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Determination of Trace Formaldehyde in Water Samples by Interfacial Chemiluminescence Method

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Abstract

Based on gallic acid-hydrogen peroxide-formaldehyde chemiluminescence system, a low concentration formaldehyde detection method was established in aqueous solution by using home-made interface Chemiluminescence tester. The influence of the concentration of gallic acid, hydrogen peroxide, sodium hydroxide and other reagents on the chemiluminescence intensity were investigated, and other parameters of the instrument were optimized. Under the optimized experimental conditions, the instrument method and phenol reagent method were compared to detect the formaldehyde content in water samples. The results showed that when 0.15 mol/L hydrogen peroxide, 0.1 mol/L sodium hydroxide and 0.030 mol/L gallic acid (containing 30% ethylene glycol and 0.40% tetrabutylammonium iodide by volume) were mixed in sequence, the length of the collecting tube was 7 cm, the formaldehyde content showed a good linear relationship in the range of 1×10^{-5}-1.5×10^{-3} mg/mL, the detection limit was 5.96×10^{-5} μg/mL, and the RSD was 0.92%. However,the detection limit of phenol reagent method was 2.14×10^{-5} μg/mL, and the RSD was 0.97%.It shows that the instrumental method has lower detection limit and higher accuracy, which meets the requirements of the determination of trace formaldehyde in water samples.

Keywords

Interfacial Chemiluminescence; Formaldehyde; Gallic Acid.

1. Introduction

Formaldehyde is a common organic poison, in daily life, formaldehyde is usually used for disinfection, sterilization, corrosion, etc., its sources are very wide, building decoration materials, leather products, car seats, cosmetics, alcohol contain formaldehyde. Formaldehyde has been recognized as a Group I carcinogen by the International ARC(International Center for Research on Cancer) [1]. Its influence on human health is mainly manifested as irritability, irritability, disease degeneration and carcinogenicity [2-3]. Long-term exposure to low concentration of formaldehyde will cause chronic respiratory diseases, inhibit the repair of damaged DNA, cause menstrual disorders in women, and lead to the decline of intelligence and memory in adolescents [4]. High concentration of formaldehyde inhalation can cause suffocation, even respiratory paralysis and death. Formaldehyde is more harmful to children, the elderly and pregnant women.

Formaldehyde in the environment has become an invisible killer threatening human health, and now it has been highly valued by people. With the continuous development of formaldehyde detection technology, how to detect formaldehyde quickly, sensitive and accurately is very important. The traditional detection methods of formaldehyde include phenolic reagent method [5], acetyl acetone method [6], gas chromatography (GC) method [7], liquid chromatography (LC) method [8], ion chromatography (IC) method [9], fluorescence method [10], etc. In recent years, there are new

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detection methods of formaldehyde: Sensor method [11], chemiluminescence method [12], potentiometric method [13], microfluidic chip technology [14], etc. So far, in order to meet the detection performance of high sensitivity and excellent selection in different fields, various combined technologies have been introduced on the basis of chemiluminescence analysis, such as flow injection-chemiluminescence method [15], high performance liquid chromatography-chemiluminescence method [16], capillary electrophoresis-chemiluminescence method[17], molecula imprinting technology-chemiluminescence method [18], etc.

In this paper, the trace formaldehyde in water samples was taken as the research object, and the chemiluminescence online detector made by the laboratory was used to detect the trace formaldehyde. First, the chemiluminescence reagent system was optimized, including ethylene glycol (cosolvent), gallic acid, hydrogen peroxide, sodium hydroxide, and the type and concentration of sensitizer. Then the effects of reagent mixing sequence and the length of liquid collecting tube on the chemiluminescence intensity were investigated. Finally, the results were compared by phenol reagent method and instrument method.

