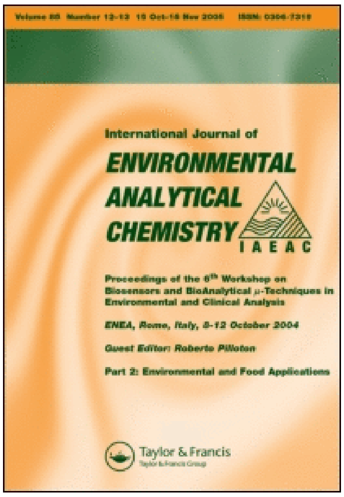

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On-Line Monitoring of Formaldehyde In Water and Air Using Chemiluminescence Detection

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ON-LINE MONITORING OF FORMALDEHYDE IN WATER AND AIR USING CHEMILUMINESCENCE DETECTION

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A rapid and sensitive chemiluminescence flow sensor for the determination of formaldehyde was proposed in this article. The analytical reagents involved in chemiluminescence (CL) reaction, luminol and KIO_4, were both immobilized on an anion-exchange column. The CL signal produced by the reaction between luminol and KIO_4, which were eluted from the column through water injection, was decreased in the presence of formaldehyde. Formaldehyde was sensed by measuring the decrement of CL intensity, which was observed linear over the logarithm of formaldehyde concentration range of 5.0–1000.0 $\mathrm{ng\,mL^{-1}}$, and the limit of detection is 1.8 $\mathrm{ng\,mL^{-1}}$ (3σ). At a flow rate of 2.0 $\mathrm{mL\,min^{-1}}$, including sampling and washing, could be performed in 0.5 min with a relative standard deviation of less than 3.0%. The flow sensor offered reagentless procedures and remarkable stability in determination of formaldehyde, and could be easily re-used over 80 h. The proposed flow microsensor was applied successfully in the determination of formaldehyde in artificial water samples and air.

Keywords: Formaldehyde; Flow sensor; Chemiluminescence; Air; Water

INTRODUCTION

Formaldehyde, a colourless, pungent-smelling gas, is an important chemical used widely by industry to manufacture building materials and numerous household products. It is also a byproduct of combustion and certain other natural processes. Thus, it may be present in substantial concentrations both indoors and outdoors.

Sources of formaldehyde in the home include cigarette smoke, gas combustion, and the use of disinfectants, fungicides, germicides, cosmetics and preservative agent [1,2]. The most significant sources of formaldehyde are likely to be pressed-wood products made using adhesives that contain urea–formaldehyde (UF) resins or phenol–formaldehyde (PF) resin. Formaldehyde in atmospheric air is mainly derived from the reaction between hydrocarbons and nitrogen oxide [3] and exhaust fumes from gasoline vehicles [4].

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When present in the air at levels about 0.1 ppm, formaldehyde can cause watery eyes, burning sensations in the eyes, nose and throat, nausea, coughing, chest tightness, wheezing, skin rashes, and allergic relations [5]. High concentrations may trigger attacks in people with asthma. It has also been shown to cause cancer in animals and may cause cancer in humans [6].

Continuing concern about the environment and human health has motivated the reaches of many different methods for determination of formaldehyde in environment samples. Various types of electrochemical methods were applied as convenient ways for the determination of formaldehyde [7–13], which involved polarography [7], potentiometry [8] and voltammetry [9–12]. One of the most widely used electrochemical methods is voltammetry, which has been directly used to monitor the variation in formaldehyde along a highway. As well, a biosensor [13] and an automated flow-through system have been developed by using a microchannel fused-silica cell in voltammetry and an Os(bisbipyridyl)2-poly(vinylpyridine) modified screen-printed electrode immobilized with formaldehyde dehydrogenase, respectively.

However, chromatographic methods are of more use in complicated mixtures for the identification of formaldehyde. HPLC [14–24] combined with sampling procedures has been widely applied to determine formaldehyde in indoor and outdoor air samples, human teeth and urine and automotive exhaust gas. Other chromatographic methods, including TLC [25–27], GC [28,29] and capillary electrophoresis [30,31], have contributed in assays of formaldehyde in tooth tissue, gaseous samples and aldehyde mixtures.

