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Biomimetic enhanced chemiluminescence of luminol–H_2O_2 system by manganese (III) deuteroporphyrin and its application in flow injection determination of phenol at trace level

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ABSTRACT

A novel, sensitive and high selective flow-injection chemiluminescence (FI-CL) method for the determination of phenol is reported, based upon its decreasing effect on the CL reaction of luminol with hydrogen peroxide catalyzed by manganese (III) deuteroporphyrin [MnDP, Scheme 1, **3**] in alkaline solution. Under the selected optimized experimental conditions, the relative CL intensity was linear with phenol in the range of 4.0×10^{-9} to 4.0×10^{-7} g mL^{-1}. The detection limit (3σ) was 6.3×10^{-10} g mL^{-1} and the relative standard deviation for 1.0×10^{-7} g mL^{-1} phenol ($n = 11$) was 2.99%. The regression equation was $I = 120.79 + 1.14 \times 1010c$ ($R = 0.9936$). This method has been applied to the determination of phenol in water with satisfactory results.

1. Introduction

Phenolic compounds are used extensively in the manufacture of a wide variety of products, such as polymers, fertilizers, adhesives, paints, pesticides and explosives [1–3]. Furthermore, these compounds are easily formed in many industrial processes (e.g. petroleum, paper, tanning dye and soap industries) and during the natural decomposition of humic substances, tannins, and lignins [4,5]. However, they are highly toxic and difficult to degrade biologically [6]. Increasing concern for public health and environmental quality has led to the establishment of rigid limits on the acceptable environmental levels of phenol, which makes the determination of phenols from waste streams a world-wide research interesting.

Several methods have been reported for the determination of phenols, such as high performance liquid chromatography (HPLC) [7,8], gas chromatography (GC) [9,10], and impedance spectroscopy (IS) [3]. Although these methods have their respective advantages, there also exist some different shortcomings, such as instrument-expensive, approach-complicated, low-sensitive or time-consuming. As a rapid, simple method with inexpensive instruments, chemiluminescence (CL) combining with flow injection has received much attention in various fields [11,12]. It is characterized by high sensitivity, fast response time, wide linear range, no disturbances or light scattering, minimum background and superduper reproducibility. The luminol–H_2O_2 system is one of the most efficient CL systems, which is mostly catalyzed by enzymes [13], metal ions [14], or metal-containing species [15,16]. Horseradish peroxidase (HRP) has long been used as an enzyme catalyst, but the instability and high cost of it has stimulated people to search for alternatives. The use of metalloporphyrin complexes as a substitute for peroxidase and cytochrome P-450 has been applied in a number of analytical applications such as fluorescence and chemiluminescence analysis [17,18]. Most are based on the use of total synthesized metalloporphyrin and their derivates or natural occurred metalloporphyrins [19,20]. In the last two decades, a number of manganese-containing biomimetic complexes such as Mn-SOD, which make use of the redox capabilities of the manganese ion(s) to catalyze a variety of important biological processes, have been widely recognized and studied and showed excellent catalytic capability [21,22]. These facts led us to consider that the manganese porphyrins should play an important role in biomimic catalyzed chemiluminescence reactions. In our research, manganese (III) deuteroporphyrin was found to greatly enhance the CL emission intensity by the reaction of the studied phenol with H_2O_2 in alkaline medium, which

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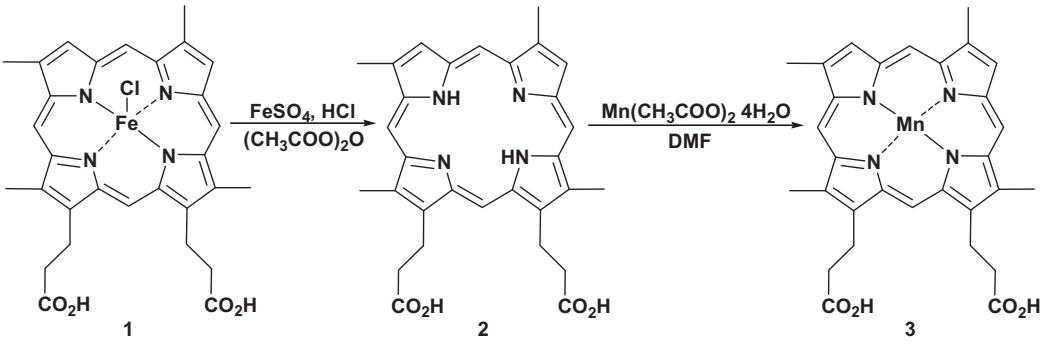


