Bull. Environ. Contam. Toxicol. (1995) 55:810–816

Bulletin of Environmental Contamination and Toxicology

Determination of Formaldehyde in Textiles Using a Diffusive Sampler

M. Naruse,[1] H. Naruse,[2] M. Aoyama[2]

[1]Department of Home Economics, Kinjo Gakuin University, Moriyama-ku,
Nagoya 463, Japan
[2]Department of Hygiene, Nagoya City University Medical School, Mizuho-ku,
Nagoya 467, Japan

Received: 28 January 1995/Accepted: 11 June 1995

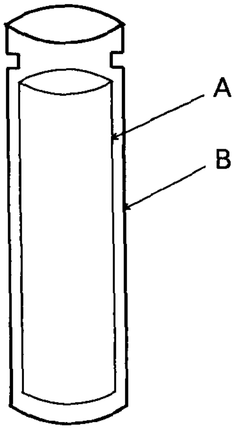
Styczynski (1989) showed the possibility of formaldehyde transfer from treated to untreated materials which are stored together. Iwama et al. (1990) also reported that untreated textiles may contain formaldehyde derived from treated textiles. Formaldehyde is one of the most significant causes of dermatoses originating from chemical textile finishes (Hatch et al. 1986; Groot et al. 1989; Fowler et al. 1992). If we could detect the presence of formaldehyde in untreated as well as treated textiles, we might lower the incidence of contact dermatitis from formaldehyde. In Japan, the standard method of detecting formaldehyde in textiles is legislated in the form of a Regulation on Toxic Substances in Home-Use Items (Ministry of Health and Welfare, 1976). We will call this Method A. Although this method has sufficient sensitivity and reproducibility to detect formaldehyde, the textiles tested must first be cut into swatches. The textiles tested are not available for wear. Such an artificial testing procedure makes it difficult to determine formaldehyde in textiles sold on the market.

In this paper, we report a new diffusive sampler we have developed utilizing the volatility of formaldehyde in order to determine its presence in textiles without cutting the sample into swatches.

MATERIALS AND METHODS

A description of the new method (Method B) is as follows; a diffusive sampling vial shown in Figure 1 is composed of a 14 mL vial (Screw Cap Vials, SV-14. Gasukuro Kogyo Inc., Japan) and one sheet of filter paper (Chromatography Paper no. 50. Labosco Co., Japan). The filter paper is moistened with distilled water. The diffusive sampling vial is transferred to a 12.7 L airtight box (Tosron. Tosron Co., LTD. Japan). The textiles are put in the box together with the vial. The box is then placed in a thermo-regulated chamber. To the vial we added 7 mL of acetylacetone solution (prepared by dissolving 150 g ammonium acetate in 800 mL distilled water, adding 3 mL of concentrated acetic acid and 2 mL

Correspondence to: M. Naruse



A: Filter paper moistened by distilled water

B: 14 ml screw cap vial (68 mm × 18 mm id.)

Figure 1. Diffusive sampling vial

acetylacetone, and adjusting the volume to 1 L with distilled water). Water is added to a total volume of 14 mL. The vial is placed for 30 min in a water bath maintained at 40 degrees centigrade. The absorbance of the above solution is measured by spectrophotometer at 414 nm. The concentration of formaldehyde in textiles is calculated by the calculation curve. We investigated: (1) storage temperature of the thermo-regulated chamber, (2) the most accurate volume of distilled water added to moisten the filter paper, (3) storage time in a thermo-regulated chamber and (4) correlation between the concentration levels measured by Method A and Method B.

RESULTS AND DISCUSSION

The relation between the amount of formaldehyde passing into a diffusive sampling vial and the storage temperature in the thermo-regulated chamber is shown in Figure 2. Six point six mg formaldehyde is added to textiles (cotton, Canequine third, 100 × 90 cm, 88 g; Japanese Industrial Standards Committee, Japan). This level corresponds to 75 ppm (criterion level indicated in Method A). The amount of formaldehyde passing into the vial increased with increasing storage temperature. Kojima et al. (1975) reported that reproducibility is reduced with increasing temperature when extracting formaldehyde from textiles because the hydrolysis of formaldehyde resin in textiles is accelerated at high temperature. Thus, a high storage temperature is not desirable. The amount of formaldehyde transferred at 40 degrees centigrade is enough for measuring the absorbance by spectrophotometer, even though the concentration of formaldehyde in textiles is 15 ppm (detectable level indicated in Method A). Therefore, the storage temperature was set at 40 degrees centigrade.

