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# Determination of cyanide using a chemiluminescence system composed of permanganate, rhodamine B, and gold nanoparticles

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**Abstract** We describe a new chemiluminescence (CL) system based on the oxidation of rhodamine B (RhoB) with alkaline potassium permanganate in the presence of gold nanoparticles (Au-NPs) and anionic detergent sodium dodecyl sulfate. Free RhoB is weakly chemiluminescent when oxidized with permanganate at alkaline pH values. However, a remarkably strong enhancement of CL is observed in the presence of Au-NPs, probably due to a strong interaction between RhoB and the NPs. The possible mechanism was studied via recording the CL emission. It is also found that the intensity of CL gradually decreases in the presence of cyanide due to its interaction with the Au-NPs. The relation between the decreased CL intensity and cyanide concentration was exploited to develop a method for the determination of cyanide in the 0.01–0.5  $\mu\text{M}$  concentration range, with a detection limit of 2.8 nM. The method was used to determine cyanide in spiked water, urine, and serum.

**Keywords** Chemiluminescence · Gold nanoparticles · Rhodamine B · Permanganate · Cyanide

## Introduction

Chemiluminescence (CL)-based analytical methods have many advantages including rapid and simple detection, wide linear dynamic range, good reproducibility, excellent detection limit and high sensitivity. Acidic potassium permanganate

as a versatile oxidizing agent is extensively used in CL reactions [1]. However, it can oxidize many species and hence, there will be many possible interferences with such CL reactions. Moreover, some species may be unstable in acidic conditions. Cyanide, for example, is protonated in acidic medium and produces dangerous HCN vapor. The use of alkaline permanganate as a CL reagent may overcome these problems. A few reports on the application of alkaline  $\text{KMnO}_4$  in CL have appeared in the literature [2–4].

In recent years, Au or Ag nanoparticles (NPs) have been favorably utilized as an active unit in the chemiluminescence assays to improve their sensitivity [5, 6]. In these systems, NPs may act as catalyst, reductant, luminophore or energy acceptor. Our group has studied the enhancing effect of metal NPs on some acidic permanganate CL reactions [7, 8]. In order to broaden the analytical applications and reduce interferences, we decided to examine the alkaline medium for such systems.

Cyanide ( $\text{CN}^-$ ) is an extremely toxic lethal poison that can rapidly cause human death only at 300 ppm amount. This effect is due to its strong propensity to suppress cellular respiration through binding to the active site of cytochrome c oxidase, interfering with electron transport and resulting in hypoxia. Low amounts of cyanide in long-term exposure can also affect the central nervous actions [9–19]. The U.S. environmental protection agency (EPA) has set the maximum contaminant level for cyanide in drinking and environmental waters, at very low levels of 200 and 5  $\mu\text{g L}^{-1}$ , respectively [20]. Cyanide poisoning can also occur from smoke inhalation from both residential and industrial fires, and in those people who work in the metal industries [12, 13, 17]. Thus the determination of blood cyanide levels in fire victims is an area of active research. Blood cyanide levels for asymptomatic persons have been reported as being  $\sim 0.3 \text{ mM}$  [9], while lethal cyanide blood levels for fire victims are in the range of 23–26 mM [12, 17].

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Several analytical methods such as colorimetric [14, 18], chromatographic [12, 21], fluorimetric [10, 13, 15, 17, 22, 23], chemiluminescence [11, 24], surface enhanced Raman spectroscopy [16, 25] and electrochemical [26] methods have been developed for cyanide detection. However, many of these methods have tedious sample pretreatment or measurement stages. Therefore, the developing simple and sensitive methods for cyanide detection, is still a valuable analytical task.

In this study, we present a new CL reaction based on rhodamine B (RhoB)-KMnO<sub>4</sub> reaction in alkaline medium. This reaction produces a very weak CL emission but, the presence of Au-NPs causes an extremely high increasing effect. We further exploited the dissolving effect of CN<sup>-</sup> on gold NPs to develop a highly sensitive CL sensor for detecting cyanide anion.

## Experimental

### Reagents

All reagents were of analytical grade and used without further purification. All solutions were prepared with deionized water (obtained from Kasra Co. Tabriz, Iran). Sodium citrate, KMnO<sub>4</sub>, NaBH<sub>4</sub>, sodium dodecyl sulfate (SDS), NaOH and RhoB were obtained from Merck (Darmstadt, Germany; [www.merck-chemicals.com](http://www.merck-chemicals.com)). Chloroauric acid (HAuCl<sub>4</sub>) was purchased from Alfa Aesar (Karlsruhe, Germany; [www.alfa.com](http://www.alfa.com)). A 1.0 mM stock solution of cyanide was prepared by dissolving appropriate amount of KCN powder (Merck) in deionized water.

