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Determination of ultra-trace formaldehyde in air using ammonium sulfate as derivatization reagent and capillary electrophoresis coupled with on-line electrochemiluminescence detection

Biyang Deng*, Yang Liu, Huihui Yin, Xi Ning, Hua Lu, Li Ye, Quanxiu Xu

Key Laboratory for the Chemistry and Molecular Engineering of Medicinal Resources (Ministry of Education of China), College of Chemistry and Chemical Engineering, Guangxi Normal University, Guilin 541004, China

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ABSTRACT

The reaction between formaldehyde and ammonium ion to produce hexamethylenetetramine is well known. The reaction conditions are very easily controlled in situ and the experiment operation is very simple. However, such derivatization reaction for trace formaldehyde determination using capillary electrophoresis (CE) electrochemiluminescence (ECL) has not been reported before. In this study, the application of ammoniun sulfate as derivatization reagent to in-situ determination of formaldehyde in air was reported. Based on ECL enhancement of tris(2,2′-bipyridyl)ruthenium(II) with hexamethylenetetramine, a novel approach for the determination of ultra-trace formaldehyde in air using CE coupled with on-line ECL of tris(2,2′-bipyridyl)ruthenium(II) has been developed. The parameters affecting separation and detection such as detection potential, concentration and pH of phosphate buffer, and electrokinetic voltage, were investigated. Under the optimal conditions, the linear concentration range of formaldehyde in air was from 0.48 μg/m^3 to 96 mg/m^3 (linear range covering 5 orders of magnitude). The limit of detection (3σ) was 0.15 μg/m^3. The relative standard deviations of peak height and migration time for six consecutive injection of 1 ng/mL formaldehyde derivative were 0.9% and 0.8%, respectively. The recoveries of formaldehyde in air were between 99.3% and 101%.

1. Introduction

Formaldehyde is the most common and the most-known indoor air pollutant [1]. Formaldehyde is a key intermediate in tropospheric photochemistry and is the most abundant carbonyl compound in the ambient atmosphere [2]. Its photolysis products impact HO_x abundance, O_3, and consequently the oxidation rates of other atmospheric gases like NO_x and SO_2. Formaldehyde is an industrial chemical that is widely used to manufacture building materials and numerous household products, as a reagent for adhesives such as urea–formaldehyde and phenol–formaldehyde resins in pressed wood products, as a preservative or disinfectant in paints, coatings or cosmetics, and as a finish in certain paper products and insulation materials. It also is a by-product of tobacco combustion and certain natural processes [3]. Formaldehyde has a great impact on human health, because of its potentially carcinogenic and mutagenic properties, and its capability of forming intermediate and stable species of toxic and phototoxic radicals [4]. The International Agency for Research on Cancer (IARC) classified it as "carcinogenic to humans" in the Group 1 [5].

Due to the influence of formaldehyde to nature and human bodies, methods for the determination of formaldehyde are receiving increased interest in environmental studies, including capillary electrophoresis [5,6], electrochemistry [7–11], high performance liquid chromatography [12–17], gas chromatography [18,19], spectrometry [20–26], chemiluminescence [27], and mass spectrometry [28,29]. However, the detection procedures with HPLC or GC/MS are expensive and unable to provide formaldehyde exposure information on a real-time basis. HPLC with 2,4-dinitrophenylhydrazine (DNPH) as a derivatization agent is one of the most frequently used methods [15]. HPLC procedures, however, are time-consuming and less adaptable to water samples. Some methods are sensitive and selective [2,21], but derivatization reactions needed complex derivatization procedures. For the analysis of formaldehyde in the outdoor environment, spectroscopic techniques are convenient. Nevertheless, the techniques usually require long optical path, which makes these methods unsuitable for routine applications. Other methods are susceptible to interference and suffer from high detection limits, such as photo-acoustic spectroscopy and proton-transfer-reaction mass

* Corresponding author. Tel.: +86 7735845726; fax: +86 7732120958.
E-mail address: dengby16@163.com (B. Deng).