Scheme 1. Synthesis of manganese (III) deuteroporphyrin.

indicates that the manganese (III) deuteroporphyrin accelerates the CL reaction between hydrogen peroxide and phenol in alkaline medium, and increases the luminescence quantum number. To the best of our knowledge, this is the first report on the use of manganese (III) deuteroporphyrin in chemiluminescence analysis for the determination of phenolic compounds. Based on this reaction, we develop an inexpensive and simple flow injection chemiluminescence method for the determination of phenol with high sensitivity and selectivity. Furthermore, the role of manganese (III) deuteroporphyrin in CL reaction and the possible reaction mechanism was also discussed in this paper.

2. Experimental

2.1. Apparatus

An AVANCE 500 Bruker spectrometer (500 MHz) was used for ^{1}HNMR spectra using DMSO-D6 as solution and tetramethylsilane (TMS) as internal standard (Bruker, German). IR spectra were obtained by a Thermo Nicolte IS10 IR instrument (Thermo, USA). ESI–MS/MS mass spectra was obtained from a Finnigan TSQ Quantum ultra AM mass spectrometer (Finnigan, USA). Elemental analysis was conducted on a PE-2004 elemental analyzer (Perkin-Elmer, USA). The UV–vis spectra was recorded on a Lambda-35 UV-spectrofluorimeter (Perkin-Elmer, USA). Chemiluminescent measurements were performed with a model IFFM-E flow injection CL analysis system (Ruimai Electronic Science Co., China). The kinetic curve and luminescence spectra were obtained on a RF-5301pc spectrofluorometer (Shimadzu, Japan).

2.2. Chemicals

All reagents used in this work were of analytical grade and obtained commercially. Double-distilled water was used throughout. A 5.0×10^{-4} mol L^{-1} stock solution of luminol (Sigma–Aldrich) was prepared by dissolving 0.0089 g luminol in 100 mL of NaOH (0.01 mol L^{-1}) solution in a brown calibrated flask. The stock standard solution (1.00×10^{-3} g mL^{-1}) of phenol was prepared by dissolving phenol (Aladdin Reagent) in water and kept in a refrigerator (4 °C). All working solutions were prepared by diluting stock solutions with water as required.

2.3. Synthesis of manganese (III) deuteroporphyrin (**3**)

Fe (III) deuteroporphyrin (Scheme 1, **1**) was synthesized as previously described from hemin [23]. Ultrasound-promoted synthesis of deuteroporphyrin was according to our previous procedure [24]. The brief process is as follows: 2.0 g Fe (III) deuteroporphyrin and 2.0 g ferrous sulfate were added to a 150 mL of 3-neck-flask. 25 mL of acetic anhydride and 5 mL of concentrated hydrochloric acid were added drop-wise at 5 °C. Then the mixture was transferred to an ultrasound bath and was irradiated by ultrasound (40 kHz) for 60 min. The pH of the mixture was adjusted to 5.0–6.0 with 2.0 mol L^{-1} NaOH. The as-obtained brown precipitates were filtrated and washed with distilled water. The residue was recrystallized from hot acetone and dried in vacuum: yield: 95%; m.p. > 300 °C; ^{1}H NMR (500 MHz, DMSO-d_6): δ/ppm = −4.03 (s, 2H, NH), 3.27–3.30 (t, J = 7.5 Hz, 4H, 13, 17-β-CH_2, α to carbonyl), 3.63–3.77 (4 s, 12H, 2, 7, 12, 18-CH_3), 4.40–4.43 (t, J = 7.5 Hz, 4H, 13, 17-α-CH_2, α to carbonyl), 9.33, 9.35 (2 s, 2H, 3, 8-H), 10.30, 10.33, 10.35, 10.36 (4 s, 4H, 5, 10, 15, 20-H), 12.1 (s, 2H, 13, 17-COOH); IR (KBr, cm^{-1}): 3460 (m, ν_{N-H}), 2916 (m, ν_{C-H}), 1725 (s, $\nu_{C=O}$), 1435 (m), 1361 (m), 1300 (w), 1235 (w), 1196 (m), 1165 (s, ν_{C-O}), 1125 (m), 894 (w); ESI$^+$–MS (45 ev, m/z), 511 [M+H]$^+$, 452 [M+H–CH_2COOH]$^+$, 437 [M+H–CH_2COOH–CH_3]$^+$, 393 [M+H–2CH_2COOH]$^+$, 379 [M+H–CH_2COOH–CH_2CH_2COOH]$^+$; UV–vis (DMF, nm), λ_{max} (relative intensities): 397.5 (1.00), 495.6 (0.092), 527.2 (0.063), 564.9 (0.051), 619.4 (0.033); Anal. Calcd for $C_{30}H_{30}N_4O_4$: C, 70.57; H, 5.92; N, 10.97. Found: C, 70.40; H, 6.06; N, 10.89.

