

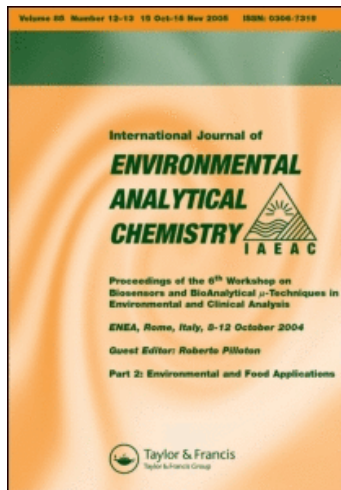
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DETERMINATION OF FORMALDEHYDE TRACES IN FABRIC AND IN INDOOR AIR BY A KINETIC FLUORIMETRIC METHOD

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A simple and sensitive kinetic fluorimetric method is reported for the determination of trace amount of formaldehyde. The proposed method is based on the catalytic effect of formaldehyde on the oxidation reaction of rhodamine B with potassium chlorate in sulfuric acid solution. Formaldehyde in the range of 0.020–0.340 µg/mL can be determined with a limit of detection of 5.73 ng/mL. The method has been used to determine trace formaldehyde in fabric and in indoor air. The results thus obtained show good agreement with those determined by acetyl acetone method.

Keywords: Kinetic fluorimetric method; Formaldehyde; Rhodamine B; Fabric; Indoor air

INTRODUCTION

Formaldehyde is used as a coating, resin and/or adhesive in many building materials, and is also widely presented in the atmosphere [1]. It is known to be irritant to the eyes, nose and throat, and has been declared a suspected mutagen and carcinogen in the laboratory animal test [2–4]. The toxicity of formaldehyde to man and animals has been subject of a number of reviews [5,6], and studies in this respect are still in progress. It is also an increasingly important environmental pollutant and in the USA the permitted upper limit for formaldehyde has recently reduced to 1.2 mg/m³ [7]. Moreover, formaldehyde is now recognized as one of the most important indoor air pollutants [8]. Since people spend about 90% of their time indoors, it is important to determine the indoor concentration levels to obtain an estimate of personal exposure. Hence it is of great concern to develop a simple and sensitive method for the measurement of formaldehyde.

Several methods for the determination of formaldehyde have been reported. The most used Spectrophotometric method that have been devised for the determination of formaldehyde are the chromotropic acid method [9]. The spectrophotometric

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method based on the formation of metal ion complexes of formaldehyde [10] have been also reported. In recent years, kinetic spectrophotometric methods [11,12] have been developed for the determination of formaldehyde. These methods have the advantages of simplicity. However, most of them are not sensitive enough or subject to numerous interferences from phenols, alcohol, cyclohexanone and some metal ion compounds. Chromatographic methods, including GC and HPLC, have been reported for the determination of formaldehyde based on pre- or post-column derivatization reaction [13–15]. They have been shown to provide adequate sensitivity. However, these methods require a fairly elaborate analytical procedure and a long measuring time per sample.

There are some fluorescence methods proposed for the determination of formaldehyde. A widely used one is acetyl acetone method and its improvement [16,17]. Many of them have been coupled with HPLC or flow injection technique. These methods are sensitive, but lack of simplicity. Houdier and coworkers [18] have recently reported a new fluorescent probe which shows adequate sensitivity for the detection of formaldehyde. A fairly sensitive fluorimetric method [19], based on the reaction of formaldehyde with 3,4-diaminoanisole, has also been reported, but the method needs a refluxing process, which is fairly tedious.

So far there is no report on the determination of formaldehyde by kinetic fluorimetric photometry. In this work, a detailed study of experimental condition for the catalytic effect of formaldehyde on the oxidation reaction of rhodamine B with potassium chlorate have been conducted. Formaldehyde in the range of 0.020–0.340 $\mu\text{g}/\text{mL}$ can be determined with a detection limit of 5.73 ng/mL . The proposed method is simple, sensitive and reliable. It has been used to determine trace formaldehyde in fabric and in indoor air. The results obtained by the present method are in quite agreement with those determined by a standard method [20,21].