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spectrometry [30]. The acetylacetone (ACAC) method, which is based on the Hantzsch synthesis, is completed within 10 min at 40 °C. The long sampling time of 40 min could be a drawback of the conventional ACAC method [1].

Capillary electrophoresis (CE) is an important and powerful analytical separation tool because of its high efficiency, resolution potential, short analysis time and minimal sample volume. In recent years, there is increasing interest in coupling CE separation with high-sensitive electrochemiluminescence (ECL) detection for alkaloids analysis, drugs and other analytes [31–35]. ECL is the production of light as the result of highly energetic electron transfer reactions between reactants that are electrochemically generated, and has become an important and available technique in analytical chemistry recently [36–45]. The detection sensitivity of amines follows the order tertiary > secondary > primary [46]. Analytes containing a tertiary amine have very high ECL intensity. Among the ECL systems, the detection sensitivity of analytes can usually be enhanced by changing their structures or derivatizing with different reagents into tertiary amines. CE coupled with ECL using $[Ru(bpy)_3]^{2+}$ offers the merits of enhanced sensitivity, improved selectivity, possible micromation and integration, and reduced cost [32].

In this study, one of products that formaldehyde reacts with ammonium ion is hexamethylenetetramine. Hexamethylenetetramine contains four tertiary amines within its molecular structure and strongly enhances the ECL emission of tris(2,2′-bipyridyl)ruthenium(II). The present study combines the powerful separation of CE with the ECL sensitivity of tris(2,2′-bipyridyl)ruthenium(II) to establish a rapid and sensitive method for determination of ultra-trace formaldehyde in air. Due to the sufficient selectivity and sensitivity, the proposed method was directly applied to the determination of formaldehyde in air without requiring any complex sample pretreatment. According to the reaction below, the concentration of formaldehyde was quantified via the increased ECL intensity. The whole experiment allowed real-time monitoring of formaldehyde in air. Analytical procedure was finished within 5 min.

$$4NH_4^+ + 6HCHO \rightleftharpoons (CH_2)_6N_4H^+ + 3H^+ + 6H_2O$$

2. Experimental

2.1. Apparatus

MPI-B CE-ECL system (Xi'an Remex Electronics Co., Ltd., Xi'an China); PHSJ-4A pH meter (Shanghai Precision Science Instrument Co., Ltd., Shanghai, China); SK3200H Ultrasonic Cleaner (Shanghai Kudos Ultrasonics Instrument Co., Ltd., Shanghai, China); Rotameter (Jiangyin Keda Instrument Factory, Jiangsu, China); Common commercially available pump (Zhongshan City Electric Co., Ltd., Zhongshan, China); A working electrode (platinum disk, 300 μm in diameter), a counter electrode (platinum wire), and an Ag/AgCl reference electrode were used in a conventional three-electrode system to generate $[Ru(bpy)_3]^{3+}$; A 50 cm uncoated silica capillary (75 μm i.d., 375 μm o.d.) (Yongnian Optical Fiber Co., Hebei, China).

2.2. Reagents

All chemicals used in this investigation were of analytical grade and double-distilled water (DDW) was used throughout. Tris(2,2′-bipyridyl)ruthenium(II) chloride hexahydrate was purchased from Alfa Aesar (A Johnson Matthey Company, Ward Hill, MA, USA) and used without further purification. Hexamethylenetetramine was offered by Hunan Chemical Reagent Factory (Hunan, China). Ammonium sulfate was obtained from Guangzhou Chemical Reagent Factory (Guangzhou, China). All stock solutions were prepared with DDW and stored in a refrigerator at 4 °C. Prior to use, the required working standard solutions were freshly prepared by precise dilution of stock solution with DDW. A phosphate buffer (Na_2HPO_4/NaH_2PO_4) was used (Hunan Reagent Company, Hunan, China). Before CE analysis, the required sample solution and phosphate buffer solution (PBS) were filtered through 0.45 μm membrane filters (Shanghai Xinya Purification Material Factory, Shanghai, China).

