

Rapid Determination of Ozone by Gas-Liquid Chemiluminescence

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Abstract

Ozone is one of the most harmful air pollutants, and the pollution degree is becoming more and more serious. However, current methods of detecting the concentration of ozone in the atmosphere are limited by large-scale equipment or complex procedures. Our study revealed that fluorescein sodium and ozone can produce a high CL signal. In this work, fast and sensitive online detection of ozone is realized based on the self-developed equipment of gas-liquid chemiluminescence (GL-CL). Phloroglucinol, TritonX-100 and UV-light could be employed to synergistically enhance the CL intensity of the fluorescein sodium-ozone. Therefore, a GL-CL assay has been developed for the detection of atmospheric ozone with a linear range of 0.4-150ppbv and a detection limit of 0.1ppbv. This method has the advantages of high sensitivity, good selectivity, high precision, and continuous online detection of ozone.

Keywords

Gas-liquid chemiluminescence equipment; Fluorescein sodium; Ozone; Online detection.

1. INTRODUCTION

Ozone is one of the most harmful air pollutants, impacting human health and the growth of plants [1-3]. Its influence on human health is mainly demonstrated in the following aspects. When people breathe in a high concentration of ozone for a short time, their respiratory system will be severely damaged [4-6]. People are at risk for neurological diseases if they live in high levels of ozone for a long time, while the risk of emphysema, bronchitis, headache, and memory decline will increase [7,8]. Ozone is also highly corrosive. If breathed in excess (3 mg /m³) [9], the bronchioles and alveoli of the lungs can be damaged, causing inflammation of lung tissue and respiratory infections. Some researchers have investigated the relationship between ozone and premature death [10-12], revealing that about 100,000 people die [13,14] prematurely every year in East Asia because of high ozone concentration.

Additionally, high ozone concentrations have influenced some particular disease, such as dry eye disease, myocardial infarction, and cardiovascular disease [15,16]. A high concentration of ozone would aggravate dry eyes in patients and significantly boost the risk of cardiovascular and cerebrovascular diseases [17]. Ozone is the most toxic pollution gas to plants [18-21]. Excessive ozone will lead to slow growth or even death and destroy photosynthesis in plants [21-25], which will die if the concentration is too high. Therefore, it is urgent to detect ozone concentration in the environment [26-29].

At present, the measurement methods of ozone gas mainly include iodine quantity method, indigo disulfonate sodium method [30], ultraviolet absorption method [31], and chemiluminescence method [32], among which the ultraviolet absorption method is majorly employed to detect ozone [33]. However, ultraviolet absorption method is severely disturbed by aromatic hydrocarbons [34,35]. In this study, setting up online equipment for rapid detection

of ozone concentration based on alcohol solution of sodium fluorescein and ozone will contribute to the generation of a good chemiluminescence signal. This system demonstrates the advantages of high sensitivity, high selectivity, low cost, simple device, and fast detection speed.

2. EXPERIMENTAL

2.1. Reagents and Apparatus.

Fluorescein sodium was purchased from Wansheng Chuandong Reagent Co., Ltd (Chongqing, China). Ethanol and Phloroglucinol were purchased from Ke Long Reagent Co., Ltd. (Chengdu, China). Triton X-100 was purchased from Tiantan Scientific Co., Ltd

Ozone generator (Type 2030, Sutron America); UV lamp (Cnlight, Shanghai, China). The GL-CL detector, Peristaltic pump, and Air pump were homemade.

The construction of the GL-CL reactor and flow schematic construction were illustrated in Figure 1 and Figure 2, respectively. During the experiment, the peristaltic pump was used to make reagents evenly enter the reactor, and the ozone produced by the type 2030 ozone generator entered the reactor at a constant velocity. Contact between ozone and detection reagent produces a chemiluminescence signal, which is converted into a weak current signal by the photomultiplier tube. Then, the signal is amplified. The collected voltage signal is related to the strength of the chemiluminescence signal, which can directly reflect the concentration of ozone in the measured sample gas.

