Membrane Solubilization Technique for Spectrophotometric Determination of Trace Formaldehyde in Rainwater

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A simple and sensitive spectrophotometry for formaldehyde in water by membrane solubilization technique was proposed. Formaldehyde was converted into a blue cationic dye with 3-methyl-2-benzothiazolinone hydrazone, and the dye was retained on a membrane filter as an ion-associate with tetraphenylborate anion. The filter retaining the blue dye was dissolved in 2-methoxyethanol containing sulfuric acid, and the absorbance of the solution was measured at 670 nm against the reagent blank. The formaldehyde from 0.007 to 0.2 mg L⁻¹ was determined with an RSD of less than 5%, and the detection limit was 0.002 mg L⁻¹. The proposed method was very simple and rapid. Twenty minutes was sufficient for the entire analytical procedure. When the method was applied to rainwater, the analytical results were in good agreement with those obtained by GC/MS.

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Introduction

Formaldehyde (HCHO) is one of the materials causing sick-house syndrome and has proved to be carcinogenic to humans.¹ Pollution of atmosphere and indoor-air with HCHO is a serious problem due to its high inhalation toxicity. HCHO is the major aldehyde in the atmosphere. The significant sources of atmospheric HCHO have been identified as primary emissions from automobiles² or industrial factories,³ and as secondary formation from photochemical reaction of hydrocarbons with atmospheric oxidants.⁴ The sick-house syndrome is caused by HCHO in indoor-air from paint and the adhesive agent in many pieces of furniture. Recently, HCHO in water is also in focus. For example, the WHO guideline value of HCHO for drinking water is 0.90 mg L⁻¹,⁵ and the regulated value in Japan for tap water is 0.08 mg L⁻¹.⁶ HCHO is very soluble in water (its Henry's law constant is 2.97×10^3 mol L⁻¹ atm⁻¹ at 25°C),⁷ so HCHO exhausted to atmosphere is scavenged by rainwater and other precipitations, and is transported to aquatic environment. A large number of researches on HCHO in the atmosphere have been reported, but few researches on HCHO in rainwater are available.⁸⁻¹¹

Many methods for the determination of HCHO in water samples have been proposed. Gas chromatography/mass spectrometry (GC/MS) or high performance liquid chromatography (HPLC) coupled with derivatization of HCHO and subsequent extraction of the derivative with organic solvent or solid-phase^{12,13} are very popular. Though these methods are sensitive and reliable, their pretreating procedures are time-consuming and cumbersome. Recently, simple and sensitive

flow-injection fluorescence methods have been proposed,¹⁴⁻¹⁶ but they required purpose-built instruments.

We proposed a simple, rapid and cost-effective visual colorimetry for HCHO in water in an accelerated publication.¹⁷ We applied it to tap water successfully. The outline of the visual method is as follows. HCHO in water was reacted with 3-methyl-2-benzothiazolinone hydrazone (MBTH) and Fe³⁺ to form a hydrophobic blue cation.¹⁸ The blue cation and a yellow cation derived from the excess MBTH were reacted with tetraphenylborate anion to form uncharged hydrophobic ion-associates. Both ion-associates were retained on a membrane filter by filtration. The color of the filter was changed from yellow to green to blue depending on the concentration of HCHO. The mechanisms of the formation of cationic dyes¹⁸ and their ion-associates are shown in Fig. 1. The HCHO in a sample solution was easily determined visually by comparing the color of membrane filter with the colors of filters obtained from standard solutions. This visual method was useful to the determination of HCHO at 0.01 – 0.07 mg L⁻¹ with precision of ± 0.01 mg L⁻¹. In that method the membrane filter acted as a medium for solid-phase extraction.