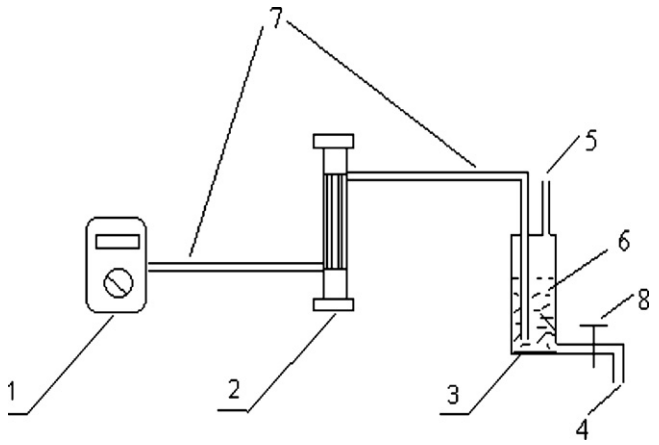

Fig. 1. Sampling equipment. 1 for pump; 2 for rotameter; 3 for reservoir bottle (1.6 cm inner diameter × 3.5 cm height); 4 for solution exit; 5 for air exit and solution entrance (located on top of the reservoir bottle); 6 for ammonium sulfate solution (0.5 mg/mL); 7 for pipe (2.0 mm inner diameter); 8 for piston with a hole.

2.3. Analytical procedure

A 75 μm i.d. 50 cm uncoated silica capillary was used as the separation capillary. The working electrode was polished with alumina powder (0.3 μm) every two weeks, and rinsed with DDW in an ultrasonic cleaner for 10 min, and then put in the cell positioned at the capillary outlet. The capillary was rinsed with 1 M NaOH for 30 min before the first use. During the entire experiment, it was necessary to rinse with 0.1 M NaOH for 10 min, DDW for 5 min, and then with corresponding running buffer for 10 min before use every day and in between each run. The axes of the working electrode and the separation capillary were aligned by setting the distance at 200 μm from each other with the aid of a microscope. A 300 μL solution of $[Ru(bpy)_3]^{2+}$ (5 mM) in PBS (50 mM, pH 8.5) was placed in the ECL detection cell for ECL measurement, 10 mM phosphate (pH 7.5) was used as running buffer. Fresh $[Ru(bpy)_3]^{2+}$-phosphate solution was replaced every 3 h in order to obtain good reproducibility. During the experiment, electrokinetic injection was used for sample introduction into the electrophoresis system at 12 kV for 10 s. The separation voltage was 15 kV. The photomultiplier tube was biased at 800 V, and the electropherogram was recorded.

2.4. Derivatization of formaldehyde

The stock solution (1 mg/mL) of ammoniun sulfate was prepared as the absorbing solution in DDW, and stored at 4 °C. Formaldehyde was absorbed into 3 mL of 0.5 mg/mL ammoniun sulfate solution containing 0.1 M HCl. The final solution was used in real-time.

2.5. Sampling equipment

The sample collection equipment is shown in Fig. 1. A branch pipe which contained absorption solution of ammonium sulfate was connected with the rotameter exit. The rotameter inlet was coupled with the air pump exit. The temperature and atmospheric

