シックハウス症候群を誘発する建築材料からの微量ホルマリンのバッチ及びFI蛍光光度分析

Batchwise and Flow Injection Spectrofluorimetry for Trace Amounts of Formaldehyde Evolved from Building Materials Caused Sick-House Syndrome

酒井忠雄†、手嶋紀雄†、田中慎一†、樋口慶郎††、浦信夫†††
Tadao SAKAI, Norio TESHIMA, Shin-ichi TANAKA, Keiro HIGUCHI, Nobuo URA

Abstract Batchwise and flow injection spectrofluorimetric methods for the trace analysis of formaldehyde evolved from building materials using 5,5-dimethyl-1,3-cyclohexanedione (dimedone) are described. These methods are based on the cyclization reaction of formaldehyde with dimedone in the presence of ammonium ion to form a fluorescent derivative (λ_{ex}, 395 nm; λ_{em}, 463 nm). Preliminary experiments by batchwise procedure were carried out in order to clarify the reactivity. They revealed that the reaction rate was very slow: the heating at 90℃ for 1 hour was required for the detection of sub-ppm levels of formaldehyde. The linear calibration curve with $r^2 = 0.995$ was obtained in the range 0.05 – 1 ppm formaldehyde. By considering the results obtained by the batchwise method, a two-channel flow system was assembled, and, the flow system was successfully applied to the determination of formaldehyde evolved from building materials such as polymer, plywood and particleboard, comparing with the results obtained by HPLC and 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole (AHMT) spectrophotometric method.

Introduction

Recently, numerous chemical products are widely used as building materials and we have received their blessings for comfortable life. However, it has been found that some toxic chemicals such as aldehydes and di-*n*-buthyl phthalate evolved from the materials. It was reported that the volatile chemicals concentrations increase in the closed room and the chemicals cause sick-house syndrome.[1)] Of aldehydes, formaldehyde is one of volatile organic compounds and a reactive molecule that irritates the eyes and lungs at quite low concentrations, just over 0.1 ppm.[2)] In Japan, the guideline value of indoor density for formaldehyde was set to 100 μ g/m^3 (0.08 ppm) in June, 1997.[3)] So, reliable methods are widely required for the measurement of ppb level of formaldehyde. Since building materials containing an adhesive and a paint evolve formaldehyde, it is important to measure the evolution amount of formaldehyde from building materials.

A gravimetric method was reported for the determination of low molecular aldehydes in smoke gases using 5,5-dimethyl-1,3-cyclohexanedione (dimedone).[4)] The analysis was accomplished by reaction of aldehydes with dimedone to form their derivatives as the precipitate. Sawicki and Carnes[5)] reported a spectrofluorimetric method for the determination of aliphatic aldehydes using dimedone and 1,3-cyclohexanedione (CHD). However, the former classical method is time-consuming, and the latter spectrofluorimetric method needs boiling water for the chemical reaction.

The reactions of aldehydes with dimedone and CHD to form a fluorescent derivative have been introduced into several instrumental analyses such as gas chromatography,[6)] high-performance liquid chromatography,[7),8)] liquid chromatography-mass spectrometry,[9)] and flow injection analysis (FIA).[10)-14)] The dimedone fluorescent derivatives of aliphatic aldehydes such as formaldehyde, acetaldehyde, propionaldehyde, and buthylaldehyde were identified by GC-MS.[6)] Colored derivatives of acetylacetone with formaldehyde, acetaldehyde, propanal, and butanal were also analyzed by LC-MS.[9)] Mopper *et al.* reported HPLC methods using dimedone[7)] and CHD[8)] for the determination of aldehydes in perfume, red wine and automobile exhaust. However, it is impossible to determine only formaldehyde with high sample throughput by these methods. Fan and Dasgupta *et al.*[10)] reported that a fast flow injection technique using CHD provided a highly selective method for formaldehyde determination over acetaldehyde. Sakai *et al.* used CHD to determine formaldehyde in automobile exhaust, thermal degradation emission gas[11)] and rainwater[12)] by a flow injection manifold. And also, we have proposed a spectrofluorimetric FIA with dimedone for the selective determination of formaldehyde in industry chimney and adhesive agents.[14)] However, these FIA methods have not been applied to building materials.