0.46 g deuteroporphyrin (Scheme 1, **2**, 0.9 mmol) was added to 30 mL DMF in a three-neck-flask. The mixture was heated to reflux and then 0.25 g manganese acetate tetrahydrate was added to the flask. The reaction was monitored by TLC. The solvents were removed after the reaction and the products were washed with distilled water for three times and dried in vacuum.

m.p. > 300 °C; ^{1}HNMR: paramagnetic; IR (KBr, cm^{-1}): 2925 (m, ν_{C-H}), 1716 (s, $\nu_{C=O}$), 1592 (m), 1449 (m), 1382 (m), 1266 (w), 1227 (w), 1026 (s, ν_{C-O}), 978 (m), 850 (w), 753 (m), 698 (m); ESI$^+$–MS (35 eV, m/z): 563 [M+H]$^+$, 504 [M+H–CH_2CO_2H]$^+$, 445 [M+H–2CH_2CO_2H]$^+$; UV–vis (DMF, nm), λ_{max} (relative intensities): 365.3 (1.00), 456.4 (0.893), 542.8 (0.158).

2.4. Experimental procedures

The flow injection analysis manifold, consisted of two peristaltic pumps (as shown in Fig. 1), was used throughout this study. One peristaltic pump (three channels) was used to deliver phenol (or sample solution), manganese (III) deuteroporphyrin and NaOH solutions at a flow rate of 2.5 mL min^{-1} (per tube). The other pump (two channels) was used to deliver luminol and H_2O_2 solutions at a flow rate of 2.0 mL min^{-1} (per tube). Polytetrafluoroethylene tube (0.8 mm i.d.) was used to connect all components in the flow system. The flow cell located in front of the detection window of the photomultiplier tube (PMT) was a coil of glass tubing (1.3 mm i.d.) spiraled to a diameter of 35 mm with five turns. The CL emission was converted by PMT to current signals and the output was fed to luminescence analyzer and recorded with a computer via special software.

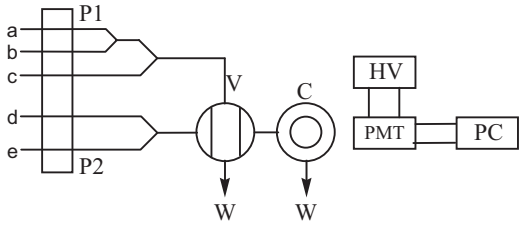


Fig. 1. Schematic diagram of flow injection CL system. (a) Phenol solution or sample solution; (b) MnDP solution; (c) sodium hydroxide solution; (d) luminol solution; (e) hydrogen peroxide solution. P, peristalticpump; V, injection valve; C, flow cell; W, waste; HV, negative high voltage; PMT, photomultiplier tube; PC, personal computer.

