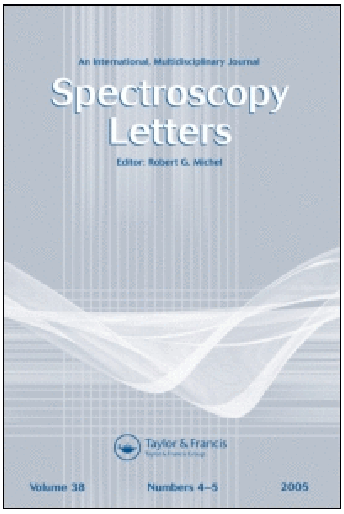

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A Flow-Injection Chemiluminescence Determination of Formaldehyde in Textiles

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ABSTRACT In the multitude of experiments on determination of formaldehyde, no experiment has made any attempt to determine the exact amount of formaldehyde in textile materials by flow-injection chemiluminescence. In this article, flow-injection chemiluminescence analysis is used effectively for the selective determination of formaldehyde in textiles. The reaction is based upon the modified Trautz–Shorigin reaction, in which formaldehyde and gallic acid are oxidized with aqueous alkaline hydrogen peroxide, producing relatively strong chemiluminescence. The effects of reagent concentrations, temperature, pH, flow rates, mixing coil length, and flow sequences on the chemiluminescence intensity were studied. Under the optimized experimental conditions, formaldehyde in an aqueous solution was determined over the concentration range from $0.20–1.0 \times 10^{-7}$ M with a linear calibration graph; the detection limit (LOD; $S/N = 3$) was 5×10^{-8} M. The relative standard deviation of 12 replicate measurements of 2×10^{-5} M formaldehyde was 1.1%. This flow-injection analysis system proved able to analyze up to 50 samples/h. The effects of various interferences possibly present in the textile samples were investigated. Most cations and anions, as well as organic compounds, do not interfere with the determination of formaldehyde in textile samples. The proposed method is very simple, rapid, inexpensive, sensitive, and can be applied to a variety of textile samples at low concentration levels without any enrichment treatment. This method was applied to the determination of formaldehyde in different textile samples and compared with the state standard method used in China.

KEYWORDS chemiluminescence, flow-injection, formaldehyde, textile

INTRODUCTION

Formaldehyde receives a great deal of attention, owing to its extensive use in industry and possible carcinogenic properties.[1] It is one of the most important indoor pollutants because of its extensive use in adhesives, bonding and laminating agents, urea-formaldehyde foam insulation, textiles, coatings, plywood, and paints. Elevated levels of HCHO, up to 300 parts per billion by volume (ppbv), have been reported in indoor air.[2] Textiles are often finished with formaldehyde-containing chemicals, which can provide crease resistance, flame retardance, and dimensional stability.[3,4]

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Its contact directly with human skin may cause an irritant effect on the mucous membrane. If inhaled, emitted formaldehyde may cause inflammation of the respiratory tract.[3,4] A rapid and sensitive method for the determination of formaldehyde in textile samples at low levels is required.

For the determination of formaldehyde, many of methods have been proposed so far. Of these, the chromotropic acid (1,8-dihydroxynaphthalene-3, 6-disulphonic acid) method,[5–7] the MBTH (3-methyl-2-benzothiazolone hydrazone) method,[8–10] the AHMT (4-amino-3-hydrazino-5-mercapto-1, 2,4-triazole) method,[11–13] and the pararosaniline method[14–17] are popular colorimetric methods for the detection of formaldehyde. In these methods, however, serious problems are present; for example, the chromotropic acid method needs hot concentrated sulphuric acid[5] or a less harmful mixture of HCl and H_2O_2.[18] The MBTH method has been less commonly used because it is very expensive and can react easily with other aldehydes, and the sample solutions should be measured immediately after sampling due to the instability of the MBTH–formaldehyde intermediate.[19,20]

Chemiluminescence (CL) methods for the determination of formaldehyde in natural and wastewater based on the Trautz–Schorigin reaction involving formaldehyde, hydrogen peroxide, and gallic acid in a strong alkaline solution was developed by Slawinska and Slawinska.[21] Afterwards, Motyaka and coworkers[22,23] modified the original configuration of the Trautz–Schorigin reaction into a form suitable for flow-injection analysis (FIA) of formaldehyde in water samples.