Many methods for determination of formaldehyde in air were based on direct spectrometric [32–37] and fluorimetric measurements [38,39]. Other methods also used include airborne tunable diode laser measurements [40], MS [41–43], as well chemometrics strategies [44] and sequential response surface methodology [45] for optimization purposes. In an environmental application, the methods reported put more efforts on the development of the method offering instrumental simplicity, sensitive detection and on-line or real-time procedure.

Chemiluminescence (CL) combined with a flow injection (FI) system is an attractive analytical method for its sensitivity and rapid detection, and offers possibilities for on-line or real-time determination. In the case of FI-CL, however, large quantities of analytical reagents must be prepared and delivered continuously into the reaction zones. This is undesirable, not only for operational convenience and simplicity of the detection device, but also for cost, environmental and resource considerations. A less expensive alternative that can provide a fast and simple quantitative measurement has been employed with CL reagents in an immobilized format in our previous work [46,47].

It is well known that the fast oxidation reaction between luminol and periodate in alkaline medium produces a strong CL signal. In this article, a simple CL sensor for formaldehyde combined with FI was presented. The CL flow sensor for formaldehyde was based on the inhibition of CL intensity generated by the luminol–periodate system, and the CL reagents, luminol and periodate, used in this sensor, were both immobilized on anion-exchange resin. Through injection of 200 μL of water, the reagents on the anion-exchange column are eluted from the resins and in presence of formaldehyde the CL reaction is inhibited, by which formaldehyde can be detected. The concentration of formaldehyde was quantified *via* the decreased CL intensity generated by the eluted CL reagents. The decreased response is linear over the logarithm of formaldehyde concentration range 5.0–1000.0 ng mL^{-1} with a relative standard deviation less than 3.0%. The method was applied successfully to the determination of formaldehyde in water and air sample.

EXPERIMENTAL

Reagents

All chemicals used were of analytical-reagent grade. Doubly distilled water was used throughout. Luminol (Fluka, Biochemika) was obtained from Xi'an Medicine Purchasing and Supply Station, China. Potassium periodate was purchased from Xi'an Chemical Reagent Plant.

Formaldehyde for calibration was prepared from formaldehyde (37%, Xi'an Chemical Reagent Plant) stored at 4°C. Luminol was used as supplied to prepare a 0.25 mol stock standard solution in 0.5 mol L^{-1} NaOH in a 1000 mL calibrated flask. A 0.04 mol L^{-1} stock standard solution of KIO_4 was made by dissolving the solid in distilled water and diluting to 250 mL in a calibrated flask.

Preparation of Resin with Immobilized Reagents

Amberlyst (from Rohm and Haas Co.) A-27 (2.0 g) was shaken with 50 mL 0.25 mol L^{-1} luminol or 0.04 mol L^{-1} potassium periodate for 12 h, then the resin was filtered, washed with doubly distillled water and dry-stored. The most convenient method to determine the amounts of luminol and potassium periodate immobilized was to measure the losses of these reagents from the immobilization solutions. The concentration was detected at 360 nm for luminol and at 225 nm for potassium periodate by UV–Vis. In the proposed method, the amounts of luminol and potassium periodate immobilized were 1.99 ($\pm$0.01, $n=3$) mmol g^{-1} and 1.01 ($\pm$0.02, $n=3$) mmol g^{-1} resin, respectively.

Apparatus of Flow Injection System

The flow injection (FI) system used in this work is shown in Fig. 1. A peristaltic pump (Shanghai meter electromotor plant, Model ND-15, 15 rev/min) was used to generate the flows. PTFE tubing (1 mm i.d.) was used in the flow system. The anion-exchange resins containing immobilized luminol (0.05 g) and potassium periodate (0.10 g) were

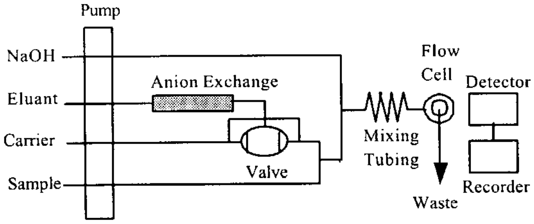

FIGURE 1 Schematic of the FI system for formaldehyde determination.

mixed together and packed into a glass column (i.d. 3 mm and total volume of about 0.5 mL) and plugged with glass wool at both ends to prevent the resins from leaking. 100 µL of eluant was injected by a six-way valve. Before reaching the flow cell, the streams of luminol, potassium periodate, sodium hydroxide and analyte were combined in mixing tube (50 mm in length). The CL emission cell is a twisty glass tube (1 mm i.d., 15 cm length) in order to produce a large surface area exposed to the adjacent photomultiplier tube (PMT) (HAMAMATSU, Model IP28). Extreme precautions were taken to ensure that the sample compartment and PMT were light-tight. The CL signal produced in flow was detected without wavelength discrimination, and the PMT output was amplified and quantified by a luminosity meter (Northwest Non-Ferrous Geology Institute of China, Model GD-1) connected to a recorder (Shanghai Dahua Instrument and Meter Plant, Model XWT-206).