2.5. Sample preparation

Samples are prepared according to official volatile phenolic compounds detection method [25]. The typical procedure is: samples obtained from the sanitary sewage at various locations were acidified to pH ≈ 4 with 1.5 mol L^{-1} phosphoric acid solution. 100 mL acidified test solution was placed in a 250 mL distillation flask. Then 1 mL $CuSO_4$ solution (0.1 g mL^{-1}), 10 mL double-distilled water, three drops of methyl orange and a few glass beads were added. The mixture was distilled until the distillate reached the mark of the receiver using a mantle heater, a 35 cm long Liebig condenser and a 100 mL receiver (volumetric flask). The distillate obtained was diluted with water (if necessary) and subjected to chemiluminescence to determine phenol as described above.

3. Results and discussion

3.1. CL kinetic characteristics

The rate of CL reaction plays an important role in the design of a flow CL system. The kinetic characteristics of the proposed CL reaction were studied before the flow-injection method was carried out. The typical intensity–time response curves are shown in Fig. 2. It indicates that the CL intensity peak reached a maximum value within 3 s since the hydrogen peroxide was injected and the CL signals decreased to the baseline within 15 s. Compared with that without phenol (Fig. 2b), the emission intensity is significantly restrained. The kinetic curve manifests that the CL method is rapid and sensitive enough for FI-CL determination of phenol.

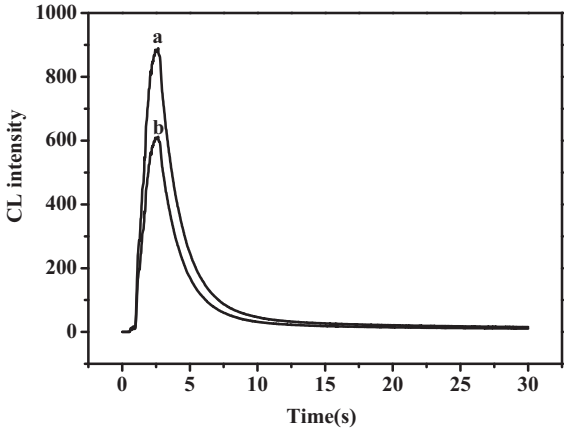


Fig. 2. Kinetic curves of chemiluminescence systems: (a) luminol + MnDP + H_2O_2 + NaOH; (b) phenol + luminol + MnDP + H_2O_2 + NaOH. The concentrations of NaOH, luminol, MnDP, H_2O_2 and phenol were 0.6 mol L^{-1}, 8.3×10^{-5} mol L^{-1}, 5.0×10^{-7} g mL^{-1}, 1.3×10^{-1} mol L^{-1} and 1.7×10^{-6} g mL^{-1}, respectively.

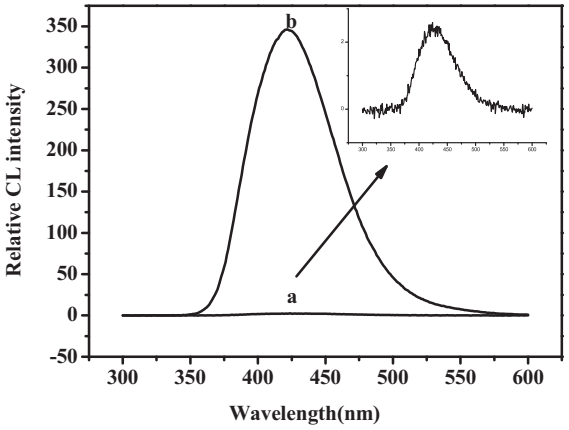


Fig. 3. Kinetic characteristics of the luminol–H_2O_2–MnDP CL system. (a) CL intensity in the absence of MnDP; (b) CL intensity in the presence of MnDP. The concentrations of NaOH, luminol, MnDP, H_2O_2 and phenol were 0.6 mol L^{-1}, 8.3×10^{-5} mol L^{-1}, 5.0×10^{-7} g mL^{-1}, 1.3×10^{-1} mol L^{-1} and 1.7×10^{-6} g mL^{-1}, respectively.