This paper deals with preliminary experiments by batchwise procedure to clarify the reactivity of formaldehyde with dimedone in the presence of ammonium ion. In addition, a rapid, selective spectrofluorimetric FIA method with the cyclization reaction is described for the determination of ppb level of formaldehyde evolved from building materials because the evolution amount from building and industrial materials gives an important suggestion for sick-house syndrome.

Experimental

All reagents were of analytical-reagent grade and were used without further purification. All solutions were prepared

†愛知工業大学　工学部　応用化学科(豊田市)
††F・I・A機器（東京都）†††相馬光学（東京都）

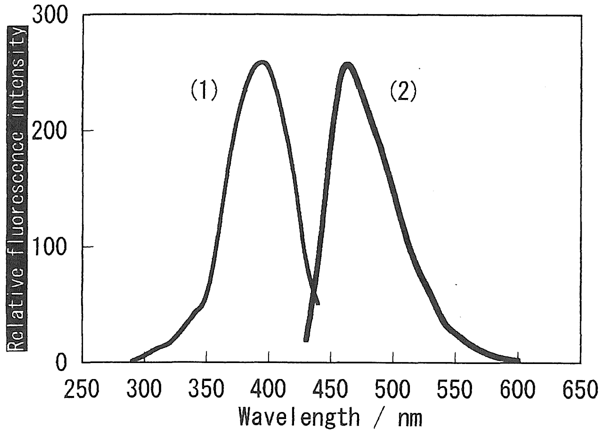

Fig. 1 Excitation and emission spectra of 5,5-dimethylcyclohexane-1,3-dione derivative. $C_{formaldehyde}$, 1 ppm; $C_{dimedone}$, 0.02 %; $C_{acetate\ buffer}$, 0.25 % (pH 4.5); reaction temperature, 90℃; reaction time, 60 min. The plotted values are subtracted the blank.

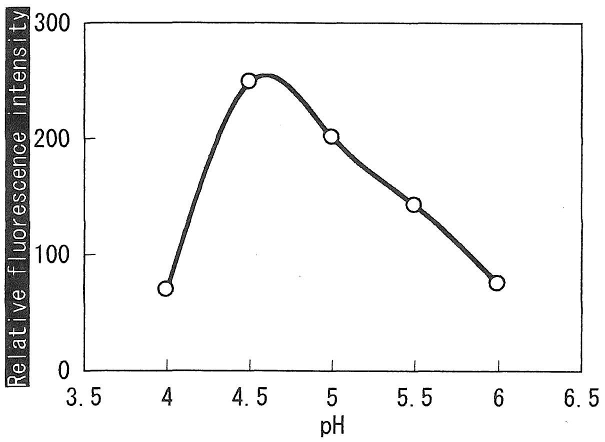

Fig. 2 Effect of pH on the relative fluorescence intensity. Conditions as in Fig. 1.

with deionized water purified with an Advantec Aquarius GSH-210 system.

Reagents for batchwise method

A commercially available formaldehyde solution (36%, Sigma Aldrich Japan, Osaka) was used and standardized by iodometry.[15] A 1 % (w/v) formaldehyde solution was daily prepared by dissolving 2.57 ml of the standardized solution in 100 ml of water, and working standard solutions were prepared by suitable dilution with water. A 0.2 % (w/v) dimedone solution was daily prepared by dissolving 0.2 g of 5,5-dimethyl-1,3-cyclohexanedione (Tokyo Kasei, Tokyo) in 100 ml of water. A 5 % ammonium acetate solution was mixed with 5 % acetic acid solution to prepare a buffer solution (pH 4.5).