The reactor is made of PTFE material. The bottom of the reactor is equipped with a long reaction bed, which is made of ultrafine polyester fiber material. The reaction bed is porous, and the surface is filled with a miniature gully structure, allowing it to effectively increase the reaction contact area between the detection reagent and the gas. The detection reagent was pumped into the GL-CL reactor and uniformly distributed over the whole fiber surface, forming a liquid membrane under the gravity and liquid spreading. Next, the sample gas was pumped into the reactor, reacted with the detection reagent, and emitted light on the surface of this liquid membrane. The CL signal was detected by a photomultiplier (PMT), and the data was processed by a computer. With the continuous entry of the detection reagent, the liquid in the reaction bed will gradually gather at the lower end of the reaction bed under the action of gravity, contributing to quickly extracting the detection liquid through the micro peristaltic pump. This process ensures the continuous updating of the detection reagents.

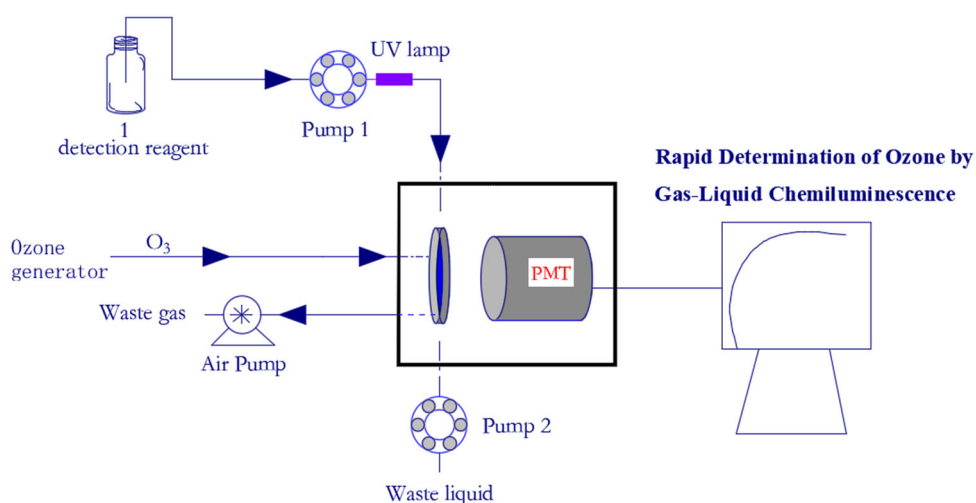


Figure 1. A schematic diagram of the flow path detecting O₃. 1 indicates the detection reagent; 2 and 3 denote Laminar flow gas quality controllers; PMT is a photomultiplier.

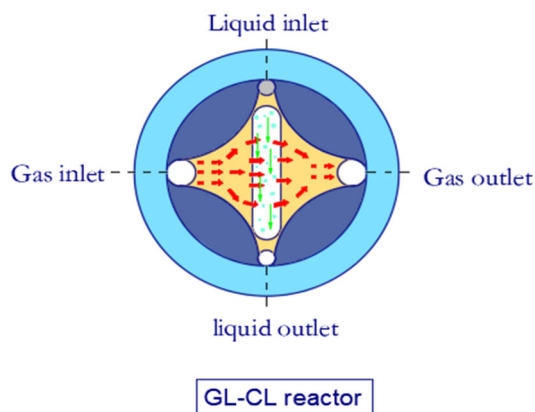


Figure 2. Schematic diagram of gas-liquid CL reactor. The white part represents the reaction bed made of hydrophilic material.

2.2. Selection of detection reagents

The CL intensity of ozone and different dyes in aqueous solution and ethanol solution were explored. The results are listed in Table 1. The concentration of ozone was 100ppbv, and the concentration of dye aqueous solution and alcohol solution was 1×10^{-3} mol/L. Besides, the selected dye aqueous solution had no luminescence response to ozone, while the dye alcohol solution had a response. The alcohol solution of fluorescein sodium exhibited a much higher signal compared to other dyes. Therefore, the fluorescein sodium ethanol system was selected to measure ozone and further optimize the system.