For the detection of formaldehyde in textile samples, however, very few attempts have been made. The colorimetric method,[24] chromotropic acid method,[25] diffusive sampler technique,[26] and interdigitated microelectrode array diffusion layer[27] are known to detect formaldehdye in textile materials. However, poor sensitivity, existence of interference, rather complicated instrumentation, and long reaction times limit the applicability of these methods for the detection of formaldehyde in textile samples. Thus, a much faster, simple, rather inexpensive, and, above all, sensitive technique was required for the direct determination of formaldehyde in textile samples.

FIA is now well established as an excellent technique for rapid, automated, quantitative analysis. It is particularly well suited to monitor transient light emission from liquid phase CL reactions due to the rapid and reproducible mixing of sample and reagent in close proximity to the detector.

In this work, a simple and sensitive method for the determination of formaldehyde in textile samples by a flow-injection CL method (FI–CL) based on the modification of the Trautz–Schorigin reaction is described for the first time. A simple FI–CL system, consisting of a pumping system, sample injection valve, reaction chamber, and a chemiluminescent detector for the formaldehyde determination in textile, is developed. The experimental results show that the method is effective for the determination of formaldehyde in textile samples.

EXPERIMENTAL

Reagents

All chemicals used were of analytical reagent grade without further purification. The concentration of formaldehyde solution (36.0–38.0%, Gongzhuling Chemical Reagent Factory, China) in the stock solution was determined by the iodometric method.[28] The concentration of hydrogen peroxide (30%, Beijing Chemical Plant, China) in the stock solution was determined by titration using the thiosulfate-iodide method.[29] Gallic acid, acetic acid, and acetyl acetone were obtained from the Tianjin Fuchen Chemical Reagent Factory (China). NaOH was obtained from Tianjin No. 1 Chemical Reagent Factory (China). Ammonium acetate was obtained from the Tianjin Guangfu Fine Chemical Research Institute (Tianjin, China). Textile samples were obtained from Jiangsu Institute of Fiber Inspection (Nanjing, China). Working standard solutions were prepared by accurate dilution of the standard stock solution just before use. The water used in all experiments had a resistivity higher than $18\,M\Omega cm^{-1}$.

Apparatus

The FIA processor (FIA-3110, Beijing Titan Instruments Co. Ltd., Beijing, China) consists of two peristaltic pumps, a 16-hole 8-way valve, and a digital system to maintain the time of flow and pressure of each pump. The CL detection system is a computerized ultra-weak luminescence analyzer (type BPCL, manufactured at the Institute of

Biophysics, Chinese Academy of Sciences, Beijing, China). The BPCL analyzer has a temperature control system that can adjust the temperature of the CL reaction chamber automatically. Emitted CL light is measured with the Photomultiplier Tubes (PMT) operating at 1080 V and 25°C with no wavelength discrimination. Resulting peaks are recorded with an FIA monitor/data processing apparatus. Flow lines are made of polytetrafluoroethylene (PTFE) tubing (0.5 mm i.d.) manufactured at Shenyang Zhaofa Institute of Automatic Analysis (China). A UV visible spectrometer Cintra 10e, GBC (Australia) was used for standard spectrophotometry.

Flow-Injection Procedure

A schematic diagram of the FI-CL employed the FIA system is presented in Fig. 1. A 0.05 M gallic acid sample and 0.2 M sodium hydroxide solutions are carried to the reaction valve through Pump A at a pump speed of 2.7 mL min^{-1}. 0.6 M H_2O_2 is introduced to the reaction valve through Pump A with a loop volume of 150 μL; pump speed is 0.9 mL min^{-1}. Finally, the mixture from Pump A is carried to the reaction valve, from where this mixture along with H_2O_2 is carried to the chemiluminescent detection chamber. The running time for Pump A was 30 s and for Pump B was 10 s.