MBTH forms more deeply colored dye with HCHO than other colorimetric reagents, thus, it was used as a postcolumn derivatization reagent in HPLC analysis¹⁹ and as a coloring reagent for gaseous HCHO in a portable system.²⁰

The great advantage of the visual colorimetry is allowed a rapid decision about whether tap water passes the quality standard in Japan becomes feasible without any analytical instrument. Therefore, this method is very convenient for screening a sample before instrumental analysis. However, this method is not suitable to obtain persuasive results because of its lower precision and sensitivity with narrow calibration range. This method should be developed to become a more reliable method of visible spectroscopy. In the present work,

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Fig. 1 Reaction of HCHO with MBTH and formation of ion-associates. B^+ , Blue cation derived from HCHO; Y^+ , yellow cation (oxidized MBTH); Ph_4B^- , tetraphenylborate anion.

spectrophotometry using a membrane-solubilization technique²¹ was proposed to improve the disadvantages of the visual method. The ion-associates retained on the membrane filter were dissolved in an organic solvent together with the filter. And the absorbance of the solution was measured against the reagent blank.

There are some reports on the spectrophotometry for HCHO in water with MBTH.^{18,22,23} In those studies, large amount of acetone or sulfamic acid was added to the sample solution to prevent precipitation of the blue cation derived from HCHO. These measures, however, produced lower sensitivities. Consequently, these methods provide unreliable results for HCHO at 0.1 mg L^{-1} . One of the most attractive points of the present work is an attainment of higher sensitivity than the previous spectrophotometries. In the present work, the details of the optimum conditions for the spectrophotometry were first investigated, because the optimization for the visual method reported in our previous paper was not sufficient to develop a novel spectrophotometry. Next, the proposed method was applied to rainwater. And finally, the analytical results were compared with those obtained by the GC/MS method.²⁴

Experimental

Reagents and chemicals

Freshly produced deionized water (Mill-Q II system, Millipore) was used for preparing the reagent solutions. A HCHO standard solution (1000 mg L^{-1} , for water quality analysis) was obtained from Kanto Chemical and it was diluted arbitrarily. A 74 mmol L^{-1} (17 g L^{-1}) 3-methyl-2-benzothiazolinone hydrazone (MBTH) solution was prepared by dissolving 0.86 g of MBTH-HCl·H₂O (Tokyo Chemical Industry, extra pure grade) in 50 mL of water. A 200 mmol L^{-1} (54 g L^{-1}) iron(III) chloride solution was prepared by dissolving 5.4 g of FeCl₃·6H₂O (Nacalai Tesque, analytical reagent grade) in 100 mL of 0.5 mol L^{-1} hydrochloric acid. An acetate buffer solution was prepared by mixing 0.1 mol L^{-1} acetic acid with 0.1 mol L^{-1} sodium acetate in the ratio of 1:25 (v/v). A $60 \text{ } \mu\text{mol L}^{-1}$ (21 mg L^{-1}) tetraphenylborate solution was prepared by dissolving 0.34 g of sodium tetraphenylborate (Dojindo Lab.) in 100 mL of water to prepare a 10 mmol L^{-1} solution and the solution was diluted. A mixed cellulose ester membrane filter (made of cellulose nitrate and cellulose acetate, with pore-size $0.45 \text{ } \mu\text{m}$, 25 mm i.d. , Advantec Toyo, A045A05A) was used.

Apparatus

A spectrophotometer (Hitachi, U-2001) equipped with a 1-cm glass cell was used. A vacuum filter holder (Sibata, 6168-2552) was used for filtration. Measurement of pH was performed with a TOA, HM-60S. A GC/MS (Shimadzu, QP5000) equipped with a head space autosampler (Perkin Elmer, Turbo Matrix 40)

Fig. 2 Effects of counter ions on the retention of the dye. ■, Tetraphenylborate ion; ●, dodecylbenzenesulfonate ion; □, dodecylsulfate ion; ▲, di(2-ethylhexyl)sulfosuccinate ion. Concentration of HCHO, 0.1 mg L^{-1} ; volume of sample, 10 mL ; volume of 2-methoxyethanol (MC), 5 mL .

was used.

Recommended procedure

Place 10 mL of sample solution in a glass tube, add 1 mL of the acetate buffer solution and 0.5 mL of the MBTH solution, and set the mixture aside for more than 10 min . Add 0.5 mL of the FeCl₃ solution, and set this mixture aside for more than 5 min . Add 5 mL of the tetraphenylborate solution, and pass the solution through the membrane filter under vacuum aspiration. Wash the tube and filtration funnel twice with *ca.* 2 mL of water and filtrate the water. Dissolve the filter with 5 mL of 2-methoxyethanol (methyl cellosolve, MC) that includes 0.1 mL of 0.01 mol L^{-1} sulfuric acid. Measure the absorbance of the solution at 670 nm against the reagent blank.