Table 1. CL signals of different dyes with ozone (The Instrument background value is 30)

Dye	Dye in aqueous	Dye in ethanol
Rhodamine B	30	42
Rhodamine 6G	31	64
Methylene blue	30	50
Sodium fluorescein	32	290
Neutral red	30	29
Methyl orange	30	38
Malachite green	29	35
Amino black10-B	30	30
Congo red	31	41
Acid red	29	32
acid blue	29	37
Oringe I	29	33

2.3. Parametric Optimization

The effect of the concentration of sodium fluorescein on CL intensity was also investigated. The concentration of sodium fluorescein was an essential factor in the CL intensity. The effect of the concentration of sodium fluorescein was researched in the range of 1-10 mM. The results were provided in Figure 3. The data indicated that the CL intensity increased with the increase in the concentration of sodium fluorescein in the range of 1-6 mM and decreased above 6 mM. The possible reason was that the high concentration of sodium fluorescein could absorb some CL because of its deeper color. Consequently, 6 mM sodium fluorescein was chosen as the optimum for further experiments.

As demonstrated in Figure 4, the effect of the concentration of Triton series on CL intensity was investigated in the range of 0-16.0 g/L. Triton is a good surfactant and can enhance CL intensity. The results revealed that TritonX-100 pairs of CL intensity increase the most since TritonX-100 had a better water solubility. The CL increased with an increase in the concentration of TritonX-100 in the range of 0-12.0g/L but decreased above 12.0 g/L. This was in that surfactant micelles were not formed at a low level, while a hydrophobic environment was created under a high concentration of surfactant, resulting in a reduction of reaction efficiency. TritonX-100 could not only significantly enhance the CL but also keep the CL signal stable.

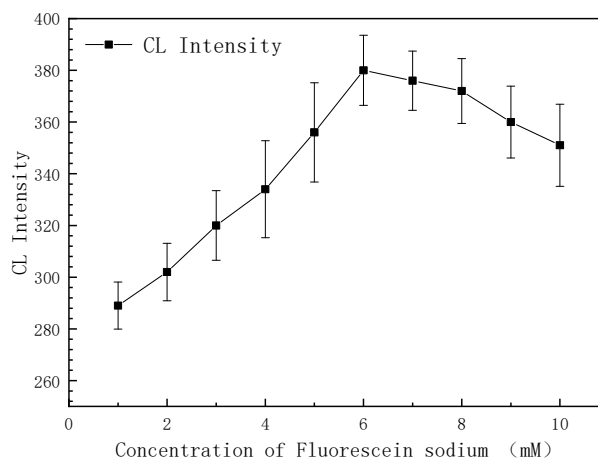


Figure 3. The effect of the concentration of sodium fluorescein on CL intensity in the range of 1-10mM.Ozone: 100 ppbv.

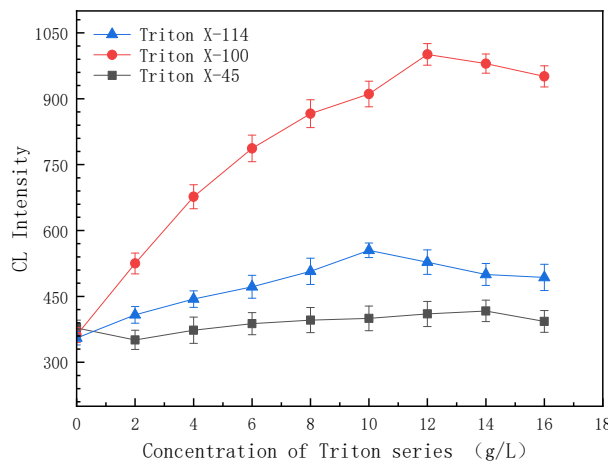


Figure 4. The effect of the concentration of Triton series on CL intensity in the range of 2-16g/L. Ozone: 100 ppbv.

The effect of resorcinol and phloroglucinol on CL intensity was demonstrated in this study. It was revealed that phenols could enhance CL intensity. Thus, the effects of the concentrations of phloroglucinol and resorcinol on CL intensity were investigated in the range of 0.5-5mM. As suggested in Figure 5, phloroglucinol has a better effect on increasing the CL signal than resorcinol. CL increased with an increase in the concentration of phloroglucinol in the range of 0.5-2mM but decreased above 2mM. Consequently, 2 mM phloroglucinol was selected as the optimum for further experiments.