2. Experimental

2.1 Reagents and Apparatus

Gallic acid, sodium hydroxide, hydrogen peroxide, ammonium ferric sulfate, ethylene glycol, hexylene tetramine, sodium hydroxymethyl sulfonyl, ethylenediamine tetracetate, cetyltrimethyl ammonium chloride, zinc nitrate (hexahydrate), nickel nitrate (hexahydrate), silver nitrate, chromium trichloride, potassium chloride and manganese chloride (tetrahydrate) were purchased from Chengdu Kelon Chemical Reagent Factory. Among them, the purity of potassium chloride and sodium hydroxide reagent is chemical pure, the purity of gallic acid reagent is 99%, the purity of hydrogen peroxide reagent is 30%, others are analytical pure; Tetrabutylammonium iodide, polyvinylpyrrolidone, sodium dodecyl sulfate, lauryl polyoxyethylene ether, cetyltrimethyl ammonium bromide, sodium methyl sulfonate, potassium hydrogen phthalate, octadecyl trimethyl ammonium chloride, and trisodium citrate (dihydrate) were all purchased from SIGMA Reagent Company in the United States. The purity of tetrabutylammonium iodide reagent was 99%.

XY-A/B/C Analytical Balance (Shanghai Shunyu Hengping Scientific Instrument Co., LTD.); ATMOS-DSI Chemiluminescence detection system (Developed by Analysis and Test Center Laboratory of Sichuan University of Light Chemical Technology); 1200UV-Visible spectrophotometer (Aoyi Instruments (Shanghai) Co., LTD.)

The schematic diagram of the experimental device is shown in **Figure 1**. Based on the chemiluminescence detector made by the laboratory [19], the reaction reagent and formaldehyde solution are mixed through the pipeline, pumped into the reactor by the peristaltic pump, and enter the reaction interface through the liquid inlet. The reaction interface is made of hydrophilic material, and the trace solution quickly infiltrates the interface and generates stable chemiluminescence reaction on it. After the reaction, the waste liquid is pumped into the waste liquid collection bottle from the outlet. The photomultiplier tube in the detector converts the detected light signal into the current signal, which is collected by the main control circuit and transmitted to the software system of the industrial control computer for processing, recording and display. Within a certain range, optimized through the experimental conditions, the higher the concentration of formaldehyde, the greater the luminescence intensity, the larger the signal data displayed by the software, so that the formaldehyde concentration can be measured through the signal data.

he reactor is made of teflon material. The bottom of the reactor is provided with a long reaction bed which is made of microfine polyester fiber material. The reaction bed is porous and the surface is filled with micro gully structure, which can effectively increase the reaction contact area between reagent and gas. The detection reagent is pumped into the reactor and evenly distributed throughout the fiber surface to form a liquid film under the action of gravity and liquid diffusion. Then, the sample formaldehyde liquid is pumped into the reactor to react with the detection reagent and emit

Volume 9 Issue 4, 2023
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light on the surface of the liquid film. CL signal is detected by photomultiplier tube (PMT), and data is processed by computer.

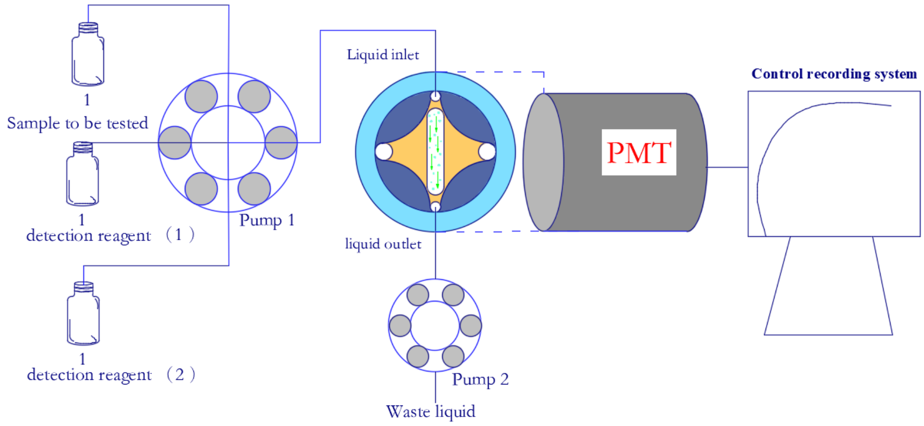

Figure 1. Schematic diagram of flow path detection; PMT is a photomultiplier tube.