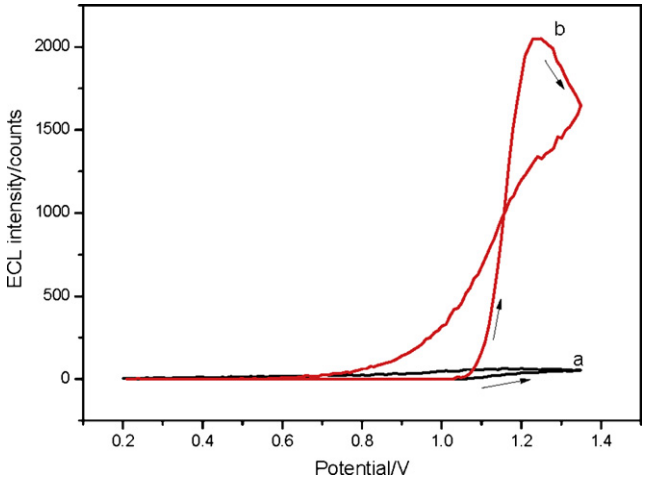

Fig. 2. The profile of electrogenerated chemiluminescence (ECL). (a) 5.0 mM $[Ru(bpy)_3]^{2+}$ + 50 mM PBS (pH 7.5), scan rate: 100 mV/s; (b) 5.0 mM $[Ru(bpy)_3]^{2+}$ + 50 mM phosphate buffer (pH 7.5) + 1.0 μg/mL hexamethylenetetramine, scan rate: 100 mV/s.

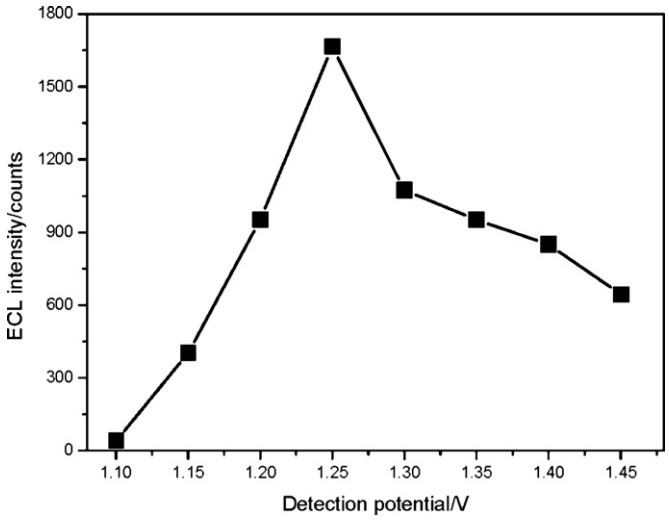

Fig. 3. Optimizing the detection potential. Detection conditions: sample: 1.0 μg/mL hexamethylenetetramine; electrokinetic injection, 10 kV × 10 s; separation buffer, 10 mM pH 7.5 PBS; separation voltage, 15 kV; in ECL cell, 5 mM $[Ru(bpy)_3]^{2+}$, 50 mM pH 7.5 phosphate buffer.

pressure at sampling location were 298 K and 101.3 kPa, respectively. The samples obtained were analyzed at room temperature.

2.6. Sample solution preparation

The indoor air samples were collected from new building of Guangxi Normal University campus. The outdoor air samples were collected from Seven Star Park and Guilin Sanjin Pharmaceutical Company in Guilin, China. The 3 mL of 0.5 mg/mL ammonium sulfate containing 0.1 M HCl was filled into the reservoir bottle. The air flow rate was set at 0.1 L/min. The sampling time was 2 min. After being absorbed and derivatized, all sample solutions were filtered with 0.45 μm membrane filters. The filtrates were transferred into a 1.5 mL polyethylene tube, and the final sample solutions were obtained.

2.7. Sample stability

Different storage conditions were investigated. After formaldehyde was derivatized using ammonium sulfate, samples of formaldehyde derivative were stored for 1 h with one batch at room temperature and another batch for 10 days. These samples were analyzed by CE-ECL. The differences among samples are negligible (all within instrument specifications). The results also show that the formaldehyde derivative was stable.