EXPERIMENTAL

Reagents

All chemicals used in the experiment were analytical reagents, and double distilled water was used throughout.

1.0 mg/mL stock solution of formaldehyde (HCHO) was prepared and standardized by the sulfite method. Working standard solutions were freshly prepared by appropriate dilution of the stock solution. 0.2 mol/L potassium chlorate, 1.0×10^{-4} mol/L rhodamine B(RhB) and 2.0 mol/L sulfuric acid solutions were prepared by standard procedure.

Apparatus

FP-6200 spectrofluorometer (JASCO, Japan); Model 930 fluorophotometer (Shanghai, China); Model 501 thermostat bath (Chongqing, China).

Procedure

0.60 mL of 1.0×10^{-4} mol/L rhodamine B, 1.80 mL of 2.0 mol/L sulfuric acid, a proper amount of formaldehyde solution and 1.5 mL of 0.2 mol/L potassium chlorate were

successively added into a 25 mL measuring flask, diluted with water up to the mark and mixed well by shaking. After heating in boiling water bath for 14 min, the sample was cooled with running water to stop the reaction. Its fluorescence value (F) and blank value (F_0) were determined at an excitation wavelength of 560.0 nm and an emission wavelength of 576.0 nm. Then the value of $\Delta F = F_0 - F$ was calculated.

RESULTS AND DISCUSSION

Rhodamine B emits very strong fluorescence. Figure 1 shows its excitation (A) and emission (B) spectra at different experimental conditions. It can be seen that addition of formaldehyde into RhB + KClO₃ and RhB + H₂SO₄ has little influence on the fluorescence value. Rhodamine B is oxidized by potassium chlorate in sulfuric acid. This oxidation reaction is speeded up in the presence of trace formaldehyde, indicating that formaldehyde can catalyze the oxidation reaction of rhodamine B with potassium chlorate. At an excitation wavelength of 560.0 nm and an emission wavelength of 576.0 nm, the ΔF values are maximum. Furthermore, it is observed that there is a linear relationship between ΔF and the concentration of formaldehyde. On the basis of this, a new kinetic fluorimetric method has been proposed for the determination of trace formaldehyde and the experimental conditions have been studied.

Effect of Variables

In order to select an optimized analytical system, various experimental parameters including medium, reaction temperature and time were studied (with formaldehyde

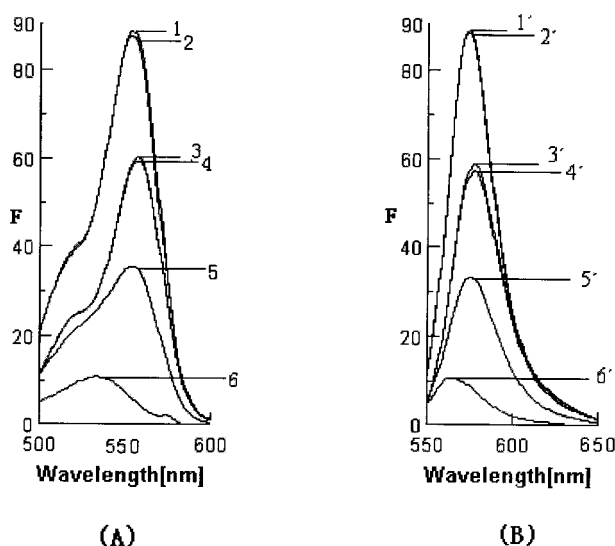


FIGURE 1 Excitation (A) and emission (B) spectra of RhB at different experimental conditions: (1-1'), RhB + KClO₃; (2-2'), RhB + KClO₃ + HCHO; (3-3'), RhB + H₂SO₄; (4-4'), RhB + H₂SO₄ + HCHO; (5-5'), RhB + H₂SO₄ + KClO₃; (6-6'), RhB + H₂SO₄ + HCHO + KClO₃. RhB, 2.4×10^{-6} mol/L; H₂SO₄, 0.144 mol/L; KClO₃, 1.2×10^{-2} mol/L; HCHO, 0.20 μ g/mL.

concentration being 0.20 $\mu\text{g/mL}$ under all conditions). These parameters were obtained by optimizing one of the parameters each time and setting all other parameters to be constant.