2.2 Parametric Optimization

Gallic acid is dissolved in a glycol-water system, and a certain concentration of glycol has a better dispersion effect on gallic acid, which affects the luminescence intensity of the system. The results were provided in **Figure 2**. With the increase of glycol concentration, the emission signal value of 1.0×10^{-3} mg/mL formaldehyde solution reached a maximum of 78 mV when the glycol concentration was 30%, so 30%(v/v) was selected as the optimal concentration of glycol.

As shown in **Figure 3**, the influence of gallic acid concentration in the range of 1.0×10^{-3}~4.0×10^{-2} mol/L on the luminescence intensity of the system was investigated. When gallic acid concentration was 0.030 mol/L, the luminescence signal value of 1.0×10^{-3} mg/mL formaldehyde solution reached the maximum value of 90 mV. Therefore, 0.030 mol/L was selected as the optimal concentration of gallic acid.

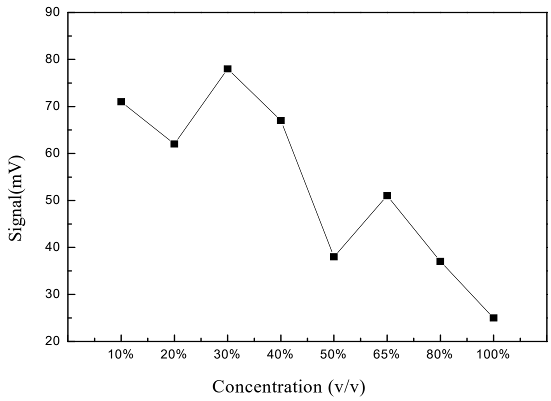

Figure 2. The effect of the concentration of ethylene glycol on CL intensity

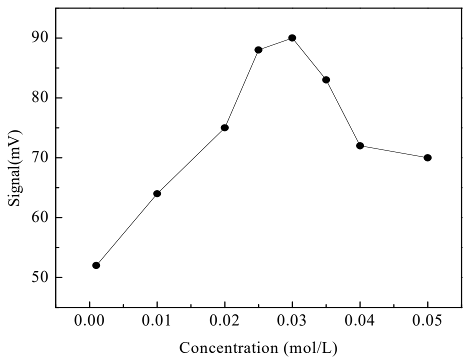

Figure 3. The effect of the concentration of gallic acid on CL intensity

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Hydrogen peroxide is the oxidant of the system. The influence of different concentrations of hydrogen peroxide on luminescence intensity was investigated in the range of 0~0.7 mol/L. As shown in **Figure 4**, the chemiluminescence intensity increases with the increase of hydrogen peroxide concentration. When the concentration of hydrogen peroxide is 0.20 mol/L, the luminescence signal value of 1.0×10^{-3} mg/mL formaldehyde solution reaches the maximum value of 95 mV. Therefore, 0.20 mol/L hydrogen peroxide concentration was selected.

The chemiluminescence of gallic acid system should be carried out under alkaline conditions. The influence of sodium hydroxide concentration on luminescence intensity was investigated in the range of 0~0.5 mol/L. The experimental results are shown in **Figure 5**. When the concentration of sodium hydroxide is 0.12 mol/L, the luminous signal value reaches the maximum value of 98 mV. Therefore, the concentration of sodium hydroxide was selected as 0.12 mol/L