Apparatus of Absorption System

A schematic diagram of the instrument used as absorption system is shown in Fig. 2. The air stream consisting of house air was artificially contaminated by purging a small bottle containing formaldehyde. The air stream flow at a rate of 200–300 mL min^{-1} for 3–5 min. The concentration of formaldehyde in the air stream can be determined by the temperature of the water bath around the bottle. The absorbent solution was pure H_2O.

Procedures

The carrier water and the solutions (NaOH, sample and eluant) were propelled at a constant flow rate on each flow line. The pump was started to wash the whole flow system until a stable baseline was recorded. Then 100 µL of eluant solution were injected into the carrier stream, luminol and periodate were eluted quantitatively, which was then mixed with the sample stream, the mixed solution was delivered to the CL cell, and the peak height of the CL signal was detected with the PMT and the luminometer. The concentration of sample was quantified by decreased CL intensity, $\Delta I = I_o - I_s$ where I_o and I_s are CL signals in the absence and in the presence of formaldehyde, respectively.

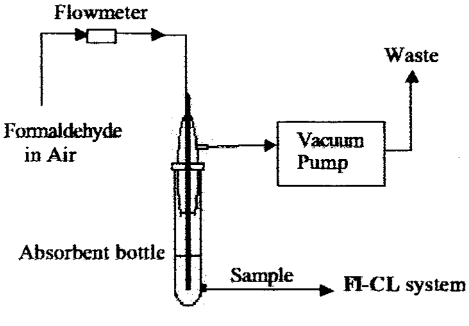

FIGURE 2 Manifold for the formaldehyde absorption system.

RESULTS AND DISCUSSION

The CL Intensity–Time Profile

Before carrying out the FI method, the batch method for the CL profiles was used. Without any special eluant, the mixture of luminol and periodate rinsed by water gave out an evident CL signal. As Fig. 3 shows, the CL intensity reached a maximum 10 s after injection, and then died within 25 s. On joining of the sample into the above mixing solution, a decreased CL signal was recorded. The peak heights of the CL emission were proportional to the logarithm of formaldehyde concentration.

Designation for the FI-CL System

The assay could be carried out by a continuous-flow mode in two different manifolds. To evaluate the different designation for the FI-CL system, Na_3PO_4 ($5.0 \times 10^{-5}\,mol\,L^{-1}$) was proposed as eluant instead of water, which was proved to be more suitable in the following section, because there would be no obvious CL intensity *vs* background when water was used as the eluant in the manifold illustrated in Fig. 3. Through injection of 100 μL eluant, the reagents on the anion-exchange resin column were eluted and in the presence of formaldehyde, the CL intensity decreased, and this decrease was recorded. It was found that while the column with immobilized reagents was put in front of or behind the valve, two significantly different results were observed. The whole analysis process, including sampling and washing, could be accomplished in 0.5 min as the column was put in front of the valve (namely Fig. 1 manifold), whereas it must take more than 2.0 min as the column was put behind the valve as shown in Fig. 4 and also the manifold in Fig. 1 gave better precision. Therefore, the manifold depicted in Fig. 1 was chosen for the subsequent work.

Selection of Eluant

100 μL of different eluants were injected through the resin column and released different amounts of luminol and periodate, thus producing the CL emission. The results are

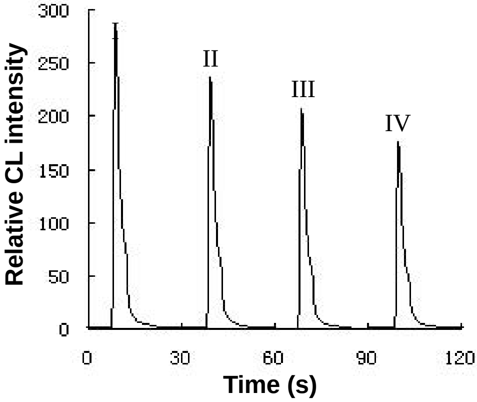

FIGURE 3 CL time profile in the batch system. I: CL intensity in the absence of formaldehyde; II: CL intensity in the presence of formaldehyde ($30.0\,ng\,mL^{-1}$); III: CL intensity in the presence of formaldehyde ($100.0\,ng\,mL^{-1}$); IV: CL intensity in the presence of formaldehyde ($700.0\,ng\,mL^{-1}$).

