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A screening method for detecting formaldehyde emitted from textile products

Abbreviated title: Screening Formaldehyde in Textiles

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ABBREVIATIONS

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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 acetylacetone method. Moreover, we estimate the effects of temperature, and suggest a formula to calculate concentration including temperature correction.

Key words: Formaldehyde; Screening; Textile; Acetylacetone method

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 $16 \mu\text{g} \cdot \text{g}^{-1}$ (e.g. diaper, diaper cover, bib, hat, bedding, underwear, nightclothes, gloves, socks, intermediate garment, outer garment), and less than $75 \mu\text{g} \cdot \text{g}^{-1}$ 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 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 equation (1):

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

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 B₀), 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 equation (2):

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

where C ($\mu\text{g/g}$) 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 S₀ with the reference solution B₀, A_A is the absorbance of the formaldehyde standard solution with the reference solution B, K_A ($\mu\text{g/mL}$) is the concentration of formaldehyde standard solution A, and m (g) is the mass of the sample.

2.6 Determining formaldehyde emitted from textiles using a sensor element at room temperature

The sensor element was prepared using the method reported previously [13], changing the quantity of 1-phenyl-1,3-butanedione (Kanto Chemical, Japan, Guaranteed reagent for JIS) to 0.471 g. The method detects the reaction of formaldehyde with 1-phenyl-1,3-butanedione and ammonium ions.

Air conditioning was used to maintain the room temperature at 27 °C. At first, as a blank check, we measured the influence of formaldehyde by placing the sensor element in an empty polyethylene bag (size 400 mm × 450 mm) for 1 h without a textile sample. Then, after absorbance of the sensor element was measured at 414 nm ($Ab_{S_{solB0}}$), both the sensor and a purchased product were put in a polyethylene bag. Figure 1 shows the measurement state. The plastic bag was placed on an indoor desk in darkness for 1 h. The element was then quickly removed and placed into an aluminum-coated polyethylene bag for 30 min, and absorbance was measured at 414 nm ($Ab_{S_{solB1}}$). The reason for keeping the sensor in darkness (in the aluminum-coated bag) for an additional 30 min is to ensure full completion of the reaction in the sensor element [14]. The change in absorbance registered by the sensor element is proportional to formaldehyde concentration in the polyethylene bag. The absorbance change was calculated using equation (3):

$$Ab_{S_{solB}} = Ab_{S_{solB1}} - Ab_{S_{solB0}} \quad (3)$$

where $Ab_{S_{solB1}}$ is absorbance of the sensor at 414 nm after exposure, $Ab_{S_{solB0}}$ is that prior to exposure, and $Ab_{S_{solB}}$ is the difference in absorbance.

2.7 Temperature dependence measured using a sensor element

We estimated temperature dependence using a temperature-controlled chamber (Kusumoto Chemicals, Japan, FPX413PH), and experiments were repeated at 10, 35, and 40 °C, in addition to the series conducted at 27 °C.

3. Results and discussion

3.1 Measurement at room temperature

It was found that very little formaldehyde was emitted from the children's underclothes (Nos. 9 and 10), the blouse (No. 2), and the T-shirt (No. 1), and these samples showed a small change in absorbance. However, each of the shirt (Nos. 3–8) and blouse (Nos. 11–13) textiles emitted varying quantities of formaldehyde.

We first measured formaldehyde emissions within the polyethylene bag. The sensor element showed a change in absorbance of 0.0034 (standard deviation 0.0039) at 414 nm. The results show that the polyethylene bag does not affect the measurement.

Figure 2 shows the relationship between the amount of formaldehyde measured via the standard L1041 method, and the change in absorbance measured by the sensing element at room temperature (27 °C). The relationship between both data series was linear, and the coefficient of determination was 0.92. The expression to convert the absorbance difference of the sensor element into formaldehyde amount using the extracting solution is expressed in (4). Based on these findings, the difference in absorbance recorded by the sensor element was converted to a formaldehyde-equivalent value obtained in the acetylacetone method, as shown in Equation (4).

$$C = 161.94 \times Abs_{solB27} \quad (4)$$

where C ($\mu\text{g/g}$) is mass concentration of formaldehyde and Abs_{solB27} is the absorbance changes at 414 nm for the sensing element at room temperature.