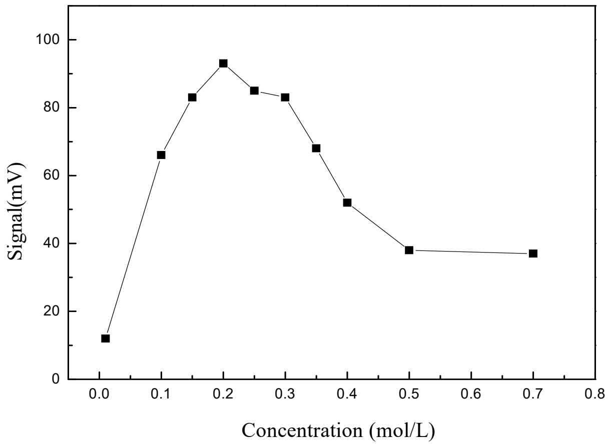

Figure 4. The effect of concentration of hydrogen peroxideon CL intensity

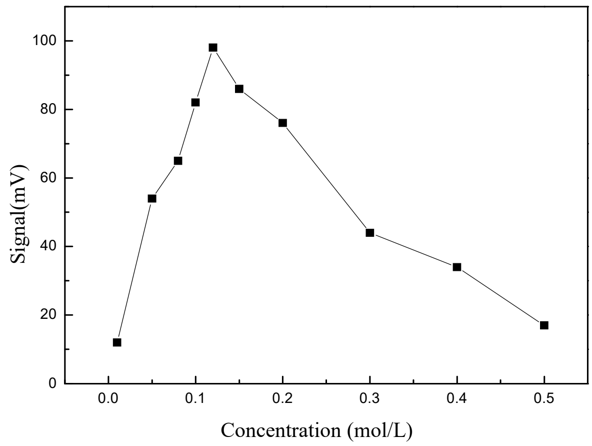

Figure 5 . The effect of concentration of sodium hydroxideon CL intensity

Effects of sensitizers such as (SAS), tetrabutylammonium iodide (TBAI), potassium hydrogen phthalate (KAP), disodium ethylenediamine tetraacetate (EDTA), cetyltrimethylammonium chloride (CTAC) and tri-sodium Citrate (Citrate) on the chemiluminescence intensity of gallic acid reagent system. The experimental results are shown in **Figure 6**. When TBAI is used, its luminescence intensity increases significantly compared with the blank group, so the best sensitizer is determined to be TBAI. Then, the influence of different concentrations of TBAI on luminescence intensity was investigated. The experimental results are shown in **Figure 7**. When the concentration of TBAI is 0.40%, the luminous signal value reaches the maximum value of 181 mV, so the concentration of TBAI is determined to be 0.40%.

 Volume 9 Issue 4, 2023
DOI: 10.6919/ICJE.202304_9(4).0027

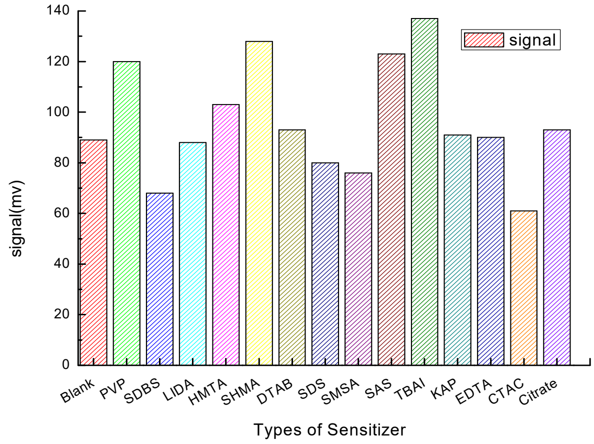

Figure 6. Curves of luminescence intensity and signal-to-noise ratio under different sensitizers.

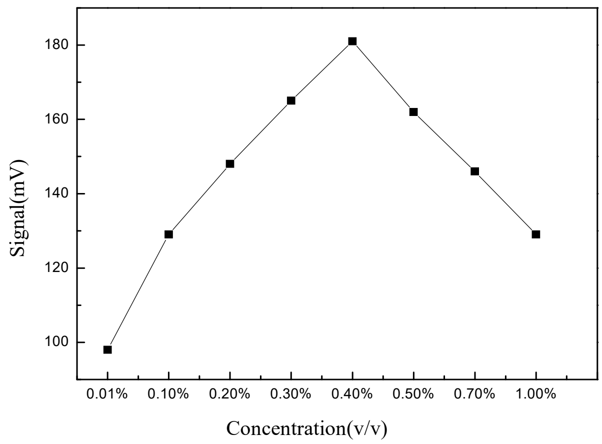

Figure 7. The effect of concentration of tetrabutylammonium iodide on CL intensity.

The influence of the length of the liquid collector on the luminescence reaction was investigated. The experimental results are shown in **Figure 8.** When the length of the liquid collector was 7cm, the luminous signal value was the largest, so the optimal length of the liquid collector was determined to be 7cm.

