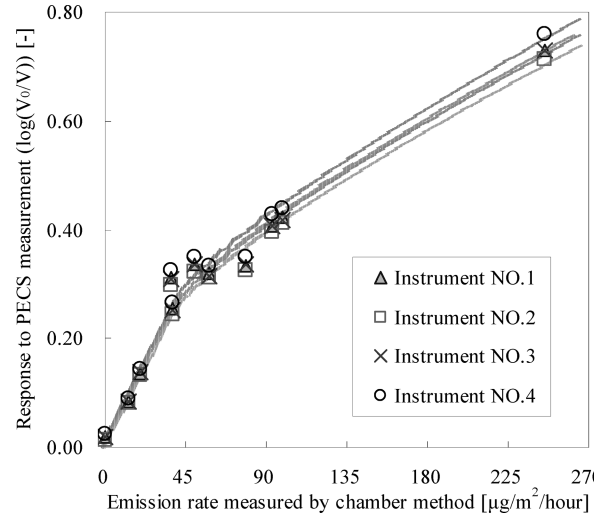

FIGURE 6. Emission from particleboard obtained by using the chamber method vs the PECS response of four reflectance photometry instruments (Nos. 1−4).

formaldehyde aqueous solution up to 28 μg/mL. The relative standard deviations (RSD) of the response of the sensor for the samples of the same concentration ($N = 7$) were less than 10% (1−28 μg/mL), and the RSDs of the response of the reflectance photometry for the same PECS ($N = 4$; Nos. 1−4) were less than 6% (1−28 μg/mL).

In the measurement of formaldehyde concentration in aqueous solution by using the PECS, the rate-determining step can be enzymatic reaction because formaldehyde can be contacted with all enzymes in the test sheet up to 28 μg/mL. The lack of INT could be considered to induce the saturation of the coloration when the concentration exceeded 28 μg/mL.

Comparison with the Desiccator Method and the Chamber Method. Compared with the results obtained using the desiccator method, visual observation of the color change of the PECS could be used to identify a highly emissive material (Figure 2). The responses to the PECS measurement obtained by using the reflectance photometry device ($\log(V_o/V)$), y, were proportional to the emission rates measured by using the desiccator method, x, below a certain value (0.35 mg/L) and were nonlinearly correlated to the emission rates measured by using the desiccator method above the value (Figure 5). A relation function between both methods was used with the response of the PECS as an independent variable. The determination coefficient was the highest ($R^2 = 0.988$) when the linear function $x = 2.27y - 0.0239$ ($\leq$0.35 mg/L) and the power function $x = 6.70 \times (y - 0.166)^{1.28} + 0.354$ (>0.35 mg/L) were used. These functions are similar to that obtained in the preliminary examination in which the intensity of the light source in the reflectance photometry device was different from the present study (*24*). The results from four reflectance photometry instruments ($N = 4$; Nos. 1−4) were highly reproducible (<10%).

The responses to the PECS measurement obtained by using the reflectance photometry device, y, were proportional to the emission rates measured by using the chamber method, x, below a certain value (38 μg/m^2/h) and were nonlinearly correlated to the emission rates measured by using the chamber method above the value, similar to the desiccator method (Figure 6). The relation function between both methods was applied, with the response of the PECS as an independent variable. The determination coefficient was the highest ($R^2 = 0.984$) when the linear function $x = 155y - 1.61$ ($\leq$38 μg/m^2/h) and the power function $x = 530 \times (y - 0.255)^{1.23} + 37.8$ (>38 μg/m^2/h) were used. The reproducibility between the different instruments ($N = 4$; Nos. 1−4) was good (<10%). Since high determination coefficients were obtained for the correlations between the PECS and the desiccator method or the chamber method, the emission rates measured by those methods could be precisely estimated from the color change of the PECS by using the correlation equations.

In the case of the formaldehyde aqueous solution, the response of the PECS ($\log(V_o/V)$) up to 0.60 linearly correlated to the concentration, whereas the response up to about 0.2−0.3 linearly correlated to the emission rate measured by using the desiccator method or the chamber method. Two reasons can be considered. A possible reason is the difference of the rate-determining step of the reaction between the concentration measurement in the aqueous solution and the emission rate measurement. In the measurement of formaldehyde concentration in aqueous solution by using the PECS, the rate-determining step can be the enzymatic reaction described above. On the other hand, in the emission rate measurement by using the PECS, the rate-determining step could be the molecular diffusion of formaldehyde in water in the PECS. Thus, the dynamic range of the emission rate measurement is considered to be narrower than that of the concentration measurement of aqueous solution. Another possible reason is the reduction of the emission rate due to narrowing the concentration gradient. In the measurement of emission rates by using the desiccator method, the chamber method, and the PECS, the emission rates can be underestimated according to the Fick's law when the emission rate is high because of the smaller gradient between the concentration on the building materials and in-desiccator concentration, in-chamber concentration, or the concentration in the surface air on the test sheet. In the PECS, formaldehyde diffused from the source to the test sheet becomes sparingly soluble in the water on the test sheet in accordance with the increase of the formaldehyde concentrations in the water on the test sheet due to Henry's law. If the concentration in the surface air on test sheet is easier to increase than the in-desiccator concentration and in-chamber concentration, the correlations against the response lose linearity at the lower response than that of formaldehyde aqueous solution.