The relation between the amount of formaldehyde passing into the sampling vial and the amount of distilled water added to the filter

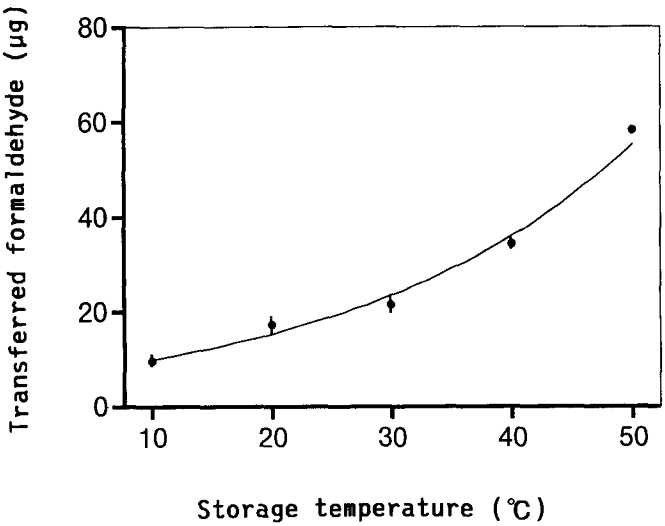


Figure 2. The relation between the amount of formaldehyde passing into a diffusive sampling vial and the storage temperature in a thermo-regulated chamber. The amount of formaldehyde added to textiles is 6.6 mg. The amount of distilled water added to moisten filter paper is 1.5 mL. The storage time in the chamber is 24 hr. ϕ : mean ± SD.

paper for moistening is shown in Figure 3. Formaldehyde is added to textiles in the same way as in Figure 2. The amount of formaldehyde passing into a sampling vial increases with the amount of distilled water up to 1 mL. Since there was no significant difference among 1.0, 1.5 and 2.0 mL, the amount of distilled water added to the filter paper was set at 1.5 mL.

The relation between the amount of formaldehyde passing into a sampling vial and the storage time in a thermo-regulated chamber is indicated in Figure 4. Formaldehyde is added to textiles in the same way as in Figure 2. The amount of formaldehyde passing into a sampling vial increased with increasing storage time. Twenty-four hr is assumed to be an adequate storage time because amount of the formaldehyde passing into the vial during 24 hr is enough for measuring the absorbance by spectrophotometer, even though the concentration of formaldehyde in textiles is at the detectable level indicated in Method A.

The amount of formaldehyde passing into a diffusive sampling vial above under the conditions is shown in Figure 5. Formaldehyde is added to textiles (cotton, Canequine third, 100 × 90 cm, 88 g) in amounts from 0.7 mg to 28 mg. These levels correspond to a range from 7.5 ppm to 300 ppm, respectively. The amount of formaldehyde passing into a vial increased with the amount of formaldehyde in the cotton. The coefficient of correlation was 0.996 ($n=40$, $p<0.001$). The equation is $Y = 4.74 X^{1.04}$, where Y is the amount of

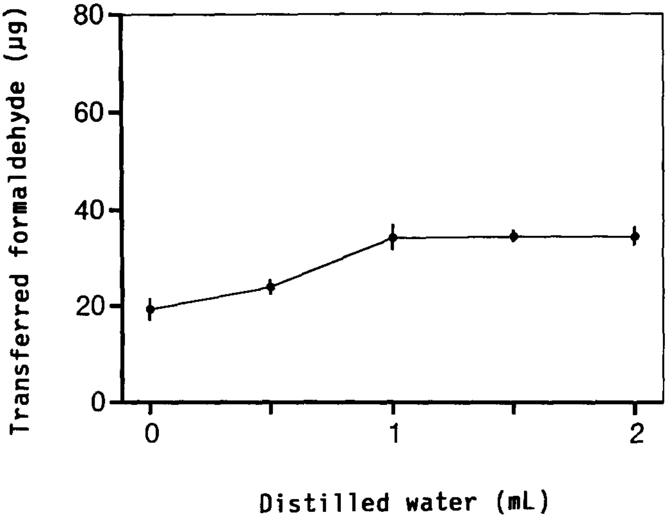


Figure 3. The relation between the amount of formaldehyde passing into a diffusive sampling vial and the amount of distilled water added to moisten filter paper. The amount of formaldehyde added to textiles is 6.6 mg. The storage time in a thermo-regulated chamber is 24 hr. The temperature of the thermo-regulated chamber is maintained at 40 degrees centigrade. ♦ : mean ± SD.