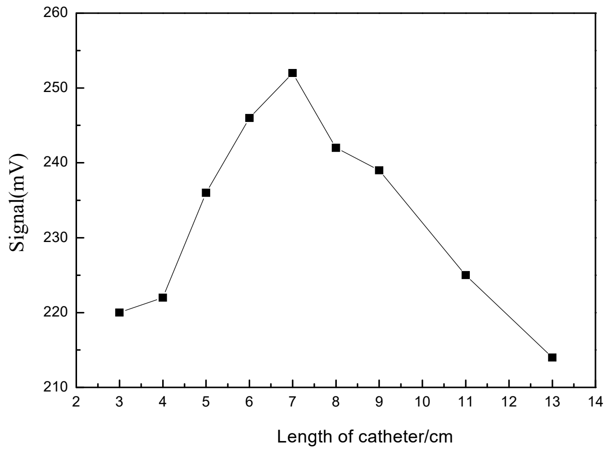

Figure 8. The luminescence intensity varies with the length of the collector.

 Volume 9 Issue 4, 2023
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3. Analytical Performance

In order to consider the validity of this experimental method, the phenol reagent method [20] was compared with the instrument method. As shown in **Figure 9**, the linear regression equation was as follows: $y = 0.344x + 0.0464$, linear correlation coefficient $R^2 = 0.999$, detection limit of the method was 2.14×10^{-2} μg/mL, and relative standard deviation RSDS were 0.97%. Under optimized experimental conditions, with formaldehyde concentration as the abscissa and luminous signal as the ordinate, as shown in **Figure 10**, the linear equation of the instrument method can be obtained as follows: $y= 243.624x +5.865$, the linear correlation coefficient $R^2 = 0.998$, the detection limit was 5.96×10^{-5} μg/mL, the relative standard deviation RSDS were 0.92%. Formaldehyde standard solution was used to configure 4 formaldehyde liquid samples of different concentrations to be tested. The standard curve method was used to parallel measure each sample for 3 times, respectively. The results are shown in Table 1.

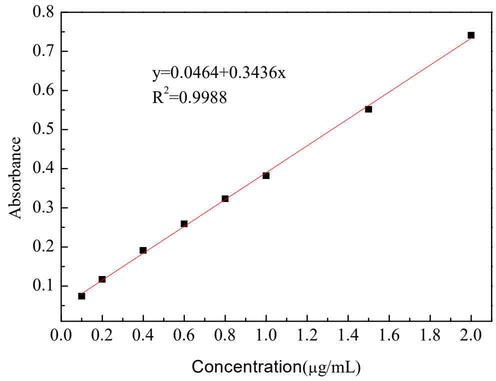

Figure 9. Standard graph of phenol reagent method.

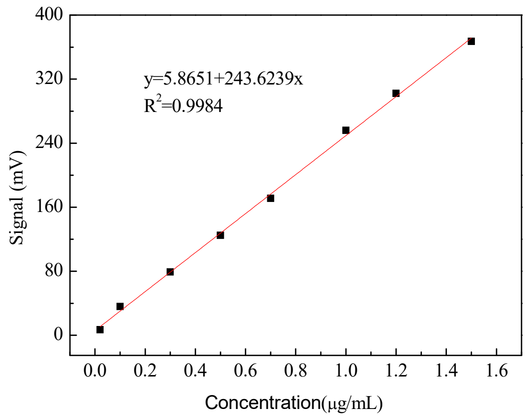

Figure 10. Standard graph of instrumental method

Table 1. Table of Test results of four kinds of samples by phenol reagent Method and Instrument method (n=3)

Test sample (μg/mL)	Phenol reagent method (μg/mL)	Instrumental method (μg/mL)
sample1 (0.500)	0.489	0.493
sample2 (0.800)	0.758	0.781
sample3 (1.200)	1.161	1.217
sample4 (1.500)	1. 451	1.546

4. Conclusion

Based on the principle of interfacial chemiluminescence, the detection method of low concentration formaldehyde solution was established by optimizing the gallic acid reagent system. The detection limit was 5.96×10^{-5} μg/mL. The comparison test with phenol reagent method showed that the method was simple and fast, sensitive and accurate, and could realize online and portable detection. It has a good application prospect in the field of trace formaldehyde detection in water

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Disclosure statement

No potential conflict of interest was reported by the author(s).

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