Table 3 shows the experimental result for the amount of formaldehyde via the standard method, and that of the sensor element calculated from Equation (4) in the 13 samples.

3.2 Temperature dependence

Figure 3 shows a common logarithm used to calculate the variation in a sensor element's absorbance at differing temperatures. The four selected samples (Nos. 5, 11, 12, and 13) were exposed for 3 h.

Each sample showed a linear relationship between temperature and the common logarithm of the sensor element's absorbance change, and the slopes were the same (0.036). The results show that emissions increased by 9% from $10^{(0.036)}$ with a 1 °C increase in temperature. This agreed well with the 10% increase reported previously [14]

Therefore, equation (5) can express the relationship of C ($\mu\text{g/g}$) to $AbsB$ within the temperature range 10 °C to 40 °C:

$$C = 161.94 \times AbsB \times 1.09^{(27-t)} \quad (5)$$

where t (°C) is ambient temperature, C ($\mu\text{g/g}$) is mass concentration of formaldehyde, and $AbsB$ is the absorbance change of the sensing element at 414 nm.

Figure 4 shows the screening method proposed in this work. This proposed method does not involve cutting the textile samples. When a textile sample was placed in a polyethylene bag with the sensing element, the obtained formaldehyde concentrations showed high correlation with those obtained via the standard method.

3.3 Sampling parts of textiles

Items of clothing may include multiple materials, for example adhesive interlining, that emit different amounts of formaldehyde compared with the other fibers or materials used in the garment. Therefore, we measured the formaldehyde emitted from the collar and chest areas of sample 13 (Figure 5), comparing the results obtained using the standard method and the developed sensor element. The results (Table 2) show that the measurements were very different in the chest area of the garment; however, the measurements in the collar area were similar to equation (4). The sensor element reacts to formaldehyde emitted from the textiles inside the polyethylene bag, and therefore indicates the mean concentration of formaldehyde in the textiles. This example shows that the screening method is effective for textiles in which formaldehyde is unevenly distributed within the constituent materials of a product.

3.4 Reading device for a sensor element

The authors developed a simple spectrophotometer that uses a 415 nm LED light source (the nearest available LED wavelength to the 414 nm peak of the sensor) and photodiodes. Figure 6 shows the correlation between the absorbance measured via the sensor element using this device, and that measured using a UV-vis spectrophotometer. This device permits easy on-site screening of textiles without the need for large-scale and high-energy apparatus such as a spectrophotometer.

4. Conclusion

In this work, a method was developed for on-site screening of formaldehyde using a sensor element. We purchased textiles, and compared the emissions of formaldehyde recorded via the standard acetylacetone method and the proposed screening method. We also determined the temperature dependence of emissions between 10 °C and 40 °C, and derived an expression to convert the change in absorbance registered at the sensor into the mass concentration of formaldehyde contained in the textile.

This approach provides a simple and reliable method for on-site screening of the formaldehyde content in textiles.

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Figure captions

Figure 1 Photograph of the measurement setup

Figure 2 Relationship between absorbance change with sensor element at 27 Celsius and quantity of formaldehyde eluted with standard L1041 method

Figure 3 Relationship between temperature and the common logarithm for change in absorbance observed using the proposed screening method (×: Sample 5, □: Sample 11, Δ: Sample 12, ○: Sample 13)

Figure 4 Proposed screening procedure

Figure 5 Sampling locations for textile sample 13

Figure 6 Comparison of absorbance measured via developed sensing element versus spectrophotometer