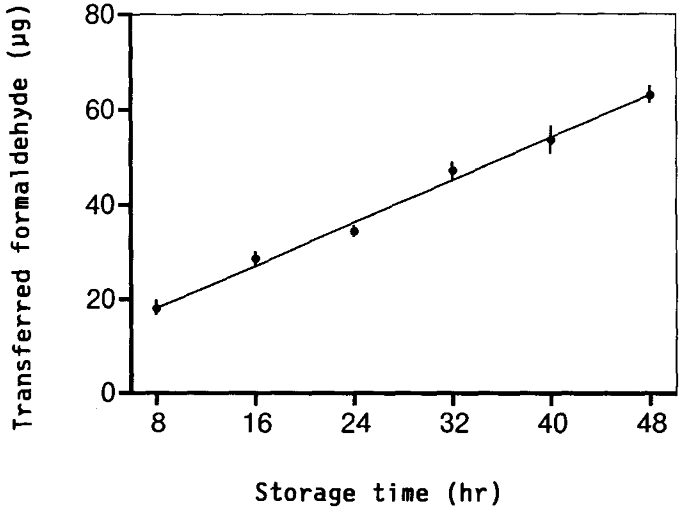


Figure 4. The relation between the amount of formaldehyde passing into a diffusive sampling vial and the storage time in a thermo-regulated chamber. The amount of formaldehyde added to textiles is 6.6 mg. The amount of distilled water added to moisten filter paper is 1.5 mL. The temperature of the thermo-regulated chamber is maintained at 40 degrees centigrade. ♦ : mean ± SD.

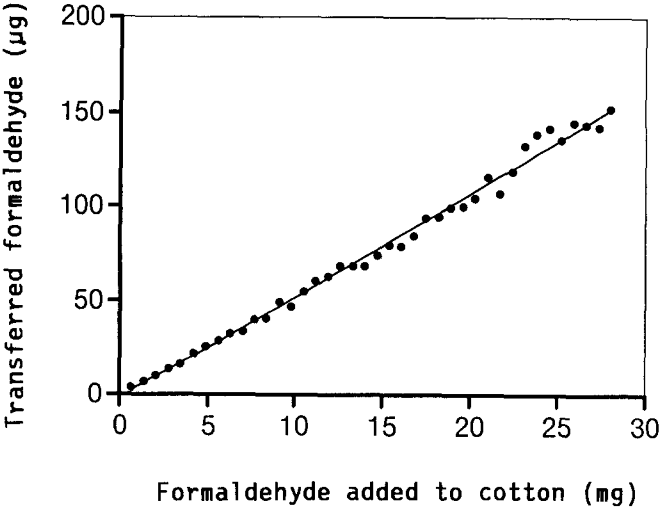


Figure 5. The amount of formaldehyde passing into a diffusive sampling vial by Method B. The amount of distilled water added to filter paper is 1.5 mL. The storage time in a chamber is 24 hr. The temperature of the chamber is maintained at 40 degrees centigrade.

formaldehyde passing into a vial, µg, and X is the amount of formaldehyde added to cotton, mg. The concentration of formaldehyde in the textiles is computed from the following equation; $A = 10^{(\log Y - \log 4.74)/1.04} \times 1000/W$, where A is the concentration of formaldehyde in ppm and W is the weight of textiles in g.

The established method is as follows : The diffusive sampling vial, which is composed of a 14 mL vial and one sheet of filter paper moistened with 1.5 mL distilled water, is transferred to a 12.7 L airtight box. The textiles are put in the box together with the vial. The box is left in a thermo-regulated chamber for 24 hr at 40 degrees centigrade. Seven mL of acetylacetone solution is added to the vial. Water is added to a total volume of 14 mL. The vial is placed for 30 min in a water bath maintained at 40 degrees centigrade. The absorbance of the above solution is measured by spectrophotometer at 414 nm. The concentration of formaldehyde in textiles is calculated by the calculation curve.