Next, it is the effect of UV radiation time. According to the previous report [36,37], photoactivation could significantly enhance CL intensity. With the increase in UV radiation time of the detection reagent, the color of sodium fluorescein solution changed to more fluorescent green. The effect of UV radiation time on CL intensity was examined in the range of 0-600 s, as

illustrated in Figure 6. CL intensity increased with the increase in the UV radiation time in the range of 0-420 s but decreased above 420 s. This was in that the active substance was consumed with a long time of UV radiation. Hence, 420s UV radiation time was selected for the following experiments.

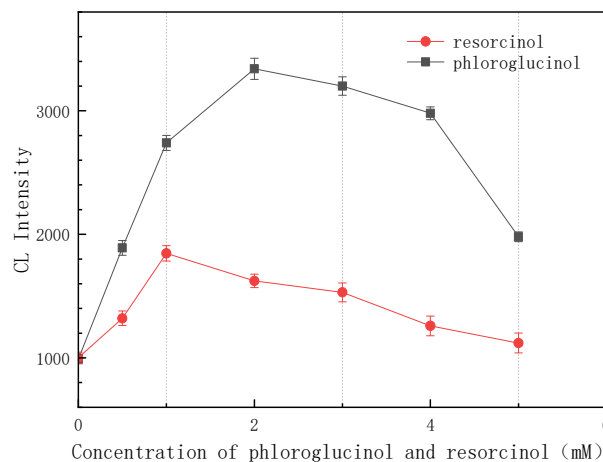


Figure 5. The effect of concentration of resorcinol and phloroglucinol on CL intensity in the range of 0.5-5mM. Ozone: 100 ppbv.

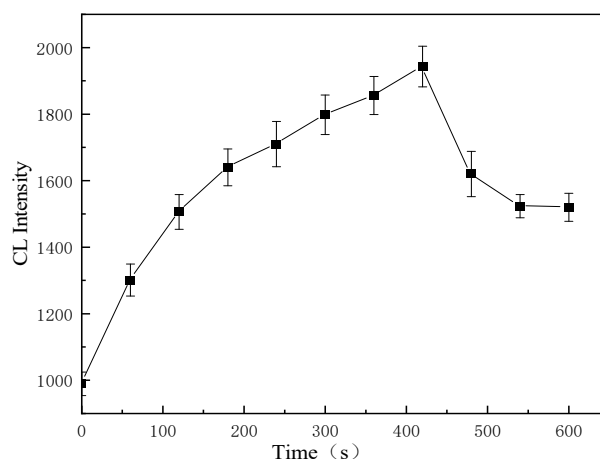


Figure 6. The effect of UV radiation time on CL intensity in the range of 0-600s. Ozone: 100 ppbv.

2.4. Mechanism Analysis

Most chemiluminescence reactions are redox reactions. In these reactions, free radicals are often involved. In sodium fluorescein - ozone chemiluminescence system, ozone is a strong oxidant, so we speculate that this reaction is also a chemiluminescence reaction involving free radicals. To test this hypothesis, we designed a free radical scavenging experiment. Add 500 μ L of 1×10^{-3} mol/L thiourea and ascorbic acid, which are hydroxyl radical scavenger and extensive free radical scavenger, to 5 mL sodium fluorescein solution of 2 groups, respectively. The two groups of solutions were activated by ultraviolet light and then reacted with ozone and the luminescence intensity was recorded. The influence of two free radical scavenger on chemiluminescence intensity is shown in Figure 7. When thiourea and ascorbic acid were added, the luminescence intensity of the system decreased by 96% and 88%, respectively. The results showed that free radicals were involved in the reaction between sodium fluorescein and ozone, and the reaction involving free radicals is the main reaction.

