Talanta 191 (2019) 422–427

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Fluorescein and its derivatives: New coreactants for luminol chemiluminescence reaction and its application for sensitive detection of cobalt ion

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ARTICLE INFO

Keywords:
Chemiluminescence
Fluorescein
Luminol
Cobalt ion
Carbonate buffer

ABSTRACT

Fluorescein and its derivatives, including 4′,5′–dibromofluorescein, 2′,7′–dichlorofluorescein and 2′,4′,5′,7′–tetrabromofluorescein can be employed as efficient coreactants for luminol reaction. Under an alkaline condition they reacted with luminol to produce measureable chemiluminescence (CL) in the absence of any extra–oxidant. Cobalt ion (Co^{2+}) significantly enhanced the CL emission of the reaction. The CL emission was strongly dependent on the concentration of carbonate buffer used; higher concentration of carbonate buffer provided more intense CL emission. The system had two emission peaks locating at 425 nm and 535 nm, respectively. With 4′,5′–dibromofluorescein as the coreactant for luminol reaction, a new CL method was developed for the detection of Co^{2+}. The procedure allowed the linear detection of Co^{2+} in the range of 5–1000 nmol/L. The limit of detection (LOD) and limit of quantitation (LOQ) were 1.8 nmol/L and 5.0 nmol/L, respectively. The intra–day precision (n = 11) and inter–day precision (n = 3) was 3.2% and 4.7% for replicated measurements of 0.2 μmol/L Co^{2+} solution. The method was successfully applied to the determination of Co^{2+} in blue silica gel samples.

1. Introduction

Chemiluminescence (CL) has been extensively utilized to determine a variety of trace inorganic and organic species in chemical, environmental, food and biological fields due to its attracting features of low detection limit and wide calibration range, both of which can be achieved with a simple and inexpensive instrumentation [1–3]. The discovery of new CL reactions is important since it is foundation for the technique. Luminol is one of the most popular liquid–phase CL agents and produces light emission following action with many familiar oxidants in alkaline condition [4]. Among them, hydrogen peroxide (H_2O_2) is unstable and susceptible to many transition metal ions, resulting in poor selectivity in the determination of metal ions. Other oxidants, e.g. $KMnO_4$ and $K_3Fe(CN)_6$, produce high background signal, thus impeding the improvement in the sensitivity for enhanced–based CL detection [5]. Therefore, it is urgent to find new chemicals that can be used as CL coreactant for luminol reaction. Thiourea dioxide [6] and N–hydroxysuccinimide [7] were previously reported to be employed for this purpose.

Since its first synthesis in 1887, fluorescein and its derivatives have been adopted as powerful fluorescent probes in the detection of different substances including metal ion, anion, small molecule and biological macromolecule [8]. More recently, fluorescein and its derivatives were reported exhibiting peroxidase–like activity as they catalyzed the oxidation of peroxidase substrate 3,3′,5,5′–tetramethylbenzidine by H_2O_2 [9,10]. Refer to their use in CL–based detection method, they were mainly utilized as energy transfer enhancers [11–13].

Cobalt is an essential nutrient for the human body and plays significant roles in various biological processes. Various analytical techniques have been reported for the determination of Co^{2+} in different matrix, including colorimetry [14], spectrophotometry [15], atomic absorption spectrometry [16], fluorescence [17], chemiluminescence [18] and voltammetry [19].

In this work, we found that fluorescein and its derivatives directly reacted with luminol to produce CL in alkaline condition without adding extra–oxidant. The CL emission was remarkably enhanced in the presence of Co^{2+}. This system was developed as a sensitive CL method for Co^{2+} assay.

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https://doi.org/10.1016/j.talanta.2018.09.007
Received 19 March 2018; Received in revised form 25 August 2018; Accepted 3 September 2018
Available online 04 September 2018
0039-9140/

2. Experimental section

2.1. Chemicals and materials

All chemicals were of analytical grade and used without further purification. Ultrapure water was produced from Molegene 1810b ultrapure water system (Chongqing Mole, China). Luminol and fluorescein were purchased from Adamas Reagent Co., Ltd (Shanghai, China). 4′,5′–Dibromofluorescein (DBF) was obtained from Shanghai Macklin Biochemical Co., Ltd (Shanghai, China). 2′,7′–Dichlorofluorescein (DCF) and 2′,4′,5′7′–tetrabromofluorescein (TBF) were bought from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Cobalt(II) sulfate heptahydrate ($CoSO_4{\cdot}7H_2O$) was provided by Xi'an Reagent Co., Ltd (Xi'an, China). Sodium bicarbonate ($NaHCO_3$) was purchased from Guangdong Guanghua Sci–Tech Co., Ltd (Guangdong, China). Other reagents were obtained from Aladdin Reagent Co., Ltd (Shanghai, China). Luminol stock solution (10.0 mmol/L) was prepared by dissolving 0.8858 g luminol in 250 mL of 0. 2 mol/L NaOH solution and diluting up to 500 mL with water. Luminol working solutions were prepared by dilution of the stock solution with carbonate buffer with desirable pH and concentration. Stock solutions (10.0 mmol/L) of fluorescein, DBF, DCF and TBF were prepared by dissolving appropriate amounts of respective solid in 6 mL of 0.1 mol/L NaOH solution and diluting to 100 mL with water. Co^{2+} stock solution was prepared by dissolving 0.2812 g $CoSO_4{\cdot}7H_2O$ in 100 mL of water to give a final concentration of 10.0 mmol/L. More dilution solutions of Co^{2+} were daily prepared by diluting the stock solution with water. The stock solutions are stable at least two months when storing in a refrigerator.