Apparatus for batchwise method

A Hitachi Model F-2000 spectrofluorimeter was used with a 10-mm light-path quartz cell for fluorescence spectra measurement. A Horiba Model F-22 pH/mV meter was used for pH adjustment. A Taiyo Kagaku Kogyo C-630 thermostat was used to maintain reaction temperature.

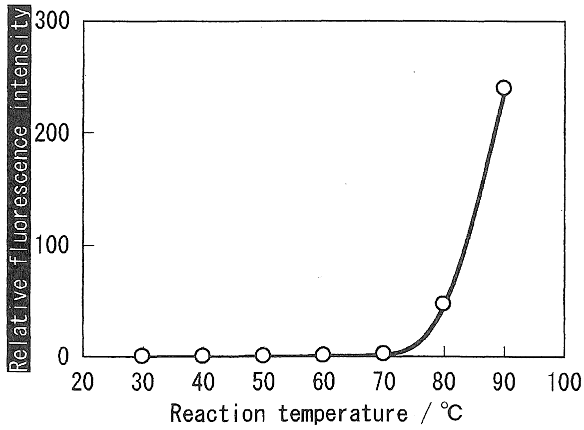

Fig. 3 Effect of reaction temperature on the relative fluorescence intensity. Conditions as in Fig. 1.

Procedure for batchwise method

To an appropriate amount of formaldehyde (0.5 – 10 μg) in a 10-ml volumetric flask, 1 ml of 0.2 % dimedone and 0.5 ml of 5 % acetate buffer (pH 5.5) are added and then the solution is diluted to the mark with water. The solution is thermostated at 90℃ for 1 hour and quenched by immersing in cool tap water for 1 min, and the fluorescence intensity is measured at 395 nm for excitation and 463 nm for emission wavelengths.

FIA system

The two-channel flow system for the determination of formaldehyde consists of a carrier solution of water and a reagent solution of 0.3% dimedone buffered at pH 5.5 with 10 % ammonium acetate-10 % acetic acid. Sample solutions containing formaldehyde evolved from various building materials are injected into the carrier stream, and the relative intensity is continuously monitored using the same wavelengths mentioned above. The reagents and apparatus were used as described previously.[14]

Results and Discussion

Fluorescence spectra

Formaldehyde reacted with dimedone to form a fluorescent derivative in the presence of ammonium ion. Figure 1 shows fluorescence spectra of the derivative, which has an excitation wavelength at 395 nm and an emission wavelength at 463 nm. We showed that the reactivities of other aldehydes such as acetaldehyde, propionaldehyde and *n*-butylaldehyde as well as ketones were quiet low under the conditions investigated in the work. Therefore, selective determination of formaldehyde can be carried out using the proposed cyclization reaction.

Variation in reaction parameters by batchwise procedure

Reaction parameters on the formation of the fluorescent derivative were studied at formaldehyde concentrations of blank and 1 ppm by batchwise procedure.

The reaction pH was varied from 4 to 6 under otherwise identical conditions: 0.25 % acetate buffer, 0.02 % dimedone, 90℃, 60 min. The result is shown in Fig. 2. The relative fluorescence intensity was maximal at pH 4.5. At higher pH range over 4.5, the intensity gradually decreased because the deprotonation of nitrogen inhibited fluorescence intensity. In a previous paper,[14] a reaction pH of 5.5 was chosen for FIA procedure. It is not clear why the optimum pH condition for FIA procedure is different from that by batchwise procedure. It