For the flow-injection system described here, the minimum cycle time (load plus inject) necessary to prevent carry-over between successive samples is 40 s, which leads to a maximum throughput rate of more than 50 samples h$^{-1.}$

Sample Preparation

At low temperatures (lower than 65°C), sorption of formaldehyde on cellulose is reversible, as indicated by complete extractability of the sorbed formaldehyde in water. At temperatures higher than 65°C, a fraction of the sorbed formaldehyde is irreversibly bound to cellulose and cannot be recovered by extraction with water.[30]

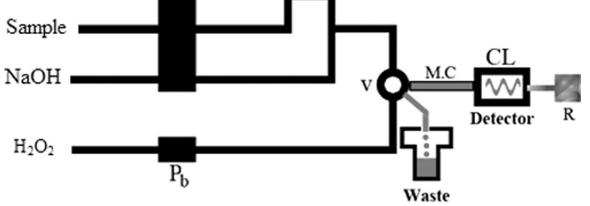

FIGURE 1 **A schematic diagram of the FIA system: G.A, gallic acid; P$_a$, Pump A; P$_b$, Pump B; V, 8-way valve; M.C, mixing coil 10 cm; R, recorder; P$_a$ = 2.70 mL min^{-1}; P$_b$ = 0.9 mL min^{-1}.**

In this experiment, formaldehyde from the textile substrate was extracted with water at 50°C. An amount of 1-g sample fragments were placed into a 250-mL conical flask, in which 50 mL of pure water was added. The flask was tightly capped and placed in a 50°C water bath for 60 min. If the concentration of the formaldehyde was above 100 mg/kg, a few milligrams of the sample were enough for the analysis. When the formaldehyde concentration is below 0.25 mg kg^{-1}, the sample amount should be increased.

Standard Spectrophotometric Method

The sample preparation and spectrophotometric determination of formaldehyde were performed according to the state standard method used in China.[31] An amount of 1-g sample fragments were placed into a 250-mL conical flask, in which 100 mL of pure water was added. The flask was tightly capped and placed in a 40°C water bath for 60 min. Five milliliters of extract was filtered and transferred into a test tube, in which 5 mL derivatization reagent was added. The test tube was tightly capped and placed in a 40°C water bath for 30 min to form the derivative. After that, the solution was laid up for 30 min at room temperature and detected at 412 nm with spectrophotometer. The reference solution consisting of 5 mL pure water and 5 mL derivatization reagent was used.

The calibration curve used in this method was constructed by mixing 5.0 mL different concentrations (5×10^{-6}–5×10^{-5} molL^{-1}) of formaldehyde standard solution with 5 mL derivatization reagent.

RESULTS AND DISCUSSION

Optimization of Flow System

During the optimization, the effects of flow rates of liquids as well as concentration of reagents on the CL signal were examined. For this purpose, at first, the various mixing sequences were investigated to find the optimal one that could produce the highest CL signal. All examined mixing sequences are