2.2. Apparatus

CL measurements were carried out on an IFFM–E mode intelligent flow injection CL analyzer (Xi'an Remax Analytical Instrument Co. Ltd., China), which consists of two peristaltic pumps, a six–way valve and a CR105 photomultiplier tube (Beijing Hamamatsu Photo Techniques Inc.). Fig. 1 shows the schematic diagram of CL flow system used. PTFE tubing (0.8 mm i. d.) was used as the connecting material in the flow system. Reagent and sample solutions were delivered with the peristaltic pumps at a flow rate of 1.4 mL/min for each channel.

Fluorescent spectra were recorded on a FluoroMax–4 fluorescence spectrophotometer (Horiba, America) with slits width for excitation and emission both at 1 nm. In the case of recording chemiluminescent spectra, the excitation source was turned off and the slit width for emission was at 20 nm. The high voltage of the photomultiplier tube was biased at 950 V during the measurements. The pH of the solution was measured with a PB–10 pH meter (Sartorius Scientific Instrument Co. Ltd., Germany).

2.3. Procedure for CL measurements

In typical experiment, flow channels were connected with different concentrations of Co^{2+} solution, 0.5 mmol/L DBF solution and 1.0 mmol/L luminol solution (in 0.6 mol/L carbonate buffer at pH 11.0), respectively. Co^{2+} solution was firstly on–line mixed with DBF solution. And then 50 μL of the mixed solution was injected into luminol solution through the six–way valve to produce CL. The CL signal produced in the spiral flow cell was measured by the photomultiplier tube with high voltage biased at 600 V. The enhanced CL intensity(ΔI), calculated as $\Delta I = I - I_b$, was used to quantification of Co^{2+}, in which I was the CL signal in the presence of Co^{2+} and I_b was the blank, respectively.

2.4. Determination of cobalt in blue silica gel by atomic absorption spectrometry

The cobalt amount in blue silica gel was determined by atomic absorption spectrometry following the procedure of National environmental protection standard of People's Republic of China suggesting for water quality (Determination of cobalt–flame atomic absorption spectrometry, HJ 95-2018) [20]. In brief, about 10 g of blue silica gel sample was accurately weighed, ground into powder and transferred into 10.0 mL of water. After dissolving with the aid of ultrasonic acid for 10 min, the solution was filtered with 0.45 μm membrane filter. The filtrate was added into 0.06 mL of 2.0% (w/v) $La(NO_3)_3$ solution to make a final total volume of 5.0 mL. The absorbance was measured on HITACHI ZA3000 atomic spectrophotometer with a cobalt hollow cathode lamp operated at a current of 15 mA and a wavelength of 240.7 nm with a spectral bandwidth of 0.2 nm. The amount of Co in blue silica gel sample was determined with calibration curve method.

3. Results and discussion

3.1. CL of luminol with fluorescein and its derivatives and enhanced by Co^{2+}

Fluorescein was reported to enhance horseradish peroxidase–catalyzing luminol–H_2O_2 CL reaction via an energy transfer process from the excited state of 3–aminophthalic ion to fluorescein molecule [11,12]. In the present work, a measurable CL signal was recorded when fluorescein and its derivatives, including DBF, DCF and TBF was injected into alkaline luminol solution in the absence of adding

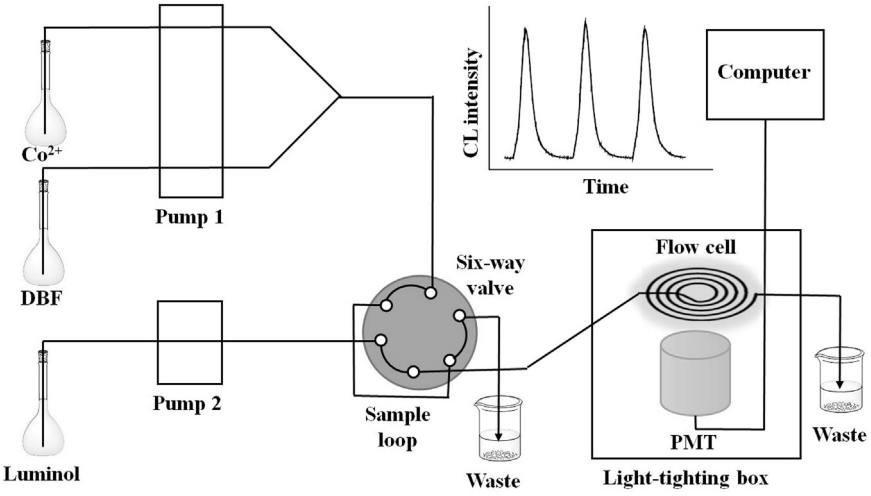

Fig. 1. Schematic diagram of the CL flow system.