### Apparatus

The chemiluminescence detection was conducted on a LUMAT LB 9507 chemiluminometer (Berthold; [www.berthold.com](http://www.berthold.com)). Ultraviolet–visible (UV–vis) spectra were recorded on a Cary-100 Spectrophotometer (Varian; [www.varianinc.com](http://www.varianinc.com)). The size and shape of the NPs were confirmed through transmission electron microscopy (TEM, Leo 906, Zeiss, Germany). Fluorescence and CL spectra were obtained on a Shimadzu RF-540 spectrofluorometer.

### Preparation of Au and Ag nanoparticles with different sizes

Au-NPs of ca. 8 nm were prepared by a reported procedure [27]. Colloidal Au-NPs of 22, 32, and 75 nm in diameter were synthesized according to Frens method [28]. For the synthesis of 22 nm gold colloids, 100 mL of HAuCl<sub>4</sub> ( $2.5 \times 10^{-4}$  M) solution was heated to boiling. While stirring vigorously, 5 mL of 1 % trisodium citrate solution was added rapidly. The solution was maintained at boiling point until a color

change to red was evident. The heating source was then removed and the solution was continuously stirred for another 2 min. Similar procedures with suitable volumes of HAuCl<sub>4</sub> and trisodium citrate solution were adopted for the synthesis of gold colloids with diameters of 32 and 75 nm. The resultant Au-NPs were stored at 4°C. The size and shape of NPs were characterized by transmission electron microscopy (TEM). Statistical analysis of TEM data revealed that the average diameters of the gold nanoparticles were about  $8 \pm 2.2$ ,  $22 \pm 1.8$ ,  $32 \pm 2.1$  and  $75 \pm 4$  nm. The concentrations of these NPs were calculated to be  $3.61 \times 10^{-8}$ ,  $9.45 \times 10^{-10}$ ,  $2.07 \times 10^{-10}$  and  $9.77 \times 10^{-12}$ , respectively, using the extinction coefficients [29].

Ag-NPs of 6, 18, and 38 nm in diameter were prepared according to references [30, 31] and [32], respectively. The resulting NPs were characterized by TEM and statistical analysis revealed that the average diameter of particles was  $6 \pm 1.2$ ,  $18 \pm 1.4$  and  $38 \pm 1$  nm. The concentrations of these NPs were calculated to be  $4.32 \times 10^{-7}$ ,  $9.17 \times 10^{-9}$  and  $2.10 \times 10^{-9}$ , respectively [33].

### Sample preparation

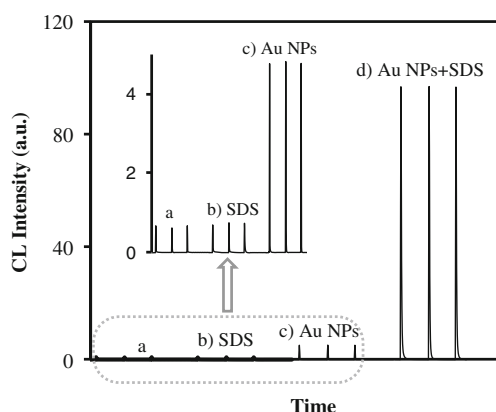
A suitable aliquot of environmental water samples was taken for the determination of CN<sup>-</sup> according to the general procedure without any pretreatment.

Human urine sample containing CN<sup>-</sup> was obtained by adding suitable concentration of standard cyanide to CN<sup>-</sup>-free urine. One mL of this sample was gently vortex-mixed with 2 mL of 0.1 M Ba(OH)<sub>2</sub> and 0.1 M ZnSO<sub>4</sub> solution, put aside at room temperature for 10 min, and then centrifuged at 4,000 rpm for 10 min. The clear supernatant was diluted to the appropriate concentration and analyzed according to the general procedure.

Human serum sample was spiked by adding suitable concentration of cyanide standard solution. One mL of the spiked serum sample was mixed with 0.5 mL of acetonitrile and centrifuged at 4,000 rpm for 10 min. The resulted supernatant was used for analysis.

### General procedure for chemiluminescence detection

Chemiluminescence measurements were done in a 3 mL tube in the batch condition. 250  $\mu$ L of RhoB (0.2 mM), 45  $\mu$ L of SDS (0.001 M), 500  $\mu$ L of NaOH (4 M), and 1,000  $\mu$ L of Au-NP solution (~22 nm) were added into the cell. Then an appropriate volume of sample or standard cyanide solution was added and the final volume was reached to 2.5 mL with deionized water. After 8 min, 75  $\mu$ L of KMnO<sub>4</sub> (0.005 M) was injected by an automatic injector and the CL signal was monitored versus time automatically. Maximum CL intensity was used as analytical signal.