Results and Discussion

Counter ion for retention of the dyes on a membrane filter

In our previous paper, tetraphenylborate anion was proposed as a counter ion to collect the blue and yellow cations as ion-associates on a membrane filter, but the optimal conditions were not studied in detail. In the present study, the effects on the absorbance of four hydrophobic organic anions: dodecylsulfate ion, dodecylbenzenesulfonate ion, di(2-ethylhexyl)sulfosuccinate ion, and tetraphenylborate ion, were investigated. The results are shown in Fig. 2. Tetraphenylborate ion, which is the most hydrophobic among the anions investigated, gave a constant and maximum absorbance by addition of over $0.2 \text{ } \mu\text{mol}$. Obviously, other anions did not give reliable results. An addition of 0.3

Fig. 3 Effect of the solvent on stability of the dye. □, 2-Methoxyethanol (MC); ■, MC containing 0.1 mL of 0.01 mol L⁻¹ sulfuric acid; ▲, dimethylsulfoxide (DMSO); ×, *N,N*-dimethylformamide (DMF). Concentration of HCHO, 0.1 mg L⁻¹; volume of sample, 10 mL; volume of solvent, 5 mL.

Fig. 4 Absorption spectra in MC containing sulfuric acid. a, 0.1 mg L⁻¹ HCHO; b, reagent blank; c, a - b. The maximal absorption wavelength of the blue cationic dye was 670 nm and that of the yellow dyes was 410 nm.

μmol, or 5 mL of 60 μmol L⁻¹ tetraphenylborate solution was recommended. This condition was the same as that reported for the visual colorimetry.

Solvent for dissolving the dye and membrane filter

The solvent for dissolving membrane filter (MF) was investigated. A mixed cellulose ester MF is easily dissolved in an organic solvent such as dimethylsulfoxide (DMSO), *N,N*-dimethylformamide (DMF) and 2-methoxyethanol (methyl cellosolve, MC). It was found that the blue dye was quickly discolored in DMF in a few minutes. And in DMSO and MC, the discoloring was slow but not suitable to obtain reliable results. The blue dye was expected to be stable under acidic condition in MC because it was produced in an acid solution. In a preliminary experiment, it was found that sulfuric acid added to MC prevented the decrease of absorbance. Figure 3 shows the effect of solvent on stability of the absorbance after the membrane filter was dissolved. When 0.1 mL of 0.001 - 6 mol L⁻¹ sulfuric acid was added to 5 mL of MC, a stable absorbance with the highest value was obtained. In this study, 0.01 mol L⁻¹ was adopted. The absorbance was constant until 30 min after dissolving MF, and decreased only 1.5% in 1 h under this condition. The use of a water-miscible organic solvent was a

Fig. 5 Effect of pH on the reaction of HCHO with MBTH to form azine. a, 0.1 mg L⁻¹ HCHO; b, reagent blank; c, a - b. Other conditions were the same as the recommended procedure.

great advantage of this method, because an aqueous acid solution could easily mix with the solvent.

Absorption spectrum

As described above, tetraphenylborate anion reacted with not only the blue cationic dye but also the yellow cationic dye to form ion-associates. The yellow dye played an important role in the visual method to make clear the color change of the filter, from yellow to green to blue, depending on the concentration of HCHO. In the present method, however, the yellow dye was only a foreign component and did not play any positive role. The absorption spectra for 0.1 mg L⁻¹ HCHO and the reagent blank are shown in Fig. 4. Obviously, the yellow cation gave little effect on the absorbance at 670 nm, where the maximum absorbance of the blue cation is present.