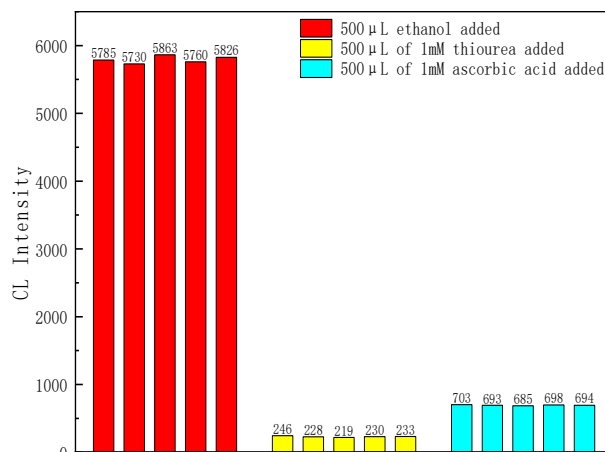


Figure 7. The effect of free radical scavengers on CL intensity .Ozone: 100 ppbv.

3. ANALYTICAL PERFORMANCE

This section details the linear relationship between the concentrations of ozone and sodium fluoresces with CL intensity. Under the optimum conditions, a series of different concentrations of ozone were adopted to construct the calibration curve, as demonstrated in Figure 8. CL intensity increased with the increase in the concentration of ozone. The calibration curve of ozone exhibited a good linear relationship between CL intensity and the concentration of ozone in a range of 0.4-150 ppbv with R2=0.998. The regression equation was $Y= 58.19C+21.63$, where Y and C represented CL intensity and volume concentration of ozone, respectively. The limit of detection (LOD) was calculated to be 0.1 ppbv.

Afterward, the precision of this method was verified. The reproducibility was tested by measuring the 100ppbv and 50ppbv ozone, and each was repeated eleven times (Figure 9).The relative standard deviation (RSD) was 1.06% and 0.92%, respectively. These results confirmed that this method had a high degree of accuracy in detecting high-level or low-level ozone.

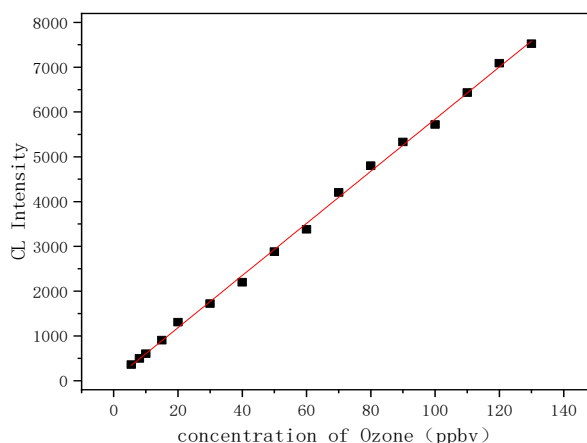


Figure 8. The linear relation between the concentration of O₃ and CL intensity

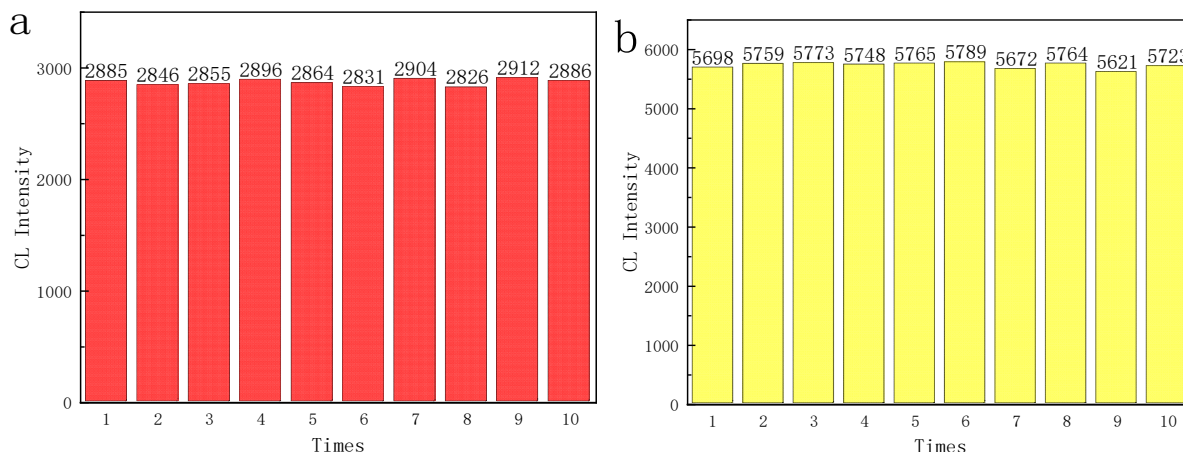


Figure 9. The repeatability of detecting different concentrations of ozone, a: 50 ppbv; b: 100 ppbv; n=10.