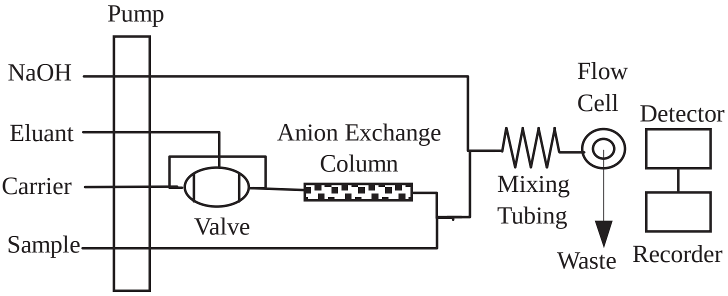

FIGURE 4 Schematic diagram of the flow-injection system for formaldehyde determination.

TABLE I Character of eluants for formaldehyde determination

Type of CL intensity	*Relative CL intensity*[a]				
	H_2O	$NaCl$	Na_2CO_3	Na_2SO_4	Na_3PO_4
I	232	362	127	498	411
II	182	291	104	389	220
III	50	71	23	109	91

[a] The concentration of each eluant was 1.0×10^{-4} mol L^{-1}. I: CL intensity in the absence of formaldehyde. II: CL intensity in the presence of 50 ng/mL^{-1} formaldehyde. III: The decrease of CL intensity.

shown in Table I. It was found that sodium sulfate gives a maximum CL emission while sodium carbonate shows some inhibitive effects on the CL reaction. Nevertheless, it was observed that a continuous flow of eluant through the column results in a rather short lifetime of the sensor down to only a few hours. It was shown that the immobilized luminol and periodate anions on the anion exchange resin undergo dissociation with water, thus releasing trace amounts of luminol and periodate from the column, and the decrease of formaldehyde CL signal could be easily observed. In this case, the column could be used over 80 h. As a compromise between higher CL intensity and longer lifetime of the column (discussed in the Applications section), water was used as eluant in subsequent work.

Effect of pH on CL and Sensor Lifetime

The best pH of eluant (water) on the performance of the system was evaluated. It was found that along with the increase of pH in eluant, the CL intensity decreased while the lifetime of the sensor decreased considerably (Fig. 5). This phenomenon is probably because the quantities of hydroxide ions in the eluant were increasing. pH 6.5 was then chosen as a compromise between lifetime and a sufficient CL intensity. In this case, the column with immobilized CL reagents could be used more than 80 h in a continuous-injection system.

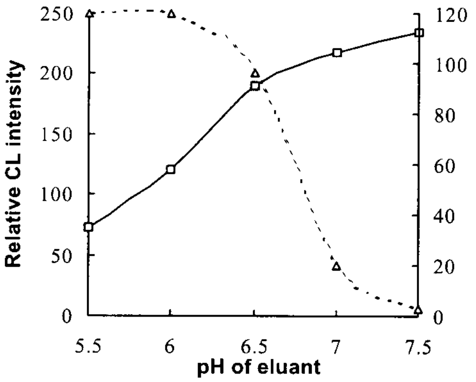

FIGURE 5 Effect of eluant pH on CL intensity (—□—) and sensor lifetime (—△—).

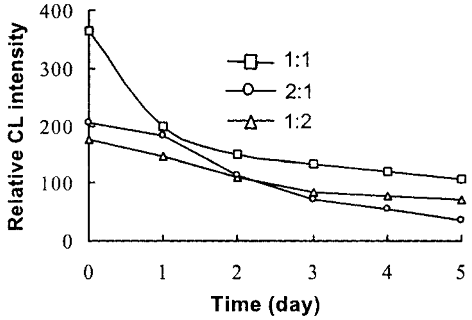

FIGURE 6 Effect of molar ratio on CL intensity and sensor lifetime.