Table 1 List of Samples

| Sample | Type | Color | Material | Processing | Weight (g) |
|--------|--------------------------------------|----------------|------------------------------------|-------------------------------|------------|
| 1 | Men's T-shirt | Blue | Polyester 100% | Sweat-absorbent, quick-drying | 134.0 |
| 2 | Women's sleeveless shirt | Red | Body: cotton 100% | - | 94.2 |
| | | | Lace: nylon 90%, polyurethane: 10% | | |
| 3 | Men's white shirt (vertical-striped) | White and blue | Cotton 52% | - | 220.0 |
| | | | Polyester 48% | | |
| 4 | Men's short-sleeve shirt | White | Cotton 50% | Permanent-press shirt | 189.9 |
| | | | Polyester 50% | | |
| 5 | Men's shirt | White | Polyester 65% | Permanent-press shirt | 221.0 |
| | | | Polyester 35% | | |
| 6 | Women's shirt | White | Cotton 50% | Permanent-press shirt | 193.0 |
| | | | Polyester 50% | | |
| 7 | Men's Oxford shirt | White | Cotton 100% | - | 215.5 |
| 8 | Women's shirt | Pink | Cotton 57% | UV protection | 150.8 |
| | | | Polyester 41% | | |
| | | | Polyurethane 2% | | |
| 9 | Baby's coverall | Pink | Cotton 100% | Reduced formaldehyde | 116.7 |
| 10 | Baby's coverall | Beige | Cotton 100% | Reduced formaldehyde | 72.8 |
| 11 | Men's short-sleeve shirt | White | Cotton 93% | Permanent-press shirt | 222.4 |
| | | | Polyester 7% | | |
| 12 | Men's short-sleeve shirt | White | Cotton 100% | Permanent-press shirt | 276.3 |
| 13 | Men's short-sleeve shirt | Light purple | Body: polyester 100% | Permanent-press shirt | 216.7 |

Table 2 Δ Abs of Sample No.13 with Standard L1041 Method

| Sampling point | Quantity of formaldehyde eluted ($\mu\text{g/g}$) |
|----------------|---|
| Collar | 6 |
| Front-1 | 1 |
| Front-2 | 0 |

Table 3 Experimental results for formaldehyde concentration
via standard and sensor methods, calculated at 27°C

| Sample | Formaldehyde concentration via standard method (µg/g) | Formaldehyde concentration via sensor element calculated from eq.(4) (µg/g) | Sample | Formaldehyde concentration via standard method (µg/g) | Formaldehyde concentration via sensor element calculated from eq.(4) (µg/g) |
|--------|---|---|--------|---|---|
| 1 | 4 | 1 | 8 | 18 | 24. |
| 2 | 2 | 1 | 9 | 2 | 0 |
| 3 | 2 | 4 | 10 | 0 | 0 |
| 4 | 2 | 5 | 11 | 46 | 52 |
| 5 | 13 | 21 | 12 | 89 | 75 |
| 6 | 9 | 19 | 13 | 6 | 19 |
| 7 | 1 | 0 | | | |