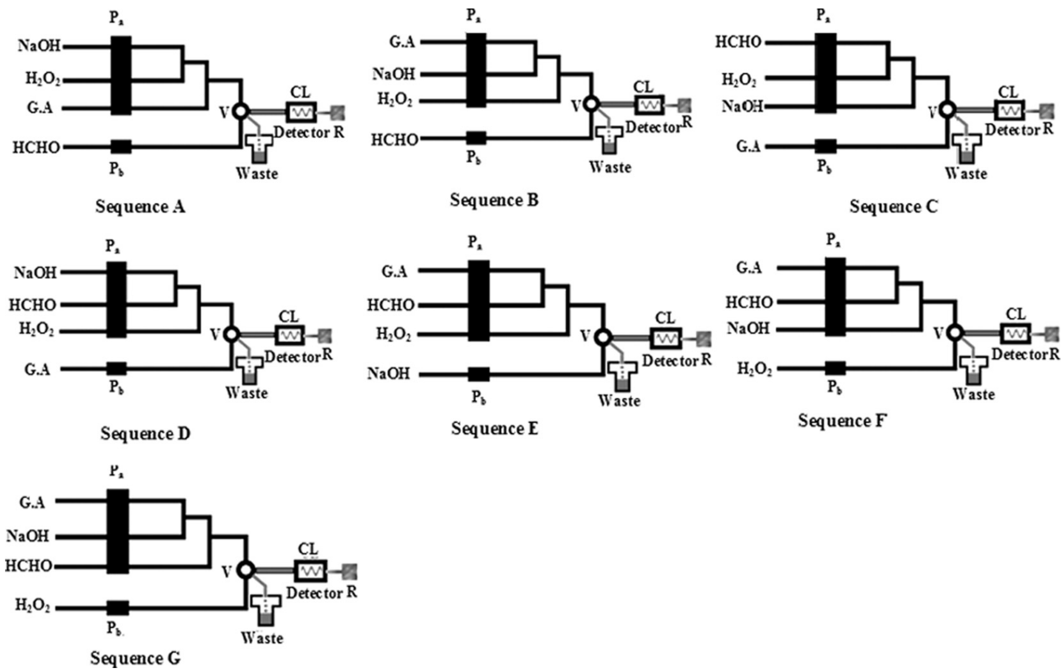

FIGURE 2 Various mixing sequences: 1×10^{-4} M HCHO; 0.05 M gallic acid; 0.6 M H_2O_2; 0.15 M NaOH; V, 8-way valve; M.C, mixing coil 10 cm; R, recorder; Pump A = 2.7 mL min^{-1}; Pump B = 0.9 mL min^{-1}.

schematically presented in Fig. 2. The mixing sequences F and G had approximately the same, but high, sensitivity compared with using the other five mixing sequences (Table 1). However, sequence F was chosen to carry out further experiments, as there was less relative standard deviation of 1.1% observed within five measurements of that sequence.

Optimization of Reagent Concentrations

The sensitivity of the modified Trautz–Schorigin reaction with respect to HCHO is markedly affected by reagent concentrations. Concentrations of gallic acid, hydrogen peroxide, and sodium hydroxide solutions were optimized individually by holding constant concentrations of three other reagents in different combinations. In all cases, the CL signal rises with the increasing concentration of reagent and, after passing, the maximum decreases. In this study, the optimum concentrations of gallic acid, H_2O_2, and NaOH are 0.05 M, 0.6 M, and 0.2 M, respectively.

TABLE 1 CL Signals for Various Mixing Sequences

Mixing sequences	S/S_{max}
A	0.23
B	0.81
C	0.61
D	0.55
E	0.49
F	1.00
G	0.97

Individual mixing sequences are shown in Fig. 2. S_{max} is the signal obtained by sequence F.

Optimization Manifold Parameters

Effect of Temperature

The effect of temperature on signal intensity was examined by varying the temperature of CL reaction chamber from 10°C to 60°C. It was seen that there is no considerable change in the chemiluminescent intensity of formaldehyde with changes in temperature. In order to select a suitable temperature, the relative standard deviation within three measurements at fixed temperature was determined. It was found that at 25°C, the relative standard deviation of 1.2% was the least (5×10^{-5} M HCHO), so the temperature of 25°C was chosen for further experiments.

Effect of pH

In the reaction of formaldehyde with the proposed reagents, the pH of the reagent solution is very important for the reaction efficiency. The effect of pH on the chemiluminescent sensitivity was investigated in the range of 6–11. The biggest CL signal was obtained when pH was about 9.8, so a pH of 9.8 is chosen for further experiments. Therefore, as the pH of the mixture was maintained at 9 by optimizing the concentrations of gallic acid and NaOH, extra chemicals (such as buffers) were not used in this method.

Effect of Mixing Coil Length

The effect of mixing coil length was examined by varying the length from 5 cm to 40. Sharp decrease in the CL intensity is observed when the mixing coil length is above 10 cm. The highest sensitivity at a coil length of 10 cm suggests that the chemiluminescent reaction is going to completion within the cell, resulting in greater peak height. While for coil lengths greater than 10 cm, chemiluminescent reaction is supposed to be completed in the mixing coil, so the CL detector did not detect intensity. Therefore, a reaction coil length of 10 cm was chosen for further experiments.