3.2. Possible CL mechanisms

In order to explore the possible mechanism, the CL emission spectrum was obtained using a RF-5301pc spectro-fluorometer, with the light source taken off, combined with a flow-injection system. The obtained CL spectrum is shown in Fig. 3. The results show that the maximum emission wavelength in both CL reactions between luminol and H_2O_2 with and without manganese (III) deuteroporphyrins is 425 nm, indicating that the luminophor in the both CL reactions is the same species which is reported to be excited-state 3-aminophthalate anions of luminol [19,26].

The UV–vis absorption spectra, as illustrated in Fig. 4, shows that in the media of NaOH (0.4 M), MnDP has two absorption peaks at 344.2 and 457.1 nm and luminol has two absorption peaks at 301.6 and 345.5 nm, respectively. Nevertheless, light absorption of the mixed system is equal to the sum of the light absorption of two individual systems. Therefore, we suggest that no effect happened between luminol and manganese (III) deuteroporphyrin. In the absence of catalysts, the oxidation of luminol by hydrogen peroxide in alkaline solution is a relatively slow reaction process and the CL intensity is relatively weak. However, the CL intensity of MnDP–luminol–H_2O_2 system is greatly enhanced and the light absorption of UV-vis spectra is greatly weakened comparing with the absorption of luminol–H_2O_2 system, which obviously indicates

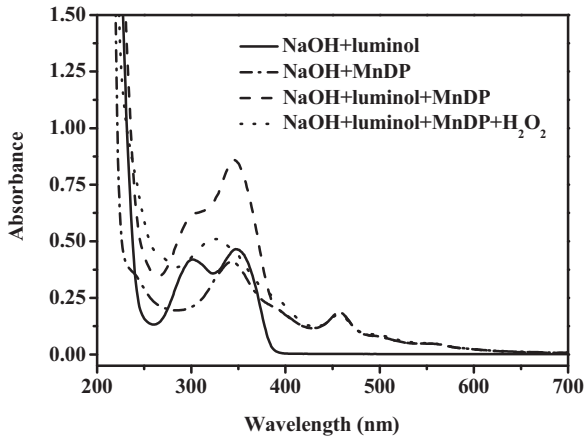
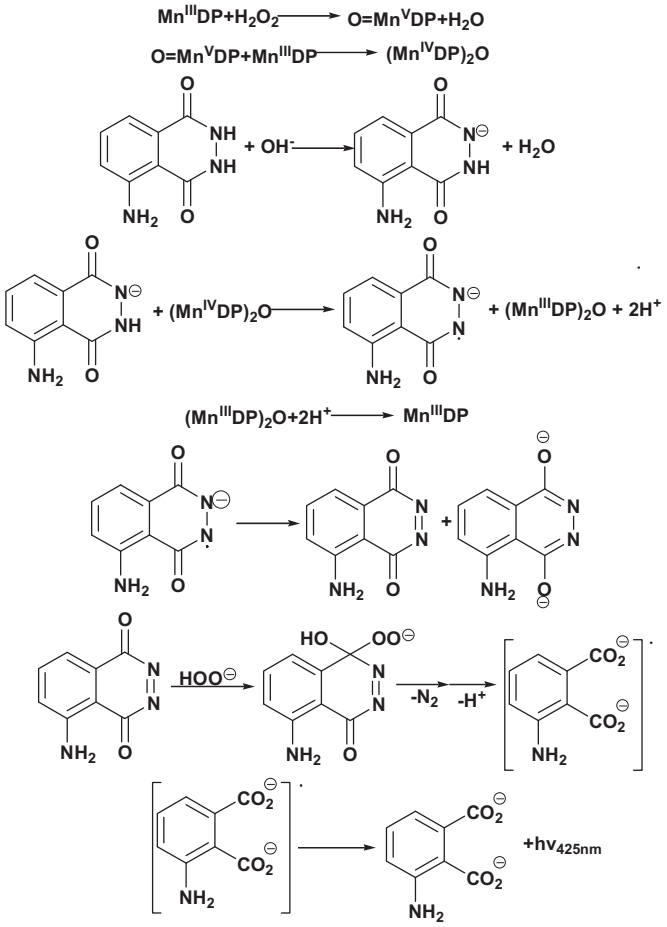


Fig. 4. UV–vis absorption spectra of MnDP–luminol–H_2O_2 system in NaOH solution. NaOH, luminol, MnDP, H_2O_2 and phenol were 0.4 mol L^{-1}, 5.0×10^{-5} mol L^{-1}, 5.0×10^{-6} g mL^{-1}, 4.8×10^{-4} mol L^{-1} and 1.0×10^{-5} g mL^{-1}.