Hydrochloric acid, phosphoric acid and sulfuric acid have been tried in the present experiments. It was found that sensitivity of the reaction is very low in hydrochloric acid and phosphoric acid media. Only in sulfuric acid, the catalyzing effect of formaldehyde is striking, the sensitivity is high and the reproducibility is good. Therefore, sulfuric acid was selected as the reaction medium.

The influence of the concentration level of sulfuric acid has been investigated. It is showed that ΔF value increases with increasing concentration of sulfuric acid in the range of 4.80×10^{-2} –0.160 mol/L. However, in the range of 0.128–0.160 mol/L, ΔF value changes slowly. So 0.144 mol/L sulfuric acid was chosen.

Similarly, it is found that ΔF value increases with increasing concentration of potassium chlorate in the range of 4.80×10^{-3} – 1.60×10^{-2} mol/L. But ΔF value changes slowly in the range of 9.60×10^{-3} – 1.60×10^{-2} mol/L. Therefore, 1.20×10^{-2} mol/L potassium chlorate was used in this work.

The influence of the concentration level of rhodmine B was studied in the range of 1.2×10^{-6} – 3.6×10^{-6} mol/L. It is noted that the lower rhodmine B concentration is, the higher the detection sensitivity. However, the reproducibility is not good when the concentration of rhodmine B is low. Thus 2.4×10^{-6} mol/L rhodmine B was selected.

The effect of reaction temperature was investigated in the range of 60–100°C. It was observed that the reaction rate increases with increasing temperature and reaches a maximum at 100°C. Moreover, $\ln(\Delta F)$ increases linearly with the reciprocal of reaction temperature in the range of 80–100°C. The regression equation is $\ln(\Delta F) = 47.05 - 1.62 \times 10^4/T$ (T is absolute temperature) with a correlation coefficient of 0.9986. The reaction activation energy $E = 134.7$ kJ/mol.

The influence of the reaction time (t) was studied in the range of 4–16 min. It was observed that ΔF value increases linearly with reaction time in the range of 6–14 min. The regression equation is $\Delta F = -11.62 + 3.49t$ (min), with a correlation coefficient of 0.9985. The apparent reaction rate constant $k = 5.82 \times 10^{-2} \text{ s}^{-1}$.

Analytical Characteristics

The calibration graph of formaldehyde was constructed under the optimum conditions described above. A linear relationship was found between ΔF and the concentration of formaldehyde in the range of 0.020–0.340 $\mu\text{g/mL}$. The regression equation is $\Delta F = 1.09 + 209.6 C_{\text{HCHO}}$ ($\mu\text{g/mL}$) with a correlation coefficient of 0.9997. The detection limit for the determination can be calculated by $C_L = KS_b/S$ recommended by IUPAC [22]. In the equation, C_L is the limit of detection; $K (= 3)$ is a constant related to confidence level; S_b is the standard derivation of the reagent blank ($n = 9$) and S is the slope of calibration graph. Thus calculated detection limit is 5.73 ng/mL, and the relative standard deviation is 1.79% for 11 determinations of 0.20 $\mu\text{g/mL}$ of formaldehyde.