The amounts of MBTH and Fe³⁺

The effects of the amounts of MBTH and Fe³⁺ on the derivation of blue cationic dye were studied using 10 mL sample solutions at 0.1 mg L⁻¹ HCHO. The investigation on MBTH was performed by the addition of 5 mL of MBTH solutions with different concentrations from 20 to 120 mmol L⁻¹. More than 60 mmol L⁻¹ of MBTH gave constant absorbance and also a constant reagent blank. In this study, 74 mmol L⁻¹ of MBTH was recommended. The effect of Fe³⁺ was studied by the addition of 0.5 mL of Fe³⁺ solutions with different concentrations from 40 to 400 mmol L⁻¹. Constant absorbance was obtained at more than 160 mmol L⁻¹ of Fe³⁺. One MBTH molecule reacts with two ferric ions to form a yellow oxidized MBTH cation. And Fe³⁺ also reacts with the intermediate of oxidized MBTH derived from HCHO (Fig. 1). Therefore, the amount of Fe³⁺ required for the reaction is at least two-fold MBTH. The reagent blank was increased at more than 320 mmol L⁻¹ of Fe³⁺; therefore, 200 mmol L⁻¹ of Fe³⁺ was recommended. These optimized conditions were the same as those in the visual method reported.

Effect of pH

The effect of pH on the reaction of HCHO with MBTH to form azine (Fig. 1) is shown in Fig. 5. A constant absorbance was obtained over the pH range of 4.0 - 7.0, and the reagent blank was constant over the pH range of 3.3 - 6.2. In this study, the pH was adjusted to 5.5 with acetate buffer solution.

Fig. 6 Reaction time for complete formation of azine. a, 0.1 mg L⁻¹ HCHO; b, reagent blank; c, a – b. Other conditions were the same as the recommended procedure.

Table 1 Precision at different concentrations of HCHO

Concentration of HCHO/mg L ⁻¹	Absorbance at 670 nm vs. reagent blank ^a	RSD ^b , %
0.020	0.075	5
0.040	0.161	2.5
0.080	0.329	0.9
0.120	0.500	0.7
0.200	0.832	0.3

a. Reagent blank was 0.044 on an average of five times, and its relative standard deviation was 5%.

b. Relative standard deviation, obtained from five different runs.

Reaction time

The reaction time required for the formation of the blue dye was investigated. As shown in Fig. 1, the formation of the blue dye consists of three reactions. Reaction 1 is the formation of azine from HCHO with MBTH. Reaction 2 is oxidation of MBTH by Fe³⁺. And reaction 3 is formation of the blue cationic dye from azine with oxidized MBTH. The effect of time on reaction 1 is shown in Fig. 6. More than 10 min was required for reaction 1. The effect of time on reactions 2 plus 3 or the time from addition of Fe³⁺ to filtration was also investigated. Three minutes was enough for the reactions; thus, 5 min was recommended.

Precision and detection limit

The mean absorbance and relative standard deviations obtained from five determinations of HCHO at different concentrations are shown in Table 1. A linear calibration curve was obtained from 2.0×10^{-2} to 2.0×10^{-1} mg L⁻¹ of HCHO with a high correlation coefficient ($R^2 > 0.999$). The detection limit based on three times the standard deviation for the reagent blank was 2.0×10^{-3} mg L⁻¹.

Effects of other aldehydes and foreign components in rainwater

HCHO is the major aldehyde in rainwater, followed by glyoxal.²⁵ Acetaldehyde, propionaldehyde and other aldehydes are minor in rainwater. The analytical responses from several aldehydes suspected to be present in rainwater were investigated. It was reported that MBTH reacts with not only HCHO but also with other aliphatic aldehydes.¹⁸ The molar absorptivities for

Table 2 Responses of aldehydes suspected to be present in rainwater

Compound	Structural formula	Molecular weight	Molar absorptivity/ 10 ⁴ mol ⁻¹ L cm ⁻¹ ^a
Formaldehyde	HCHO	30.0	6.5
Acetaldehyde	CH ₃ CHO	44.1	6.0
Propionaldehyde	C ₂ H ₅ CHO	58.1	5.0
Acrolein	CH ₂ CHCHO	56.1	7.0
Glyoxal	OHCCCHO	58.0	0.8

a. Calculated from the absorbance of 2-methoxyethanol solution obtained from a standard solution of each aldehyde divided by 5 mL and by the number of moles in the 10 mL of initial aqueous solution.