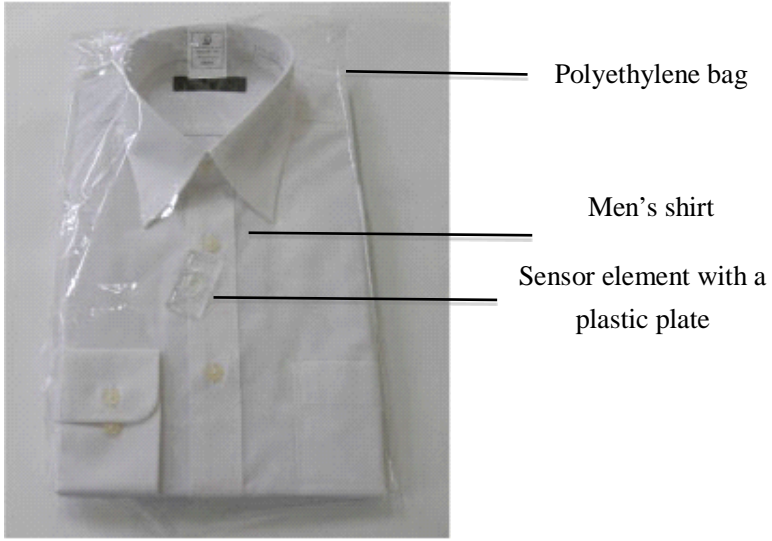


Figure 1

Photo: Yasuko Y. Maruo

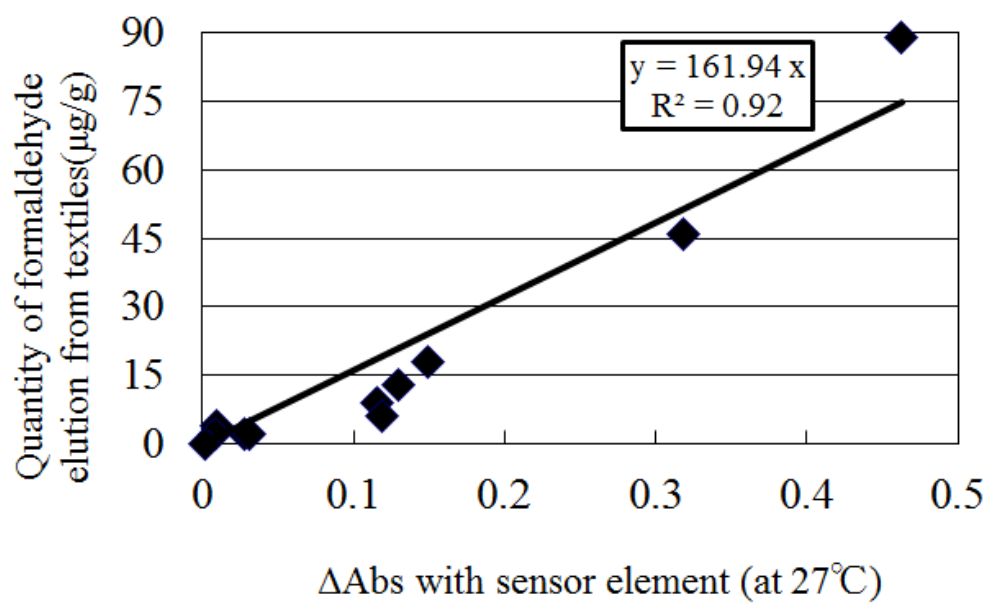


Figure 2

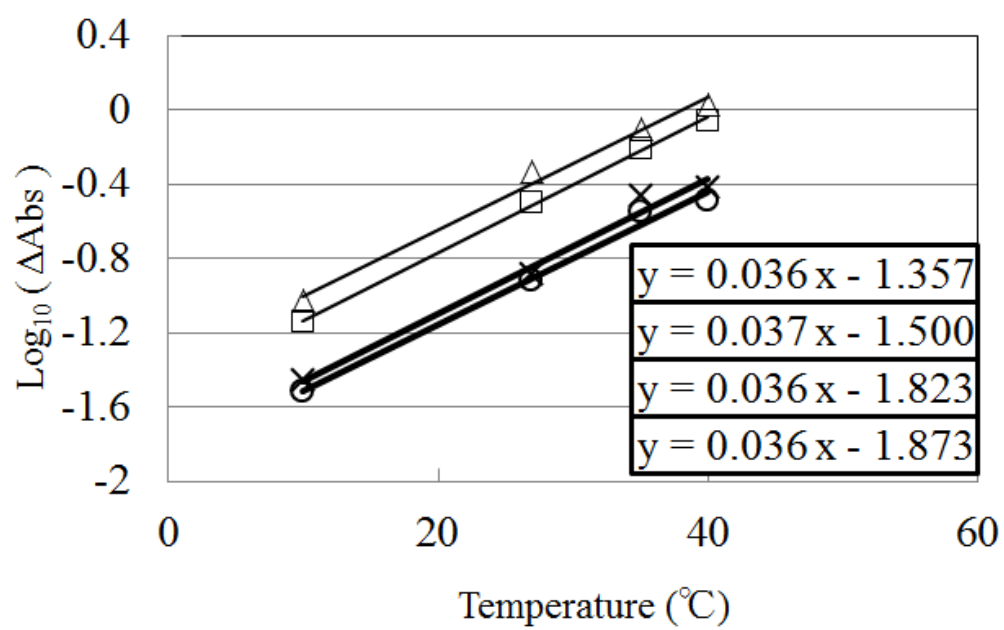


Figure 3