3. Results and discussion

3.1. ECL behavior of hexamethylenetetramine

Cyclic voltammetry and the corresponding electrochemiluminescence (ECL) emission were used to characterize the electrochemical and ECL behavior of $[Ru(bpy)_3]^{2+}$/hexamethylenetetramine. The ECL behavior of $[Ru(bpy)_3]^{2+}$/hexamethylenetetramine has been studied by starting at approximately 0.20 V and ending at 1.4 V. There was an obvious rise at about 1.2 V in the presence of 1.0 μg/mL hexamethylenetetramine (Fig. 2). The ECL intensity of hexamethylenetetramine in PBS is distinctly different from the ECL intensity of blank PBS.

3.2. Optimization of applied potential

Electrochemiluminescence intensity is dependent on the rate of the light-emitting chemical reaction between the analyte and ruthenium species, which is in turn dependent on the potential applied to the electrode. The relationship between ECL intensity and the applied potential in the range of 1.10–1.45 V was investigated in detail (Fig. 3). The ECL intensity increased accordingly, and reached a maximum value at 1.25 V. When the potential exceeded 1.25 V, the ECL intensity decreased markedly. Hence, in the following experiment, the detection potential was kept at 1.25 V.

3.3. Optimization of concentration and pH of PBS in ECL cell

One of the most important detection parameters is the optimal concentration of $[Ru(bpy)_3]^{2+}$ added in the detection cell. A low $[Ru(bpy)_3]^{2+}$ concentration leads to a low background noise, however, the ECL intensity and the sensitivity were simultaneously low. High sensitivity was obtained with the increase of $[Ru(bpy)_3]^{2+}$ concentration, and the background noise increased simultaneously. 5 mM $[Ru(bpy)_3]^{2+}$ was chosen as a compromise in the experiment with respect of the high S/N value and the high ECL efficiency. After 3 h of operation, the $[Ru(bpy)_3]^{2+}$ solution was restored to eliminate the $[Ru(bpy)_3]^{2+}$ concentration change and maintain good reproducibility.

The detection buffer concentration also plays an important role in ECL intensity. Its optimal concentration has been well studied in previous literature [31], so the detection buffer concentration was fixed at 50 mM.

Since the ECL reaction of $[Ru(bpy)_3]^{2+}$ with alkylamine depends on the buffer pH value to a great extent, the ECL intensity as a function of the buffer pH value in the range of 6.0–10.5 was investigated (Fig. 4a). Maximum ECL intensity was displayed at pH 8.5 and then the ECL intensity decreased slightly. Thus, the optimized pH value was set at 8.5 in this study.

3.4. Optimization of running buffer

The pH of the running buffer affected the ECL intensity directly because the reaction is pH dependant. The pH value strongly influenced the electroosmotic flow (EOF), the analyte ionization, and the migration time. When the pH varies, the state of the

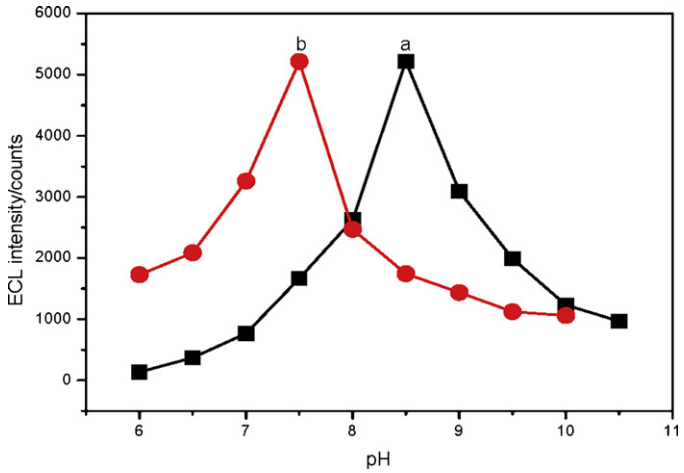

Fig. 4. Effects of pH of PBS in ECL cell (a) and PBS in capillary (b) on ECL intensity. Detection conditions: (a) detection potential, 1.25 V; other conditions as in Fig. 3. (b) pH 8.5 PBS in ECL cell; other conditions as in (a).