Table 3 Recovery tests for rainwater samples and seawater samples

Water	HCHO added/ mg L ⁻¹	HCHO found/ mg L ⁻¹	RSD, ^a %	Recovery of added HCHO	
				mg L ⁻¹	%
Rainwater ^b	0	0.029	2	—	—
	0.040	0.071	2	0.042	106
	0.080	0.11	1.0	0.080	100
	0.120	0.15	0.3	0.12	101
Seawater ^c	0	N.D.	—	—	—
	0.080	0.082	7	0.079	98
	0.200	0.196	1.3	0.19	97

a. Relative standard deviation, obtained from five different runs.

b. Sampled at campus of University of Toyama in urban area.

c. Coastal surface water of the Bay of Toyama.

some aldehydes obtained by the proposed method for HCHO are shown in Table 2. The monovalent aldehydes, acetaldehyde, propionaldehyde and acrolein gave values that were very close to the value obtained with HCHO. Glyoxal, a bivalent aldehyde, gave a much lower response. Formate, which has the property of aldehyde in addition to that of carboxylic acid, did not interrupt at all. Therefore, the proposed method gives total molar concentration of these aldehydes. In rainwater, however, the concentrations of other aldehydes are much lower than HCHO; thus, the contribution of other aldehydes to the analytical results would be very small, as shown later.

Hydrogen peroxide at high concentration changed the color of the filter to slightly brown. And it gave a species having a maximum absorbance at 513 nm in the dissolving medium. Hydrogen peroxide at 10 μmol L⁻¹ caused about 7% positive error for 0.1 mg L⁻¹ (3.3 μmol L⁻¹) of HCHO. A 50 μmol L⁻¹ portion of sulfite completely prevented the coloration of 0.1 mg L⁻¹ HCHO. It was reported that sulfite reacts with HCHO to form hydroxymethanesulfonate, which is not active to MBTH.¹⁹ Nitrite did not interfere with the determination even at 50 μmol L⁻¹. As will be shown in the next section on the recovery tests for rainwater and seawater, major ions in rainwater, such as Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca²⁺, Cl⁻, NO₃⁻, and SO₄²⁻, did not interfere with the determination.

Application to rainwater

Recovery tests. The recoveries of HCHO added to rainwater and seawater at different levels are shown in Table 3. Quantitative recoveries were obtained for both samples with high precision even at lower levels. Clearly, the proposed method is applicable

Fig. 7 Analytical results of HCHO in rainwater. The error bar gives two-fold standard deviation. GC/MS was according to the method proposed by Sugaya *et al.*²⁴

not only to rainwater but also to seawater without interference from their matrices.

Comparisons of the analytical results with GC/MS. The comparisons of the analytical results obtained by the proposed spectrophotometry and those obtained by head space-GC/MS²⁴ for the same rainwater samples taken at urban areas are shown in Fig. 7. The two results were in very good agreement. The GC/MS results also showed that the concentrations of other aldehydes such as acetaldehyde and propionaldehyde were very low in the rainwater samples investigated. Therefore, the interference from other aldehydes with the spectrophotometry was very little. Obviously, the proposed spectrophotometry was successfully applied to rainwater. The procedure is simpler, more rapid and cost-effective than GC/MS, and the analytical results are as reliable as those of GC/MS. The analytical results also strongly suggest that the rainwater pollution with HCHO was serious at the urban area where the rainwater was taken.

Conclusions

A simple and sensitive spectrophotometry for the determination of HCHO in water using an organic solvent-soluble membrane filter was developed. A linear calibration was obtained from 0.007 to 0.2 mg L⁻¹ of HCHO with satisfactory precision. Twenty minutes was sufficient for entire analytical procedure without any skill. The proposed method was three times as sensitive as the common MBTH method proposed by Hauser *et al.*²² Improvement of this method to be more sensitive is expected by increasing the sample volume or reducing the organic solvent volume. The analytical results for HCHO in rainwater were in good agreement with those obtained by GC/MS. Therefore, the proposed spectrophotometry will be a

convenient and practical tool for the investigation of rainwater pollution with HCHO.

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