The important factor determining whether a detection method is superior is whether the method has fast response speed and good stability. As demonstrated in Figure 10, the sample repeatedly switched between 50ppbv and 100ppbv ozone, recording the CL signal, indicating that the response time was less than 0.5s. As suggested in Figure 11, ozone at 100ppbv was measured continuously for 30min. It can be seen that CL signals generated within 30min are very stable, so CL signals generated by this method have good stability. To confirm the selectivity of this method for ozone detection under optimal ozone detection conditions, interference experiments were studied by measuring a range of other gases at different concentrations, the results showed that 0.5ppmv NO₂, 2ppmv SO₂, 4ppm CH₂O, 5000ppmv CO₂ and H₂O₂ had no interference on measuring 50ppbv ozone. This indicated that this method had a good selectivity for measuring ozone.

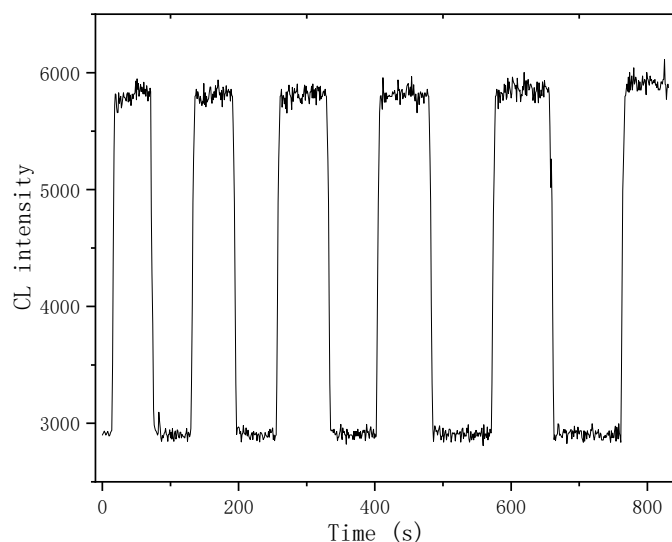


Figure 10. The change of CL intensity by repeatedly switching between 50ppbv-100ppbv ozone.

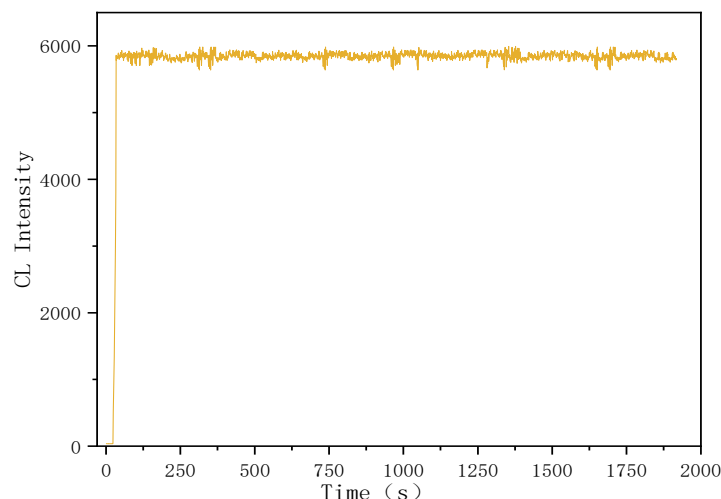


Figure 11. Ozone was measured at 100ppbv for 30 consecutive minutes.

4. CONCLUSION

Main Text Paragraph. In this study, the CL intensity of fluoresces in the sodium-O₃ system was remarkably enhanced in the presence of phloroglucinol, TritonX-100, and UV radiation. Therefore, a CL method with high sensitivity, high selectivity, low cost, fast detection speed, and portable device size for online-detecting ozone in the atmosphere was successfully developed. This method was ideally suited for transportable online detection of ozone.

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DISCLOSURE STATEMENT

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

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