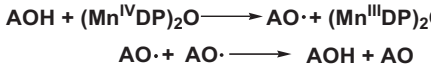


Scheme 2. The mechanism of MnDP catalyzed oxidation of luminol.

that manganese (III) deuteroporphyrin play a key role in this CL reaction.

Although the transformation of manganese (III) deuteroporphyrin in this reaction is not completely understood, it is accepted high-valent oxometalloporphyrin complexes play an important role in a variety of reactions catalyzed by biomimetic metalloporphyrin molecules of cytochrome P450 [27,28]. The mechanism of chemiluminescence reactions catalyzed by manganese (III) porphyrins in the presence of hydrogen peroxide also involves the formation of oxidizing intermediates that are formally "Mn (V)" species. Even the intermediate has not been directly detected in the process of our CL reaction, the formation of Mn (V) porphyrin species has been proved by Groves et al. [29,30] and others [28]. In the oxidation of manganese (III) porphyrins, the Mn (V) intermediate is reactive [19,29,30] and quickly reduced by manganese (III) porphyrins to a formal Mn (IV) species, which is possibly a dimeric Mn (III)-porphyrin π-cation radical complex (Scheme 2). This species is supposed to be responsible for luminol oxidation and the initiation of the reaction sequence leading finally to the production of exited 3-aminophthalate, with subsequent light emission intensity.

When antiradical molecules such as phenol is added to the system, the antiradical molecules will compete with luminol for the manganese (III) porphyrin-derived oxidizing intermediates and any other oxidant species present in the reaction mixture as well as intercept luminol-derived free radicals. The main pathway for the disappearance of the generated phenoxyl radicals is its dismutation, leading to the formation of quinoid analogues (AO) (Scheme 3) [19,31]. Thus, chemiluminescence emission will be suppressed until all antiradical compounds are completely consumed.



Scheme 3. The reaction between phenol and Mn(V)deuteroporphyrin intermediate.

3.3. Optimization of the working conditions

In order to obtain the highest sensitivity of measurements, optimization of the CL reaction conditions was performed to optimize the CL parameters, which included the component concentration and flow rate.

3.3.1. The effect of NaOH concentration

This CL reaction was performed in alkaline condition and the alkalinity of reaction medium played an important role in it. The effect of sodium hydroxide concentration on the CL reaction was studied over the range from 0.05 to 0.4 mol L^{-1} (Fig. 5a). It noticed that the relative CL intensity increased with the NaOH concentration from 0.05 to 0.1 mol L^{-1} and the maximal relative CL intensity could be obtained at the NaOH concentration of 0.1 mol L^{-1}. The relative CL intensity reduced probably because of the instability of phenol in strong basic solution above the NaOH concentration of 0.1 mol L^{-1}.

3.3.2. The effect of luminol concentration

The effect of luminol concentration on the CL signal was investigated over the range 1.0×10^{-8} to 1.2×10^{-7} mol L^{-1} (Fig. 5b). The result showed that the intensity increased with increasing luminol concentration in the whole range, but the signal to blank ratio (S/B) reached a maximum at 8.0×10^{-8} mol L^{-1}. Therefore, 8.0×10^{-8} mol L^{-1} luminol was adopted as the optimum concentration for further use.

3.3.3. The effect of manganese (III) deuteroporphyrins concentration

The effect of the manganese (III) deuteroporphyrin concentration in the range from 5.0×10^{-7} to 1.0×10^{-5} g mL^{-1} was investigated (Fig. 5c). The result showed that the relative CL intensity increased with increasing manganese (III) deuteroporphyrin concentration. When the concentration was higher than 3.0×10^{-6} g mL^{-1}, the relative CL intensity declined. Thus, the optimal concentration of manganese (III) deuteroporphyrin was 1.2×10^{-6} g mL^{-1}.