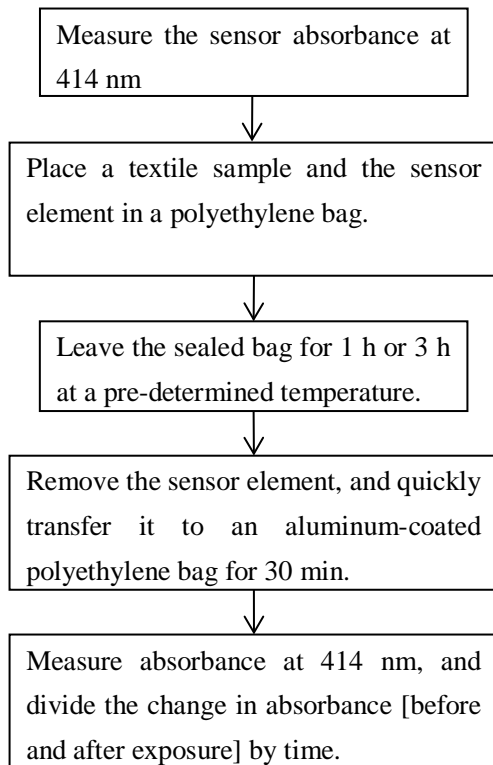


Figure 4

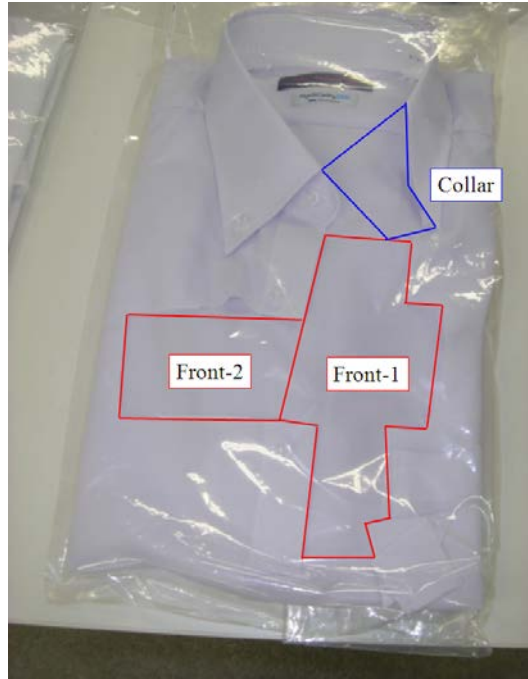


Figure 5

Photo: Yoshiyuki Kawakami

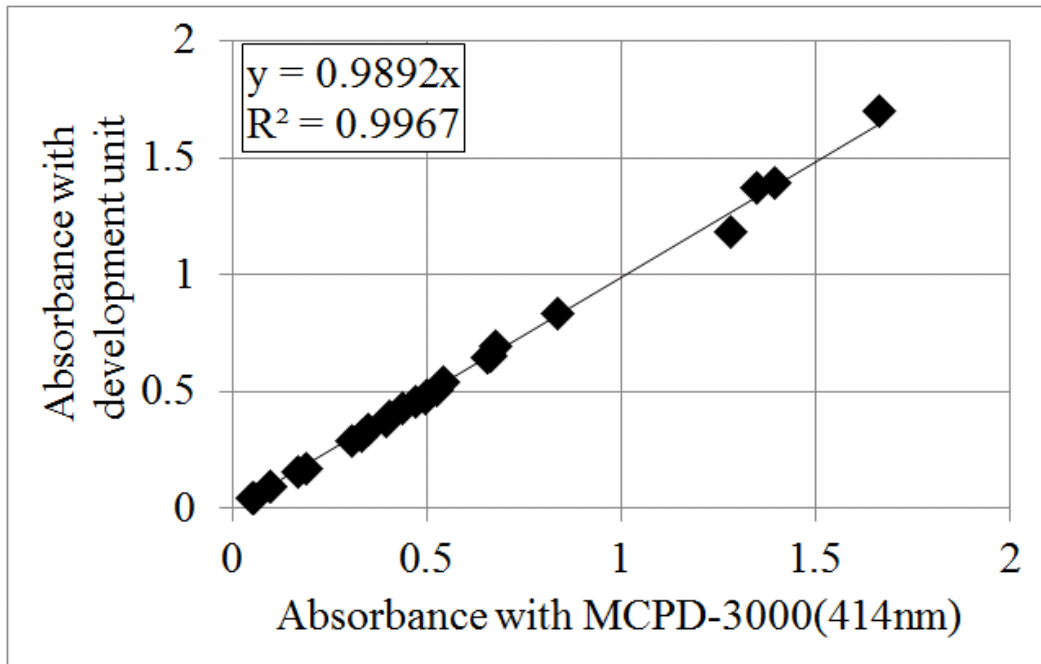


Figure 6