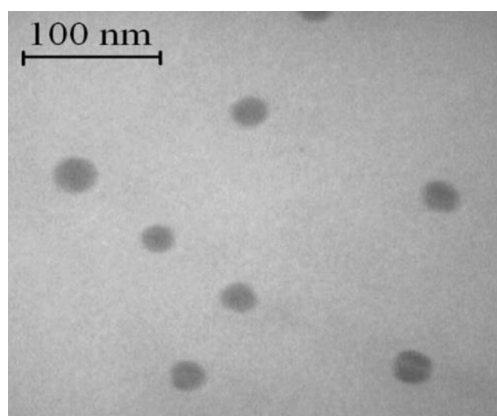


**Fig. 1** CL profiles of alkaline  $\text{KMnO}_4$ -RhoB **a, b** and alkaline  $\text{KMnO}_4$ -RhoB-Au-NPs **c, d** systems in presence **b, d** and absence **a, c** of SDS. The concentrations of RhoB, NaOH, SDS and  $\text{KMnO}_4$  were 0.02, 0.8,  $1.8 \times 10^{-5}$  and  $1.5 \times 10^{-4}$  M, respectively. 1,000  $\mu\text{L}$  of Au-NPs was used

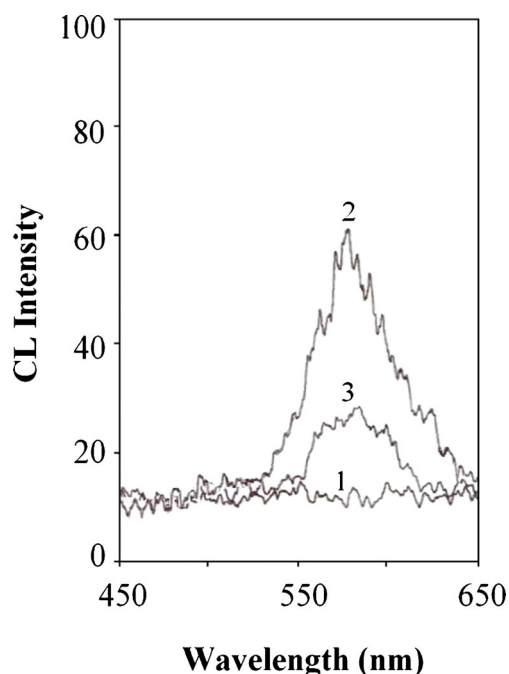
## Results and discussion

### Alkaline $\text{KMnO}_4$ -rhodamine B chemiluminescence system and effect of Au nanoparticles

The CL system in this work is based on the oxidation of RhoB by permanganate in alkaline medium which, to the best of our knowledge, has not been introduced in the literature up to now. It was found in preliminary experiments that RhoB- $\text{KMnO}_4$  in alkaline medium produces an ultra-weak CL, which can be enhanced remarkably in the presence of Au or Ag-NPs (Fig. 1). Furthermore, it was observed that addition of anionic surfactant SDS together with NPs considerably increases the CL intensity (Fig. 1). Effect of NPs on  $\text{KMnO}_4$  CL systems in alkaline condition is more considerable than that in acidic medium. Acidic solution can destroy the NPs and decrease their catalytic ability. Moreover, as mentioned before, in alkaline media  $\text{KMnO}_4$  cannot oxidize many species and, so, most of interferences are eliminated.

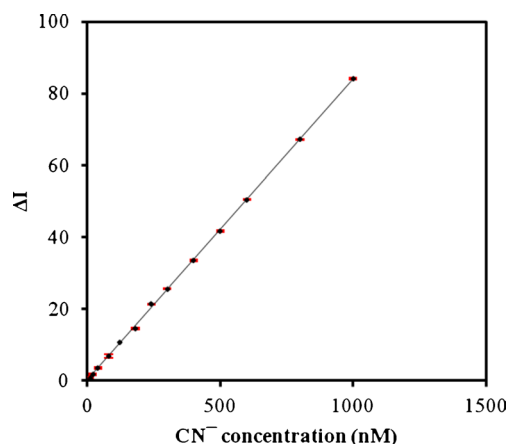


**Fig. 2** TEM image of applied Au-NPs



**Fig. 3** CL spectrum of alkaline  $\text{KMnO}_4$ -RhoB-SDS system (1) together with Au-NPs in the absence (3) and presence of  $\text{CN}^-$  (1.0  $\mu\text{M}$ ) (2). The spectra were obtained with continuous flow of reagents.  $\text{KMnO}_4$  ( $3 \times 10^{-4}$  M) in one line and NaOH (1.2 M), SDS ( $4 \times 10^{-5}$  M) and RhoB (0.04 M) with or without Au-NPs in the other line

Table S1 (Electronic Supplementary Material, ESM) shows the effect of Au and Ag-NPs with different sizes on alkaline permanganate-RhoB CL reaction. Each nanoparticle was tested at various concentrations and the maximum responses are indicated in Table S1. As can be seen, the enhancing effect of Au-NPs with average size of about 22 nm is the most remarkable compared to other examined NPs. Figure 2 shows TEM image of the synthesized Au-NPs which confirms their proper synthesis and sizes.