3.3.4. The effect of H_2O_2 concentration

In the CL system, H_2O_2 was the CL oxidant, which influenced the CL emission. The effect of hydrogen peroxide concentrations on relative CL intensity was studied in the range from 1.0×10^{-5} to 1.4×10^{-4} mol L^{-1} (Fig. 5d). It was found that the signal increases significantly with the increasing of H_2O_2 concentrations and the signal to blank ratio (*S*/*B*) reached a maximum at 6.0×10^{-5} mol L^{-1}. So, 6.0×10^{-5} mol L^{-1} hydrogen peroxide was chosen as the optimum concentration in this study.

3.3.5. The effect of flow rate

Flow rate is an important factor in flow-injection chemiluminescence system. The effect of flow rate on the intensity of chemiluminescence was studied over the range 0.5–4.5 mL min^{-1} in each stream. It was found that the chemiluminescence intensity increased with increasing flow rate of phenol, manganese (III) deuteroporphyrin and NaOH up to 2.5 mL min^{-1}, and luminol and H_2O_2 up to 2.0 mL min^{-1}, after which the CL intensity reached the maximum and remained constant. Therefore, flow rate of 2.5 mL min^{-1} and 2.0 mL min^{-1} were chosen for subsequent work.

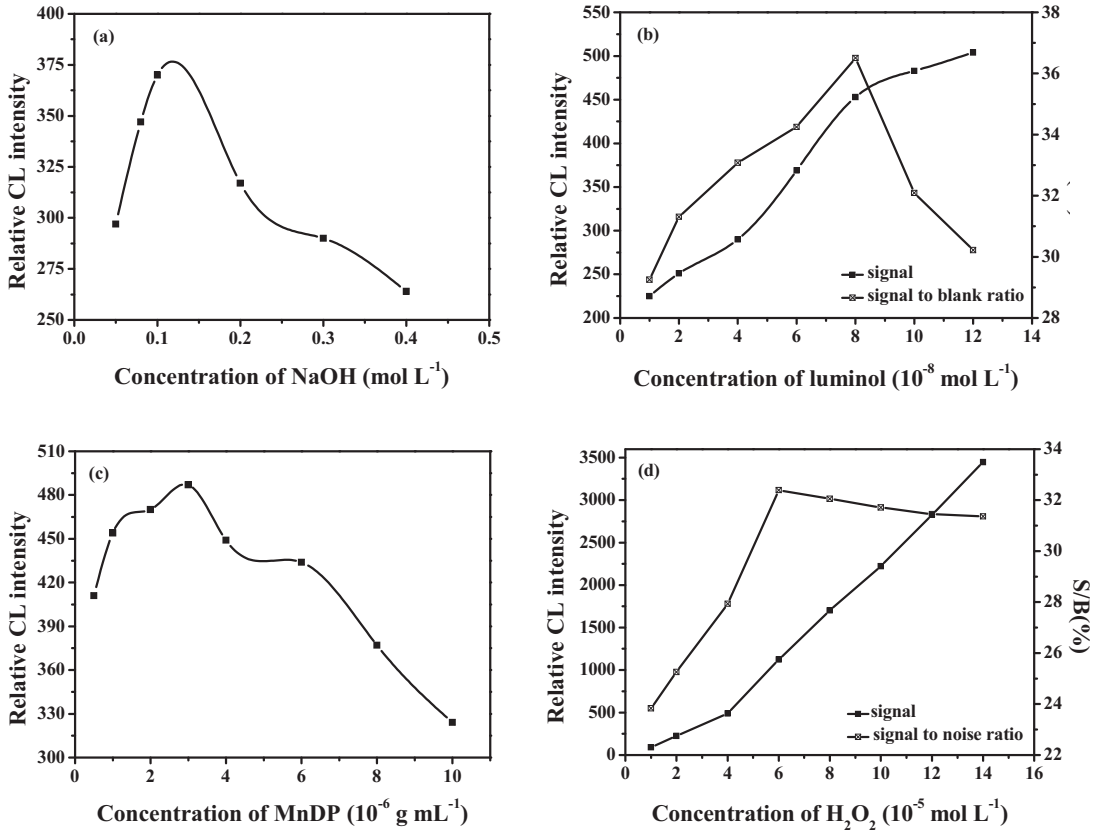


Fig. 5. Effect of concentrations of NaOH (a), luminol (b), MnDP (c) and H_2O_2 (d) on the CL intensity. (a) The concentration of luminol, manganese (III) deuteroporphyrin, H_2O_2 and phenol were 6.0×10^{-8} mol L^{-1}, 1.0×10^{-6} g mL^{-1}, 4.0×10^{-5} mol L^{-1} and 1.0×10^{-7} g mL^{-1}, respectively. (b) The concentration of NaOH, manganese (III) deuteroporphyrin, H_2O_2 and phenol were 0.1 mol L^{-1}, 1.0×10^{-6} g mL^{-1}, 4.0×10^{-5} mol L^{-1} and 1.0×10^{-7} g mL^{-1}, respectively. (c) The concentration of NaOH, luminol, H_2O_2 and phenol were 0.1 mol L^{-1}, 8.0×10^{-8} mol L^{-1}, 4.0×10^{-5} mol L^{-1} and 1.0×10^{-7} g mL^{-1}, respectively. (d) The concentration of NaOH, luminol, manganese (III) deuteroporphyrin and phenol were 0.1 mol L^{-1}, 8.0×10^{-8} mol L^{-1}, 3.0×10^{-6} g mL^{-1} and 1.0×10^{-7} g mL^{-1}, respectively.

3.4. Analytical performance