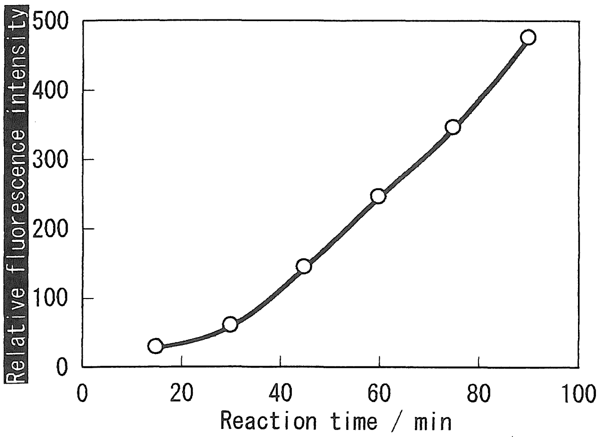

Fig. 4 Effect of reaction time on the relative fluorescence intensity. Conditions as in Fig. 1.

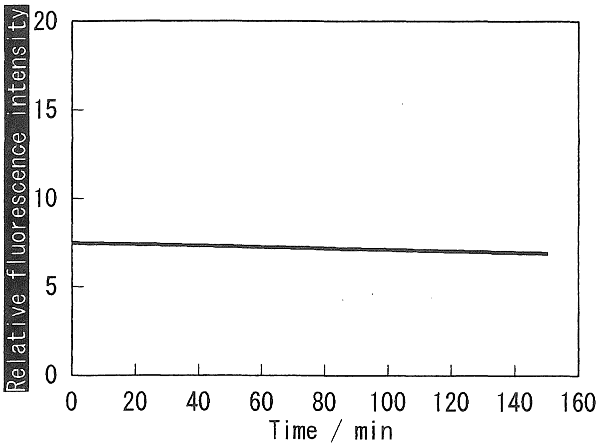

Fig. 5 Effect of standing time on the relative fluorescence intensity of mixed solution of dimedone and acetate buffer as a reagent stream for FIA. C_{dimedone}, 0.3 %; $C_{\text{acetate buffer}}$, 10 % (pH 5.5).

seems that the reason is probably related to the reaction time. Mopper *et al.*[7] reported that when the derivatization reaction was done at 100℃ for 20 min, maximum and constant fluorescence intensity was observed at pH range from 5.0 to 6.5. This experimental evidence supports our result by FIA procedure.

Ammonium ion plays an important role in the cyclization reaction of formaldehyde with dimedone. The effect of acetate buffer concentration on the intensity was examined over the range from 0.05 to 0.5 %. The intensity increased with increasing the concentration up to 0.5 %. However, the intensity of blank also increased with an increase in the ammonium ion concentration. A 0.25 % acetate buffer concentration was thus chosen.

The dimedone concentration was varied from 0.005 to 0.04 %. The fluorescence intensity was maximal and constant over the concentration of 0.02 %, and a 0.02 % dimedone concentration was selected.

Since the cyclization reaction to produce a fluorescence derivative is very slow, the previous spectrofluorimetric method[5] and the precolumn derivatization for HPLC[7] needed boiling water to accelerate the reaction. The effect of temperature on the fluorescence intensity was investigated in the range from 30 to 90℃. As can be seen in Fig. 3, the intensity increased remarkably at temperature over 80℃. Figure 4 shows the effect of reaction time on the intensity. The reaction did not go to completion even the reaction time of 90 min. A reaction time of 60 min was chosen, taking into account sample throughput.

Under the conditions above mentioned, a calibration curve for formaldehyde was prepared in the range from 0.05 to 1 ppm. The linearity was good: r^2 = 0.995. The relative standard deviation was 2.5% for five determinations of 0.5 ppm formaldehyde. The sensitivity is higher than that of the conventional spectrophotometric method with AHMT, which reliable and determinable range is from 0.3 to 50 ppm. The present batchwise method was applied to the determination of formaldehyde in a commercially available adhesive. A 2.0 g of the adhesive on a laboratory dish was put in a 20 l Tedlar bag. After sealing, the sample stood in the bag for 24 hours. Gaseous formaldehyde evolved from the materials was aspirated into water. The sample solution was analyzed by the proposed method, and the analytical values was converted to gaseous formaldehyde concentration (*C*) at 20℃ and 1 atm by using the equation as shown in ref 14. The gaseous concentration of formaldehyde obtained by the proposed method was 95 ppb. Although the same sample was also analyzed by AHMT method, formaldehyde was not detected because of the low sensitivity. When a few samples are analyzed without an FIA instrument, the proposed batchwise method is useful for the determination of such ppb levels of formaldehyde.