ionization of analytes in the sample zone and their effective charges will change correspondingly. The effect of pH on the ECL intensity of hexamethylenetetramine was investigated in the range of pH 6.0–10.0 using phosphate as the running buffer (Fig. 4b). The results showed that the ECL intensity increased with increasing pH from 6.0 to 7.5, and the maximum intensity was obtained at a slightly alkaline condition (pH 7.5), while higher than 7.5, the ECL intensity decreased. This was because the hexamethylenetetramine was positively charged and its protonated degree diminished with the increase of pH value. In addition, OH^- ions were assumed to be at considerable concentration level, which caused the competitive reaction between $[Ru(bpy)_3]^{3+}$ and OH^- ions at high pH value. It resulted in the reduced availability of $[Ru(bpy)_3]^{3+}$. Therefore, the pH of 7.5 was chosen for further experiments.

The effect of the running buffer concentration on ECL intensity was also studied. As illustrated in Fig. 5, and when the buffer concentration was adjusted from 5 to 20 mM, the highest ECL signal was obtained at 10 mM. It was also found that with the increase of buffer concentration, the migration time of hexamethylenetetramine increased, and the baseline became unstable. Therefore, 10 mM of the buffer concentration was chosen as the optimum condition.

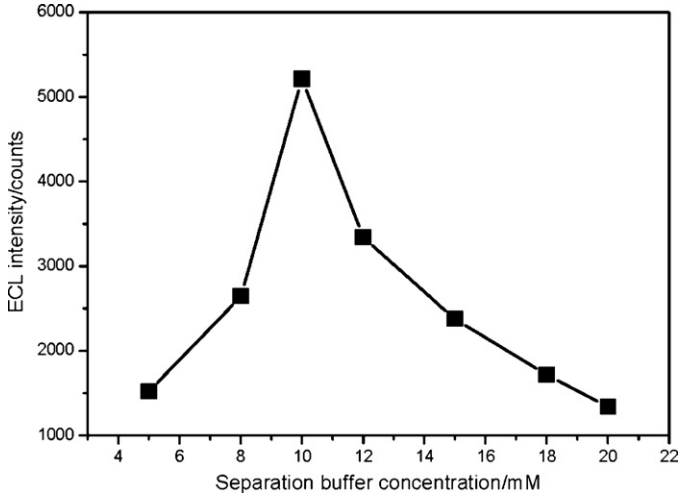

Fig. 5. Optimizing the separation buffer concentration. Detection conditions: separation buffer of pH 7.5 PBS; other conditions as in Fig. 4b.

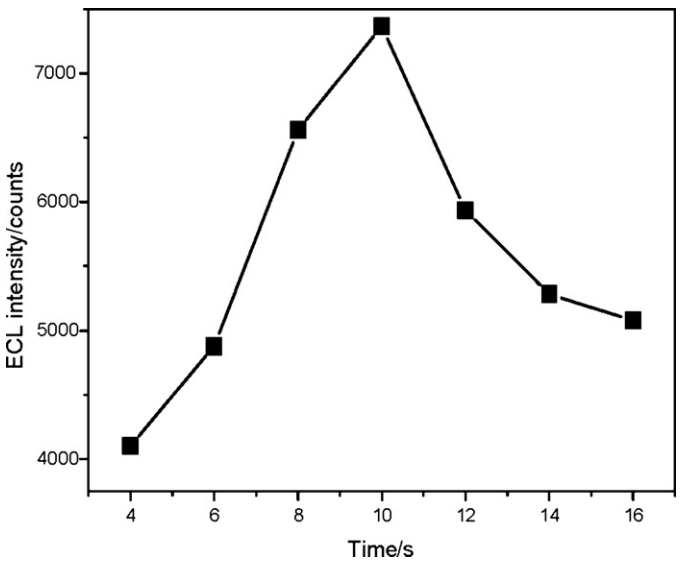

Fig. 6. Optimizing the injection time. Detection conditions: separation buffer of 10 mM PBS; separation voltage of 15 kV; injection voltage of 12 kV; other conditions as in Fig. 5.