Under the optimized experimental conditions showed above, the relative CL intensity (ΔI) was linearly proportional to the phenol concentration (c, g mL^{-1}) in the range of 4.0×10^{-9} to 4.0×10^{-7} g mL^{-1} with the regression equation $I = 120.79 + 1.14 \times 10^{10} c$ ($R = 0.9936$). The detection limit (3σ) was 6.3×10^{-10} g mL^{-1} and the relative standard deviation for 1.0×10^{-7} g mL^{-1} phenol ($n = 11$) was 2.99%.

3.5. Interference

The influence of other metal ions is often found in environmental samples on the determination of phenol by the developed FI-CL method. In order to determine phenol in water, the interference of common ions was investigated using a standard solution of phenol (1.0×10^{-7} g mL^{-1}) into which increasing amount of interfering analytes was added. The tolerable limit of a foreign species was taken if it caused a relative error of less than 5% and the result was shown in Table 1.

Table 1
Interference study of some ions.

Interferences	Tolerance ratio (species: phenol)
Na^+, K^+, Cl^-, NH_4^+	1000
CO_3^{2-}	600
Br^-	500
Ga^{2+}, Pb^{2+}, PO_4^{3-}	100
Al^{3+}	50
Ba^{2+}	30
Cr^{3+}, I^-	15
Zn^{2+}, Ni^{2+}	10
Mn^{2+}	1
Fe^{3+}, Cu^{2+}	0.5

Table 2
Determination of phenol in water.

Sample	Spectrophotometry [25] (g mL^{-1}, $n = 7$)	Proposed method (g mL^{-1}, $n = 7$)	R.S.D. (%)
1	3.17×10^{-7}	3.16×10^{-7}	2.50
2	6.85×10^{-7}	6.99×10^{-7}	2.55
3	1.87×10^{-6}	1.90×10^{-6}	2.09

3.6. Applications

The proposed method was applied to the determination of phenol in waste water samples and compared with official 4-AAP spectrophotometric method [25]. The results were shown in Table 2 and agreed well with those detected by official spectrophotometric method.

4. Conclusions

A sensitive, specific, accurate and rapid FI-CL method was developed for the determination of phenol, using manganese (III) deuteroporphyrin enhanced luminol–H_2O_2 CL system. The optimization of the experimental parameters has been carried out. The

sensitivity, simplicity and stability of the analysis procedure make the developed method as an attractive alternative to other ones.

Acknowledgments

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