Effect of Flow Rates

Flow rate is an important parameter in CL detection, because the time taken to transfer the excited product into the flow cell is critical for maximum collection of the emitted light.[32] CL intensity was found to increase with increasing flow rates for both Pump A and Pump B. The increase in CL intensity suggests that the chemiluminescent reaction is going to completion within the cell; at higher flow rates, more light is emitted per unit time, resulting in greater peak height. However, an increase in flow rate has a negative effect on reproducibility. The method could be made more sensitive to HCHO concentration but only at the sacrifice of precision. Therefore, accepting a reasonable compromise, the total flow rate of 2.70 mL min^{-1} was chosen collectively for the sample, 0.05 M gallic acid and 0.2 M NaOH through Pump A, while 0.9 mL min^{-1} was the optimized flow rate for 0.6 M H_2O_2 that flows through Pump B.

Interferences

The influences of foreign species were examined by adding a certain amount of interfering species in 1×10^{-5} M HCHO solution. Tolerable concentrations, defined as the concentrations of foreign species causing less than ±5% relative error, were examined. The tolerance limits of the interfering ions in the determination of 1×10^{-5} M formaldehyde are summarized in Table 2. From Table 2, it can be seen that no interference was observed from Na^+, K^+, and Cl^-, even when they were present in 10,000-fold excess over formaldehyde. CO_3^{2-} did not interfere up to 5000-fold excess over formaldehyde. Ba^{2+}, ClO_4^{2-}, PO_4^{3-}, Fe^{3+}, Ca^{2+}, and NO_3^-, SO_4^{2-}, glyoxal, and ethanol did not affect till 1000-fold excess over

TABLE 2 **Tolerable Concentration of Foreign Species for the Determination of 1×10^{-5} M HCHO**

Foreign species	Tolerable conc. (M)	Fold of foreign species of not causing interference	Relative error (%)
Na^+, Cl^-	1×10^{-1}	10,000	−0.17
K^+	1×10^{-1}	10,000	0.28
CO_3^{2-}	5×10^{-2}	5000	−3.23
Ba^{2+}, Fe^{3+}	1×10^{-2}	1000	−0.14
SO_4^{2-}	1×10^{-2}	1000	−2.40
ClO_4^{2-}, Ca^{2+}	1×10^{-2}	1000	−0.17
PO_4^{3-}, NO_3^{1-}	1×10^{-2}	1000	−4.00
Glyoxal, CH_3CH_2OH	1×10^{-2}	1000	−1.30
Pb^{2+}, CH_3OH, Ni^{2+}	5×10^{-3}	500	1.85
Cd^{2+}, Co^{2+}, CH_3CHO, Benzaldehyde	1×10^{-3}	100	1.90
Cr^{3+}, CH_3COCH_3	1×10^{-3}	100	0.80

TABLE 3 **Determination of Formaldehyde in Different Textile Samples and Comparison with Standard Method**

	Contents of formaldehyde in textile samples (mol L^{-1}) (mean ± SD, n = 3)	
Textile	This technique	Standard method (spectrophotometry)
Cotton	$5.2 \times 10^{-5} \pm 1.1$	$4.5 \times 10^{-5} \pm 2.1$
Cotton	$1.7 \times 10^{-5} \pm 1.3$	$1.65 \times 10^{-5} \pm 1.8$
Cotton	$7.4 \times 10^{-6} \pm 1.4$	$7.35 \times 10^{-6} \pm 2.2$
Wool	$7.0 \times 10^{-6} \pm 0.6$	$6.2 \times 10^{-6} \pm 1.7$
Wool	$5.5 \times 10^{-6} \pm 1.2$	$5.3 \times 10^{-6} \pm 1.9$
Cotton/viscose	$1.2 \times 10^{-5} \pm 0.3$	$9.7 \times 10^{-6} \pm 2.2$
Wool/tyrelene	$4.6 \times 10^{-6} \pm 1.1$	$3.9 \times 10^{-6} \pm 1.1$
Wool/viscose	$4.7 \times 10^{-7} \pm 0.5$	$4.55 \times 10^{-7} \pm 2.1$
Tyrelene	$2.3 \times 10^{-7} \pm 1.2$	$2.29 \times 10^{-7} \pm 1.7$
Nylon	$1.15 \times 10^{-7} \pm 1.3$	$1.13 \times 10^{-7} \pm 2.3$