Effect of the Molar Ratio of Immobilized Luminol and Periodate

To examine the influence of the mixing ratio, resins (0.15 g) with different mixing ratios were packed into a column with the same internal diameter and volume. By the injection of water at a fixed volume of 100 μL different amounts of luminol and periodate were eluated from the resins and emitted CL signals with different intensity. As Fig. 6 shows, the CL intensity dropped drastically from the start to the next day, then it decreased slowly. The most stable CL signal was found with a molar ratio of 1 : 2 (luminol to periodate) and a middling CL intensity is in favor of measuring an inhibitive effect of formaldehyde on CL reaction.

Effect of NaOH Concentration

It was found that luminol reacts with periodate and emits CL signals only in an alkaline medium. As Fig. 7 shows, an NaOH concentration less than 0.05 M lead to an apparent decrease in ΔI. The maximum intensity was found with 0.1 M NaOH. While concentration of NaOH is higher than 0.2 M, there is a scattering effect in flow cells due to the discrepancy between refractive index of various components. Thus 0.1 M NaOH was selected as an optimal condition.

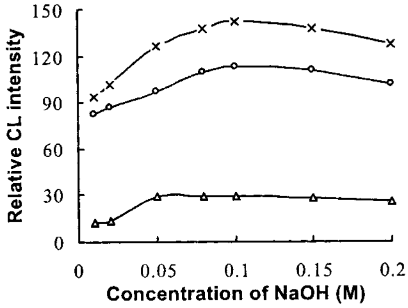

FIGURE 7 Effect of concentration of NaOH on CL intensity (—o—), in the presence of formaldehyde (I_s); —×—, in the absence of formaldehyde (I_o); —△—, decrease in CL intensity ($\triangle I$).

Effect of Flow Rate and the Length of Mixing Tubing

The CL signal was also dependent on the flow rate of carrier and eluant. The signal-to-noise rate decreased at a higher flow rate because the higher flow rate would impact the rate of contact of sample molecules with the ion-exchange resin. The lower flow rate caused broadening of the peak and slowing down of the sampling rates. Nevertheless, the high flow rate could lead to an unstable baseline and a shortening of the sensor lifetime. A rate of 2.0 mL min^{-1} was then chosen as a compromise between good precision and lower reagent consumption.

The length of the mixing tubing was also adjusted to yield maximum light emission in the cell. It was found that a 5.0 cm of mixing tubing afforded the best results as regards sensitivity and reproducibility.

Performance of the Sensor for Formaldehyde Measurements

Under the above optimum conditions, the linearity of formaldehyde was tested by determining a series of standard solutions with the flow sensor. The inhibited CL intensity was found to be proportional with the logarithm of formaldehyde concentration. As Fig. 8 shows, the linear range is from 5.0 ng mL^{-1} to 1000.0 ng mL^{-1} and the regression equation is:

$$\Delta I = 46.32\,\mathrm{Log}\,C_{\mathrm{formaldehyde}} - 54.512, \quad r^2 = 0.9971.$$

The relative standard deviation of five determinations were 1.99, 1.74 and 1.04% with formaldehyde concentration of 7.0, 70.0 and 700.0 ng mL^{-1}, respectively. The limit of detection was 1.8 ng mL^{-1}. At a flow rate of 2.0 mL min^{-1}, the determination of analyte could be performed in 0.5 min, including sampling and washing, giving a throughput of about 100 times per hour with a relative standard deviation of less than 3.0%.

Interference Studies

The effect of foreign ions was tested by analyzing a standard solution of formaldehyde (20.0 ng mL^{-1}) to which increasing amounts of interfering ions were added. The tolerable concentration ratios with respect to 20.0 ng mL^{-1} formaldehyde for interference at 3% level were over 900 for Cl^-, NO_3^-, Ac^-, I^-, SO_4^{2-}, PO_4^{3-}, $Cr_2O_7^{2-}$, borate, oxalate, urea, and 700 for NH_4^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Zn^{2+}, Ni^{2+}, Mn^{2+}, Cr^{3+}, and 500 for methanol, ethanol, and CO_3^{2-}, and 8 for Cu^{2+}, resorcinol, and 1 for hydroquinone and

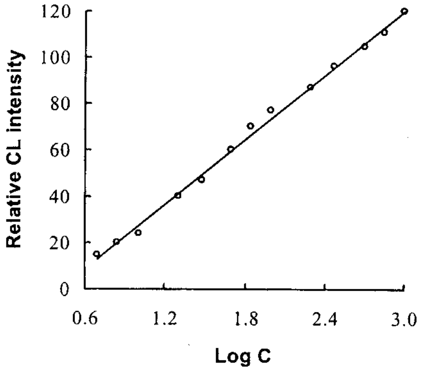

FIGURE 8 I *vs.* logarithm of formaldehyde concentration (5.0–1000.0 ng mL^{-1}).