3.5. Optimization of separation voltage and injection parameters

Separation voltage simultaneously impacted on the ECL intensity and migration speed. The study on the influence of separation voltage was carried out from 6 to 20 kV. When increasing the separation voltage, the ECL intensity was enhanced and the analysis time was shortened. When the separation voltage was higher than 15 kV, the baseline noise was enhanced, which was attributed to the increase of Joule heating in the capillary. The strong flow of effluent from the capillary may reduce the concentration of $[Ru(bpy)_3]^{2+}$ on the electrode surface and the efficiency of light emission. After comprehensive consideration for the ECL intensity and migration time, 15 kV was selected as the optimized separation voltage for further experiments.

The effect of injection voltage from 4 to 18 kV on the ECL intensity was investigated at the injection time of 10 s. Fig. 6 shows the ECL intensity was influenced by the injection time ranging from 4 to 16 s at the injection voltage of 12 kV. In general, ECL intensity increased with an increase in injection voltage and injection time. However, both the repeatability and the resolution became worse when an excessive voltage or sample volume was introduced. It can be seen in Fig. 6 that when the injection voltage was lower and the injection time was shortened, it was difficult to obtain a favorable ECL intensity because only little analyte would be in the detection cell. It was also found that the increasing injection voltage and injection time improved the ECL intensity until 12 kV × 10 s. The probable reason is that the higher the injection voltage and the longer injection time, the more analyte got into the reservoir, which resulted in higher ECL intensity. However, the analyte could not reach the electrode surface immediately and diffuse into the solution, and causing the peak profile become worse and the ECL intensity decreased. So as a compromise of the high ECL intensity and improved capillary efficiency, the injection parameters of 10 s at 12 kV was chosen.

3.6. Analytical figures of merit

Under optimized CE-ECL conditions, corresponding linear concentration of formaldehyde in air ranged from 0.48 μg/m^3 to 96 mg/m^3 with correlation coefficient of 0.9996. The linear range covering five orders of magnitude was not obtained before. The

Table 1
Effect of potential interfering substances.

Coexisting substance	Concentration (μg/mL)	Relative error of formaldehyde ECL intensity (%)
Acetaldehyde	200	<1
Propionaldehyde	200	<1
Acetone	200	<1
Methanol	200	1.5
Ethanol	200	1.6
Benzene	200	<1
Toluene	200	1.4
Carbon dioxide	200	2.1
Sulfur dioxide	20	3.8
Hydrogen sulfide	10	4.3
Nitrogen dioxide	200	4.1

limit of detection for formaldehyde (3σ) in air was 0.15 μg/m^3. According to the result compared with electrochemistry, high performance liquid chromatography, gas chromatography, spectrometry, chemiluminescence and mass spectrometry, the limit of detection using the method was better than those previously reported [6–24,26–30] but higher than that obtained using fluorescence energy transfer technique [25]. The relative standard deviations of peak height and migration time for six consecutive injection of 1 ng/mL formaldehyde derivative were 0.9% and 0.8%, respectively. The calibration was repeated every day within 6 days. The R.S.D. of the slopes and intercepts for 6 calibrations was less than 1.6%. The proposed method used simple and inexpensive equipment, and has a wide linear range, good reproducibility, small consumption of reagents and samples, and high sensitivity. The excellent performance of the present method is suitable for determination of formaldehyde in air.