From a practical point of view, it is possible to obtain the emission rate using the PECS, because the reproducibility is high. The sensitivity of the sensor was confirmed to differ less than 10% between 5 and 30 °C in the preliminary experiment (*24*). Thus, the emission rates in the actual environment which has a different temperature can be obtained by using the PECS with the correlation equation

TABLE 1. Ratios of the Colorimetric Response of the PECS of Samples with Added Solvent to Those of Formaldehyde Aqueous Solutions

	methanol (μg/mL)			
HCHO concentration (μg/mL)	10	100	1000	5000
5	107% ± 6.3%	100% ± 6.0%	104% ± 3.2%	101% ± 3.4%
10	102% ± 3.8%	98.8% ± 0.84%	98.7% ± 3.0%	102% ± 3.5%
20	103% ± 3.7%	100% ± 1.7%	102% ± 3.9%	105% ± 3.0%
	ethanol (μg/mL)			
HCHO concentration (μg/mL)	10	100	1000	5000
5	101% ± 5.8%	101% ± 3.6%	109% ± 3.6%	118% ± 5.6%
10	98.1% ± 2.6%	104% ± 1.5%	107% ± 1.5%	109% ± 2.4%
20	103% ± 1.1%	105% ± 2.1%	107% ± 2.1%	110% ± 2.0%
	acetone (μg/mL)			
HCHO concentration (μg/mL)	10	100	1000	5000
5	101% ± 0.93%	97.1% ± 3.0%	108% ± 1.1%	99.9% ± 2.8%
10	96.9% ± 2.0%	98.8% ± 0.93%	98.2% ± 2.2%	102% ± 9.8%
20	101% ± 0.45%	100% ± 1.0%	101% ± 1.0%	101% ± 3.0%

	toluene (μg/mL)	xylene (μg/mL)
HCHO concentration (μg/mL)	150[a]	100[a]
5	96.4% ± 2.1%	104% ± 3.2%
10	107% ± 4.2%	104% ± 1.5%
20	103% ± 0.44%	101% ± 2.2%

[a] Saturated aqueous solutions were made for toluene and xylene. These concentrations were saturated concentrations described in refs *25, 26*.

for the chamber method. The emission rates in the actual environment, however, can not be expressed by the results of the desiccator method because the emission rates of the desiccator method are expediency indication as a concentration of formaldehyde under the specific condition (100% relative humidity). Thus, the correlation equation for the desiccator method can be used to obtain the emission rate in the desiccator method provided in the Japanese regulation.

Limit of Detection. The standard deviation of the response ($\log(V_o/V)$ for the blank samples was less than 0.010. The LOD of the PECS, which was calculated using 3σ of the mean blank sample response, was 0.22 μg/mL for the concentration of the formaldehyde aqueous solution. The LODs of the PECS were 0.051 mg/L using the desiccator method and 3.1 μg/m^2/h using the chamber method.

In Japan, only plywood or particleboard of F four-star class (<0.3 mg/L (desiccator method) or <5.0 μg/m^2/h (chamber method)), categorized according to Japanese Industrial Standards (JIS) and Japanese Agricultural Standards (JAS), can be used in houses without limitation according to Japanese building codes. Considering the LOD and precision (<10%) of the PECS, emission rates from building materials or furniture classified as even F four-star can be measured and compared by using the PECS. If the sampling time is longer, the lower emission rates can be measured. On the other hand, if the sampling time is shorter, the higher emission rates can be measured. Since the building materials of class F one-star are prohibited from use in Japan, we considered that the emission rates of F three-star and F four-star classes have to be measured more sensitively and precisely than the emission rates of F one-star class although the emission rates of F one-star have to be determined. Thirty minutes was the most appropriate sampling time to obtain the wide dynamic range between F one-star and F four-star classes.

In a square room (area: 25 m^2, height: 2.5 m, air exchange rate: 0.5 /h), if all walls, ceiling, and floor are made of a material which have the same emission rates as the detection limit (3.1 μg/m^2/h), the indoor concentration in the steady state will be 9.9 μg/m^3. This concentration is one tenth of the indoor guidelines (100 μg/m^3) from the Japanese government and the WHO. Thus, by using the PECS, we can identify the major emission sources of formaldehyde in indoor environments and select better materials.

Interference of Other Indoor Chemicals. The ratios of the colorimetric response of the samples with solvent added to those of pure formaldehyde aqueous solutions are shown in Table 1. For aqueous solutions with methanol, acetone, toluene, and xylene, there were no differences in the colorimetric response. For samples with ethanol, concentrations of 1000 and 5000 μg/mL of ethanol enhanced the colorimetric response by about 10%.

Acknowledgments

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