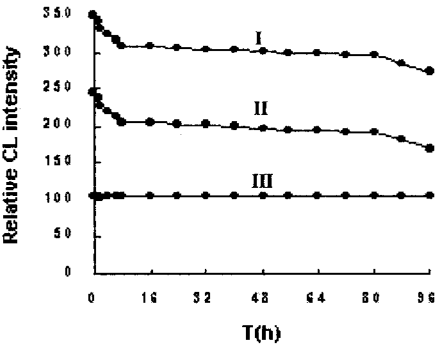

FIGURE 9 Stability of the flow sensors CL intensity in the absence of formaldehyde (I, I_o); in the presence of 300 ng mL^{-1} formaldehyde (II, I_s). III, decrease in CL intensity ($\triangle I$).

catechol, respectively. However, it should be noted that some phenols (e.g. hydroquinone and catechol) do significantly interfere with the determination of the formaldehyde.

Operational Stability of the Sensor

100 μL of eluant (water) were flow-injected through the system in presence of 30 ng mL^{-1} formaldehyde solution and the $\Delta I(I_o - I_s)$ was recorded to test the operational stability of the sensor. The experiment lasted for 10 days and the flow system was regularly used over 8 h per day. Figure 9 showed the stability of the flow sensor, and the average ΔI was calculated in ten spot-check determinations with RSD less than 3.0%. The flow sensor showed remarkable stability and could be easily reused over 80 h.

APPLICATIONS

Determination of Formaldehyde in Water and Air Samples

Following the procedure described in the Experimental section, formaldehyde can be determined in water samples after addition to tap water and drinking water.

TABLE II Results of formaldehyde in water samples[a]

Sample	*Added* (ng mL^{-1})	*Found* (ng mL^{-1})	*Recovery%* ($N = 5$)	*RSD%* ($N = 5$)	*t* ($t_{0.01,4} = 4.60$)
Tap water 1	10.0	10.1	101	1.99	1.11
Tap water 2	100	97.3	97.3	1.62	3.83
Tap water 3	50.0	49.5	99.0	1.77	1.28
Drinking water 1	40.0	41.2	103	1.62	4.02
Drinking water 2	10.0	11.0	110	2.94	6.91

[a] The average of five determinations.

TABLE III Results of formaldehyde in air samples[a]

Sample	*Found* (ng mL^{-1})	*Added* (ng mL^{-1})	*Total* (ng mL^{-1})	*Recovery%* ($N = 5$)	*RSD%* ($N = 5$)	*Content* (mg M^{-3})
1	141.6	50.0	195.8	108.4	2.76	0.78
2	128.0	70.0	200.0	102.9	1.83	0.64
3	122.9	50.0	172.1	98.4	1.94	0.61
4	119.5	70.0	191.7	103.2	2.06	0.59

[a] The average of five determinations.

Combined with the absorption system designed as shown in Fig. 2, the proposed sensor is also employed for detection of formaldehyde in air samples. Samples are collected for 3–5 min at 300–500 mL min^{-1} flow rate. The samples are collected inside the isolated Chemical Lab containing vapor of formaldehyde. The recovery studies were performed on each of the analyzed samples by adding a known amount of formaldehyde to the sample before the recommended treatment and the experimental results were also verified by *t*-test. The results are shown in Tables II and III.

CONCLUSION

By combination with a flow injection system, a novel chemiluminescence sensor was constructed by using control-reagent-release technology for quantitative analysis of formaldehyde in water and air samples in this article. The sensor was successfully applied in analysis of formaldehyde in artificial water samples and air samples. Compared with other methods for determination of formaldehyde, the proposed flow sensor put more effort on the development of the method offering instrumental simplicity, sensitive detection and on-line or real-time procedure for the environmental application.

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