TABLE 4 **Analytical Results for the Determination of Formaldehyde in Textile**

Sample	HCHO found (mol L^{-1})	HCHO added (mol L^{-1})	HCHO found(mol L^{-1})	Recovery (%)
Cotton	$5.2 \times 10^{-5} \pm 1.1$	2×10^{-5}	$7.0 \times 10^{-5} \pm 0.5$	98
		4.5×10^{-5}	$9.4 \times 10^{-5} \pm 0.7$	97
	$1.9 \times 10^{-5} \pm 0.3$	4×10^{-5}	$6.2 \times 10^{-5} \pm 0.6$	103
Cotton/viscose		3×10^{-5}	$5.1 \times 10^{-5} \pm 0.3$	102
	$7.0 \times 10^{-6} \pm 0.6$	2.0×10^{-6}	$9.1 \times 10^{-6} \pm 0.5$	101
Wool		2.5×10^{-6}	$9.3 \times 10^{-6} \pm 0.8$	98

formaldehyde. Pb^{2+}, CH_3OH, and Ni^{2+} did not interfere up to 500-fold excess over formaldehyde. For CH_3CHO, Cd^{2+}, Cr^{3+}, Co^{2+}, benzaldehdye, and CH_3COCH_3, tolerable limits were 100-fold. Therefore, the proposed method is free from the interference with the determination of formaldehyde in textile samples.

Calibration Graph and Analytical Features

The relation between the concentration of formaldehyde and the CL signal were further studied under the optimal conditions in this work. Under the optimal conditions, a calibration graph can be obtained over the concentration range of 0.20–1×10^{-7} M formaldehyde. The correlation coefficient is 0.9987. Relative standard deviation of 12 replicate injections of 2×10^{-5} M formaldehyde was 1.1%. LOD, calculated as the concentration corresponding to three times of the baseline noise ($S/N = 3$), was 5×10^{-8} M.

Determination of Formaldehyde in Textile Sample

The developed procedure was applied to the determination of formaldehyde in textile samples. Different textile samples (cotton, wool, tyrelene, nylon, etc.) were analyzed as shown in Table 3. Data summarized in Table 3 shows good agreement of results acquired by the proposed FI-CL method with those obtained by the state standard method.[31] Data were evaluated by *t*-test, and calculated *t*-value (2.14) did not exceed the tabulated value (2.26 for degrees of freedom of 9 and the level of significance of 0.05), which shows that results are not significantly different between two methods. It is evident that proposed method is sensitive and fully sufficient for the analysis of formaldehyde in textile samples. The results offer the application of the proposed CL method as a suitable and efficient alternative to other existing methods for the determination of HCHO in textile samples.

The contents of formaldehyde in textiles made from natural products, such as cotton and wool, were higher than in textiles made from synthetic products, such as tyrelene or nylon. This is because the natural-product textiles are wrinkled; more formaldehyde-based resins, such as urea–formaldehyde resin, would be used for crease-resistance treatment.[33]

Recovery tests were performed on the formaldehyde solutions of three different textile samples (cotton, cotton/viscose, wool). The analytical results are listed in Table 4. The recoveries were found to be in the range 97–103%, indicating that the proposed FI-CL system is reproducible and permits determination of formaldehyde in textile samples.

CONCLUSION

To the knowledge of the authors, this combination has not been used thus far for the measurement of formaldehyde in textile materials. The method provides simple, selective (no interference of other co-pollutants), and sensitive determination of trace levels of formaldehyde in textile samples.

The CL flow technique and high-standard electronic equipment made it possible to increase the sensitivity and to shorten the time of analysis to less than 1 min. The FI-CL technique offers several advantages. As the CL reaction is essentially instantaneous, HCHO analysis is not delayed by long reaction times. The pump system maintains uniform continuous flow, and time control is fully automated. Instrumentation is minimal; only a pump system and a photo-multiplier with basic electronic equipment are required. The reagents used are normally found in the laboratory, and their cost is very low. The amount of sample required for the detection of HCHO is less than 0.5 mL, which is far less than other methods. This method is expected to be especially useful for continuous routine determination of HCHO in textiles and offers possibilities of automation.

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