3.7. Selectivity of method

To study the selectivity of the proposed method, the effect of various potential components (acetaldehyde, propionaldehyde, acetone, methanol, ethanol, benzene, toluene, carbon dioxide, sulfur dioxide, hydrogen sulfide, and nitrogen dioxide) concurrently present in air on the determination of formaldehyde by the proposed method was investigated. The interference tests of sulfur dioxide, hydrogen sulfide, carbon dioxide and nitrogen dioxide were replaced by sodium sulfite, sodium sulfide, sodium carbonate and sodium nitrite, respectively. To examine the response for formaldehyde in the presence of another gas, the mixture containing 0.2 μg/mL of formaldehyde and 20 μg/mL of sulfur dioxide (replaced by 39.4 μg/mL sodium sulfite) was studied. As a result, the relative error of the ECL intensities of containing sulfur dioxide and not containing sulfur dioxide was less than 4%. Our results showed that sodium sulfite did not interfere the determination of formaldehyde in 0.1 M HCl at a hundred times the formaldehyde concentration. The formaldehyde content was successfully determined under an excess amount of sulfur dioxide. The effect of coexisting substances for a formaldehyde concentration of 0.2 μg/mL on the response of formaldehyde is shown in Table 1. The results show that most of the coexisting gases can be allowed at very high concentrations. Therefore, the present method has good selectivity and is free from interferences in routine analysis.

3.8. Application to air samples

The proposed method was applied to the determination of formaldehyde in local indoor and outdoor air samples under the optimal conditions. Electropherograms are illustrated in Fig. 7. The concentrations of formaldehyde in the indoor air of new building (located at Guangxi Normal University campus) were 18.2 and

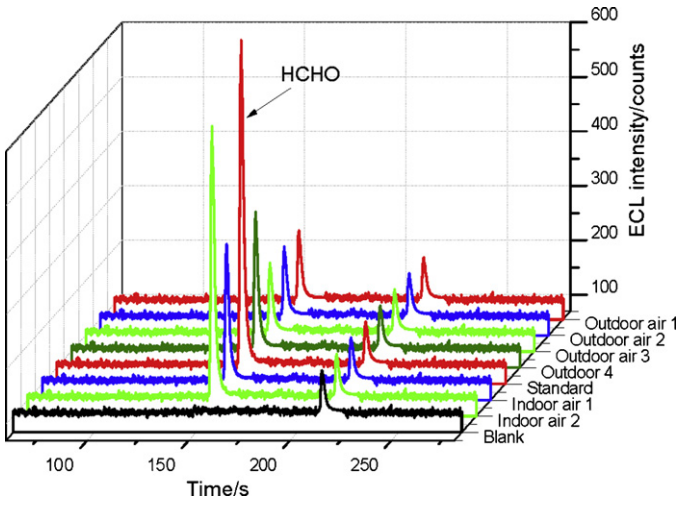

Fig. 7. CE-ECL electropherograms of blank sample, formaldehyde standard of 50 μg/m^3, and six air samples. Detection conditions were shown in Section 2.3.

40.6 μg/m^3. The concentrations of formaldehyde in the outdoor air of Seven Star Park and Guilin Sanjin Pharmaceutical Company were from 7.6 to 21.3 μg/m^3. For the recovery test, a known amount of formaldehyde solution (100 ng/mL) with 0.1 mL was injected into the bag contained air, heated to aid evaporation, and then kept for 1 h to reach equilibrium. Then the gas was drawn out using sampling device. By comparison of the measured and theoretical formaldehyde concentrations, we could determine the recovery as mentioned above (in Section 2.3). The recoveries of formaldehyde in air ranged from 99.3% to 101% ($n = 5$). The relative standard deviation of ECL peak intensity was less than 1.2%.

4. Conclusion

A novel CE-ECL method has been successfully developed to determine formaldehyde concentration in air. The formaldehyde in air was collected by $(NH_4)_2SO_4$-containing system and derivatized into hexamethylenetetramine determined by CE-ECL. The developed CE-ECL method had excellent performance with wide linear range, high sensitivity, and good reproducibility. The requirement of small sampling volume and short sampling time would enable temporal or local monitoring of formaldehyde in air. The potential application of this method in other samples such as food and environmental water is also possible.

Acknowledgements

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