Kojima et al. (1975) reported that high levels of formaldehyde were found in cuprammonium rayon and cotton. We applied Method B to determine formaldehyde in cuprammonium rayon textiles and cotton bought at a dry goods store in Aichi, Japan. The correlation between the concentration levels measured by Method A and B is shown in Figure 6. The equation of the regression line is $Y = 0.615\ X - 3.77$, where X and Y correspond to the concentration of formaldehyde measured by Method A and B, respectively. Method A measures not only free formaldehyde but also that which is decomposed from formaldehyde resin during extraction with water,

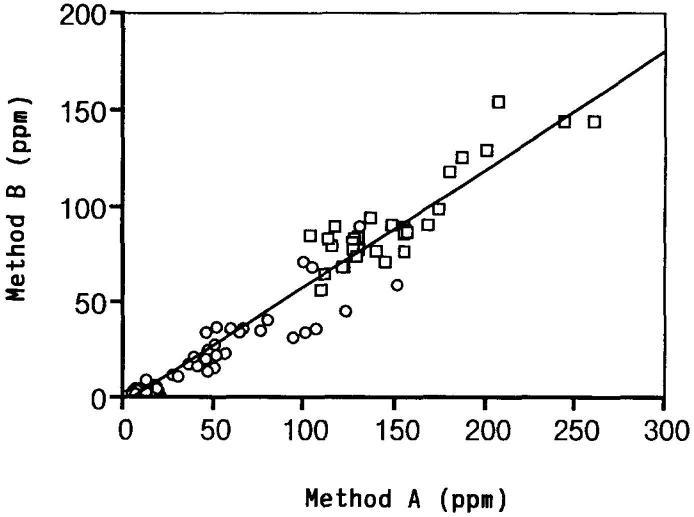


Figure 6. Correlation between the concentration levels measured by method A and method B. □ : cuprammonium rayon ○ : cotton

at which time some of the resin is hydrolyzed (Naruse et al. 1980). Kojima et al. (1975) reported that the amount of free formaldehyde was 77 percent of the amount of formaldehyde determined by Method A. The Method B dose did not involve the treatment of extraction with water. The only formaldehyde measured by Method B seemed to be free. For that reason, the slope of the regression line is low crossing the transverse axis. Nevertheless, the line shows good agreement between Method A and B with a coefficient of correlation of 0.972 ($n=98$, $p<0.001$). The concentration of formaldehyde measured by Method A is accurately estimated by Method B when the concentration of formaldehyde in textiles is at least 15 ppm.

These results make it clear that the proposed vial is a useful diffusive sampler for monitoring the concentration of formaldehyde in textiles.

Acknowledgments. We wish to thank Dr. T. Itani and Dr. N. Tachi for their valuable advice and assistance.

REFERENCES

Fowler JF, Skinner SM, Belsito DV (1992) Allergic contact dermatitis from formaldehyde resins in permanent press clothing: An underdiagnosed cause of generalized dermatitis. J Am Academy Dermatol 27:962-968

de Groot AC, Gerkens F (1989) Contact urticaria from a chemical textile finish. Contact Dermatitis 20:63-64

Hatch KL, Maibach HI (1986) Textile chemical finish dermatitis. Contact Dermatitis 14:1-13

Iwama M, Nakashima S, Aoyama T, Naruse M, Ohno H, Tsuyama A, Ishihara T (1990) Formaldehyde transference to textile goods at clothing shops, supermarkets and a hat workshop. Annual Report of Nagoya City Health Research Institute 36:58-63

Kojima S, Oba T (1975) Determination of free formaldehyde in underwears. Bunseki Kagaku 24:294-298 (Japanese)

Ministry of Health and Welfare, Environment Sanitation Bureau (1976) Regulation on toxic substance in home-use items. 145-174 (Japanese)

Naruse M, Aoyama M (1980) Washing effect on elimination of formaldehyde from clothes treated with formalin resin and formaldehyde-absorbed clothes. Nagoya Med J 30:515-521

Styczynski P (1989) Detection of the presence of formaldehyde in textiles by using color tests with acetylacetone and chromotropic acid. Przegl Dermatol 76:123-126.