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A screening method for detecting formaldehyde emitted from textile products

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ABSTRACT

Formaldehyde is widely used to improve textile quality, but it is categorized as a potential carcinogen in humans. The concentration of formaldehyde emitted from textile products therefore has implications for public health. The standard method uses acetylacetone for determining formaldehyde extracted from textile products, but requires a water solution and the use of an analyzer. In this study, we present a method for screening textile-emitted formaldehyde via a porous glass sensor that we previously developed. Our method is suitable for on-site screening, whereas the commonly used method is not. The glass sensor was used to measure formaldehyde concentrations emitted from several kinds of textile products. The results showed good agreement (coefficient 0.92) with those of the acetyl-acetone method. Moreover, we estimate the effects of temperature, and suggest a formula to calculate concentration including temperature correction.

1. Introduction

Formaldehyde has been used for many years in the textile industry [1]. Textile products are commonly processed to improve characteristics such as wrinkle resistance and shape retention, using chemicals that often contain formaldehyde, for example urea-formaldehyde resin. Formaldehyde may cause various allergic reactions, and in 2004 it was classified as a Group 1 chemical ("Carcinogenic to humans") by the International Agency for Research on Cancer (IARC) [2]. Therefore, each country sets a limit for formaldehyde content in textile products. In Japan, the formaldehyde content of textile products for infants aged

up to 24 months must be less than 16 $\mu g\,g^{-1}$ (e.g. diaper, diaper cover, bib, hat, bedding, underwear, nightclothes, gloves, socks, intermediate garment, outer garment), and less than 75 $\mu g\,g^{-1}$ in textiles for others (e.g. underwear, nightclothes, gloves, socks, Japanese tabi socks). Nevertheless, textile products are often recalled due to excessive formaldehyde content [2–5], which suggests the need for an improved method of on-site measurement during production. Moreover, the standard method involves destructive testing.

An acetylacetone method is often used to measure formaldehyde emitted from textiles: ISO 14184-1:2011 [6] internationally, and JIS-L1041 in Japan [7,8], which provides simple operation, with high sensitivity and reproducibility. However, this method is not suitable for on-site measurement, because it requires cutting cloths for extraction with water solution and treating the water solutions.

Many alternative methods have been reported (e.g. bioindicative measuring method [9], liquid-phase

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microextraction with in-drop derivatization combined with microvolume fluorospectrometry [10], dynamic ultrasound-assisted extraction coupled on-line with solid support derivatization and high-performance liquid chromatography [11], and flow-injection chemiluminescence [1]). These methods can measure formaldehyde with high sensitivity and reproducibility. However, on-site measurement is made more difficult by the complexity of such procedures and the need for large measurement instruments.

Several passive methods are reported for detecting formaldehyde in ambient air [12], and these methods may be appropriate for on-site screening of textiles. In addition, this method of testing is nondestructive.

The authors previously developed a passive method that uses a porous glass sensor element impregnated with β-diketone, which can measure formaldehyde in indoor air [13–15]. In this report, we apply the sensor element to a screening method for on-site measurement of formaldehyde in textiles.

2. Material and methods

2.1. Determining quantity of formaldehyde in textiles

We used the water extraction method specified in JIS L1041 (*Test methods for resin finished textiles*) to measure formaldehyde in textiles.

2.2. Acetyl acetone and buffer reagents

The acetyl acetone reagent consisted of a water solution containing 1.89 mol/l ammonium acetate (Kanto Chemical, Japan, Guaranteed reagent for JIS), 0.05 mol/l acetic acid (Kanto Chemical, Japan, Guaranteed reagent for JIS), and 0.02 mol/l acetyl acetone (Kanto Chemical, Japan, Guaranteed reagent for JIS). The buffer reagent was a water solution containing 1.89 mol/l ammonium acetate and 0.02 mol/l acetic acid. All reagents were used without further purification.

2.3. Formaldehyde standard solution and concentration estimation

We used a 36–38% solution of formaldehyde (Kanto Chemical, Japan, Guaranteed reagent for JIS). The formaldehyde concentration of the solution was measured accurately as follows. A 1.0 g sample of the formaldehyde solution was accurately measured, and distilled water was added to a volume of 100 ml. Then, 10 ml of this solution with 50 ml of 0.05 mol/l iodine solution (Kanto Chemical, Japan) and 20 ml of 1 mol/l potassium hydroxide (Kanto Chemical, Japan, Guaranteed reagent for JIS) were mixed in a flask and kept at room temperature for 15 min. A 15 ml sample of 18.01 mol/l sulfuric acid (Kanto Chemical, Japan, Guaranteed reagent for JIS) was added to this solution. The mixture was then titrated with 0.1 mol/l sodium thiosulfate solution (Kanto Chemical, Japan) using a starch reagent as an indicator. V_1 requires blank examination, so a blank test was performed using 10 ml of water

rather than the formaldehyde solution. The quantity of formaldehyde was calculated using Eq. (1):

$$C_p = 1.5013 \times (V_1 - V_2) \times f/1000 \times 100/10 \times 1/m \times 100 \tag{1}$$

where C_p (%) is mass formaldehyde concentration of the formaldehyde standard solution, V_1 (ml) is a titer of the sodium thiosulfate solution in the blank examination, V_2 (ml) is a titer of the sodium thiosulfate solution in the examination, f is a titer of the sodium thiosulfate solution, 1.5013 (mg) represents formaldehyde equivalency mass of the iodine solution, and m (g) is the weight of the formaldehyde solution.

A $400/C_p$ (g) sample of the formaldehyde solution was accurately measured and distilled water was added up to 100 ml. This solution was diluted to 100,000 times with water, and was used as the formaldehyde standard solution (solution A).

2.4. Textile products

We purchased 13 textile products to conduct formaldehyde measurement at room temperature without cutting the textiles. Samples comprised shirt, blouse, T-shirt, and children's underwear. Table 1 shows the categories, textiles, and weights of the 13 samples. Four samples (Nos. 5, 11, 12, and 13) were selected for the temperature dependence experiments.

2.5. Extraction, coloration and measurement

A 2.5 g sample of textile products was cut into pieces 10 mm × 30 mm, then placed in a 250 ml flask with 100 ml of distilled water and capped tightly. The solution was then extracted at 40 °C for 1 h using a water launch (Advantec Toyo, Japan, TBS271SA). The hot extracted solution was filtered using a glass filter (Sibata Scientific Technology, Japan, 17G). The obtained solution was used as the extraction solution.

Acetyl acetone reagent 5 ml was added to 5 ml of the extraction solution (solution S) or 5 ml of distilled water (reference solution S_0), respectively. These were warmed at 40 °C for 30 min and then kept at room temperature for 30 min.

A 5 ml sample of buffer reagent was added to 5 ml of the extraction solution (solution B) or 5 ml of distilled water (reference solution B_0), respectively. These solutions were processed via the same method described above.

The absorbance characteristics of these solutions at 414 nm were measured using a UV–vis spectrophotometer (Otsuka Electronics, Japan, MCPD-3000). The quantity of formaldehyde elution was calculated using Eq. (2):

$$C = K_A \times (A - A_0/A_A) \times 100 \times 1/m \tag{2}$$

where C (μg/g) is quantity of formaldehyde eluted from 1 g sample, A is the absorbance of solution S with the reference solution B, A_0 is the absorbance of solution S_0 with the reference solution B_0, A_A is the absorbance of the formaldehyde standard solution with the reference solution B, K_A