On the other hand, when lots of samples are treated, a fast and reproducible FIA method is suitable for quality control analysis of building materials. It is worthwhile to determine the evolution amount of formaldehyde from building materials because so far the amount has not been well known. And also, it was reported that the concentration range of formaldehyde in indoor environment was from 2.8 to 175 ppb.[16] In order to obtain highly sample throughput and sensitivity, an FIA method was adapted to the cyclization reaction.

Table 1 Analytical results of formaldehyde from polymer and wood

Sample	Found / ppb	
	Proposed method[a]	HPLC[b]
Polymer A	135±1	185
Polymer B	520±4	424
Plywood A	179±3	192
Plywood B	146±1	157

a. Average of three determinations.
b. ODS column: 4 mm × 10 mm; eluting solution: 45 % CH_3CN + 55 % water.

Analysis of formaldehyde evolved from polymer and plywood used as building materials by the proposed FIA

The two-channel flow system consists of water as a carrier solution, and dimedone/acetate buffer as a reagent solution. The stability of the reagent solution was investigated to assemble the flow system. The result is shown in Fig. 5. The fluorescence intensity of mixed solution of dimedone and acetate buffer was low and almost constant for at least 150 min. This stability led to a stable baseline of FIA study as described below.

Gaseous formaldehyde evolved from polymer and plywood as building materials was collected into water according to JIS A 5908[17] for particleboards. Each sample

Table 2 Analytical results of formaldehyde from particleboards by FIA method

Sample	Found /ppb	
	Proposed method[a]	AHMT method
A	82±2	91
B	787±4	780

a. Average of three determinations.

solution was diluted with water if necessary and was analyzed by the present FIA method and HPLC method with UV detection. The results are summarized in Table 1. The values obtained by the proposed method were in agreement with those by HPLC method. A rapid measurement of the evolution amount of formaldehyde from building materials can be possible by the proposed method rather than HPLC method.

Analysis of formaldehyde evolved from particleboard as a building material by the proposed FIA

Particleboards are made by chips of wood with an adhesive and classified into three types (E_0, E_1 and E_2) by the amount of formaldehyde emission from them.[17)] The formaldehyde concentrations of E_0, E_1 and E_2 are ≦0.5 mg/l, ≦1.5 mg/l and ≦5.0 mg/l, respectively. According to JIS A 5908,[17)] gaseous formaldehyde evolved from particleboards was collected into water. The analytical results by the present method and 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole (AHMT) spectrophotometric method[15)] are summarized in Table 2. A 100 μl aliquot of the sample solution containing formaldehyde from particleboards is required for a measurement in the case of the proposed FIA method, while 2 ml of the sample solution is required for AHMT method. And also, it is possible to carry out rapidly a quality test of particleboards by the proposed FIA method.

Conclusion

The batchwise method using the cyclization of formaldehyde with dimedone was proposed for the spectrofluorimetric determination of trace amounts of formaldehyde. Because formaldehyde as low as 50 ppb levels can be determined by the proposed batch method, the simple method without FI instrument is applicable to quality control analysis of a few building materials. Adaptation of a fast FI technique to the same reaction system provided a rapid and highly sensitive method compared with HPLC and AHMT methods. The present method was successfully applied to the determination of formaldehyde evolved from various kinds of building materials. Although the concentration of formaldehyde in indoor environment is as low as ppb levels, the present FIA method has a sufficient sensitivity for the detection of such low levels of formaldehyde and would be useful for an assessment of sick-house syndrome.

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