Interference of Matrix Compounds

In order to apply this method to the determination of formaldehyde in fabric and in indoor air samples, the influence of common ions and organic compounds on the determination of 0.20 $\mu\text{g/mL}$ formaldehyde was investigated in detail with $\pm 5\%$

TABLE I The influence of matrix compounds

<i>Matrix compounds</i>	<i>Ratio^a [ion]/[HCHO]</i>	<i>Matrix compounds</i>	<i>Ratio^a [ion]/[HCHO]</i>
Na ⁺	1.01×10^3	SO ₄ ²⁻	2.11×10^3
Cl ⁻	2.00×10	K ⁺	5.07×10^2
CO ₃ ²⁻	3.33×10^2	NO ₃ ⁻	8.27×10^2
Ca ²⁺	1.33×10^2	Al ³⁺	4.00×10
Ni ²⁺	5.00×10^3	Ac ⁻	3.33×10^2
C ₂ O ₄ ²⁻	1.33×10^2	Mn ²⁻	6.57×10^2
Uric acid	6.6	Cd ²⁺	1.33×10^2
Urea	2.00×10^2	Benzoic acid	1.00×10^3
Ethanol	1.58×10^2	Formic acid	3.00×10^2
Glucose	1.00×10^2	Acetic acid	7.00×10^2
NH ₄ ⁺	6.67×10^2	Benzene	5.86×10^2
Methyl benzene	4.50×10^2	Acetone	7.90×10^2
F ⁻	4.84×10	Methanol	1.06×10^3
HCO ₃ ⁻	6.67×10^2	Phenol	2.00×10^2
PO ₄ ³⁻	1.67×10	SO ₃ ⁻	3.30×10
Acrolein	1.10×10	Acetaldehyde	2.0

^a"Ratio" stands for the ratio of concentration between the interfering substance and formaldehyde.

permitted relative derivation from ΔF value. The results are summarized in Table I. It is clear that the interference of most common ions and organic compounds are very small, except for uric acid and acetaldehyde. This is advantageous to the determination of formaldehyde in real samples.

Sample Analysis

Determination of Trace Formaldehyde in Fabric

Add 100 mL double distilled water into a wide-mouth bottle with ground stopper and keep it at $65 \pm 1^\circ\text{C}$ for 20–30 min in a blasting torrefaction box. Then weigh accurately about 1 g cloth sample and hang it in the bottle for 4 h at the same temperature (the water inside and the wall of the bottle can not be touched by the samples). Then take the bottle out of the box, and cool it to room temperature. Take out the cloth sample, and shake the bottle to mix the solution uniformly. Then, a known amount of extract solution was taken and used to determine formaldehyde by the proposed method and the acetyl acetone spectrophotometric method [20], respectively. The results are presented in Table II. It is evident from the calculated *t*-test values that our results are in good agreement with those obtained by the reference method.

Determination of Trace Formaldehyde in Indoor Air

Using a air sampler, the air was drawn through 10 mL water at a rate of 0.5 L/min for 30 min in order to extract formaldehyde in air. The aqueous solution thus obtained was transferred into a 25 mL calibrated flask, diluted to the mark with water, and used to determine formaldehyde by the proposed method and the acetyl acetone spectrophotometric method [21], respectively. The results obtained for four samples are shown in Table III. Obviously, our results are in good agreement with the reference method.

TABLE II The results of formaldehyde in fabric

No.	This work		Acetyl acetone method ($\mu\text{g/g}$)	t^b
	Mean ($\mu\text{g/g}$)	RSD (%)		
1	1334.5	2.60	1388.6	2.32
2	342.4	2.34	327.4	1.91
3	299.7	1.38	289.6	1.75
4	157.6	1.82	148.9	2.38

^bTheoretical value = 2.78, $n = 5$ with 95% confidence limit.

TABLE III The results of formaldehyde in indoor air

No.	This work		Acetyl acetone method ($\mu\text{g/L}$)	t^c
	Mean ($\mu\text{g/L}$)	RSD (%)		
1	2.453	2.04	2.313	2.52
2	0.637	2.90	0.606	2.04
3	1.476	1.56	1.400	2.18
4	1.207	4.12	1.147	1.68

^cTheoretical value = 2.78, $n = 5$ with 95% confidence limit.

Acknowledgments

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