**Fig. 4** Calibration graph for  $\text{CN}^-$  using the CL system at the optimum conditions

**Table 1** Summary of the published NP- or CL- based methods for determination of cyanide

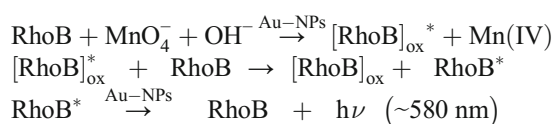
| Method   | Linear range ( $\mu\text{M}$ ) | Sample                              | Limit of detection (nM) | Ref. |
|--|--------------------------------|-------------------------------------|-------------------------|------|
| Nanostructured gold surface-enhanced Raman       | 0.077–7.7                      | Water samples                       | 27                      | [25] |
| CL (Luminol- <i>p</i> -nitrobenzaldehyde- hemin) | 0.02–2                         | –                                   | 4                       | [24] |
| CL (Luminol- $\text{H}_2\text{O}_2$ )            | 0.5–50                         | Blood sample or rabbit              | 230                     | [11] |
| CdSe fluorescence                                | 20–100                         | Water samples                       | –                       | [10] |
| Fluorescence-inner filter effect of Au-NPs       | 1–600                          | Water samples                       | 600                     | [22] |
| Fluorescent- $\text{Cu}^{2+}$ modified CdTe      | 0.3–12                         | Water samples and biological fluids | 150                     | [13] |
| Colorimetric, Au-NPs                             | –                              | Water samples and biological fluids | 10,000                  | [14] |
| Fluorescence- polymer coated Au-NPs              | –                              | Water samples                       | 300                     | [15] |
| Gold NPs surface-enhanced Raman                  | 4–156 nM                       | Water samples                       | –                       | [16] |
| The present method                               | 0.01–0.5                       | Water samples and biological fluids | 2.8                     | –    |

### Possible mechanism for chemiluminescence reaction

In order to characterize the possible emitting species, the CL emission spectrum was recorded for alkaline  $\text{KMnO}_4$ - RhoB system in the presence of Au-NPs using a spectrofluorimeter with closed excitation slit (Fig. 3). As can be seen, a characteristic peak around 580 nm has been obtained which is similar to the fluorescence spectrum of RhoB in alkaline medium ( $\lambda_{\text{em}}=585$  nm and  $\lambda_{\text{ex}}=558$  nm). This reveals that the emitting species in the CL reaction is probably RhoB.

It has been demonstrated that RhoB molecules can noncovalently adsorb on the surfaces of Au-NPs [34]. This is obvious from severe quenching of RhoB fluorescence in the presence of Au-NPs. A combination of the electrostatic and  $\pi$ - $\pi$  interactions between the negative citrate moieties and the positive groups of RhoB molecules controlled the interaction between Au-NPs and RhoB [34, 35].

The fluorescence intensity of RhoB decreases strongly after addition of  $\text{KMnO}_4$  which indicates that a reaction occurs between  $\text{KMnO}_4$  and RhoB. It can be suggested that RhoB oxidation by permanganate, can result in the production of an excited-state intermediate which then, transfer its energy to RhoB molecules and emission occurs from them. In presence of Au-NPs, the rate of RhoB oxidation or energy transferring efficiency may be improved.



### Optimization of chemical conditions.

As mentioned before, the addition of SDS to the CL system increases the emission intensity. We investigated the effect of some other surfactants (AOT, Triton  $\times 100$  and CTAB) at various concentrations on the CL system in the presence of Au-NPs and observed that only SDS increases the CL signal. Figure S1-a (ESM) shows that the maximum CL intensity was obtained at  $3 \times 10^{-5}$  M SDS concentration. This is quite below the critical micellar concentration (CMC) of SDS. Therefore, the significant enhancement effect of this surfactant is not a micellar phenomenon, and may be related to the electrostatic interaction between RhoB and SDS and/or to the change of the microenvironment of the reaction.

To investigate the effect of concentration of NaOH, different concentrations were tested and the maximum CL response was achieved at 0.8 M (Fig. S1-b, ESM). Probably, at lower NaOH concentrations, the rate of the reaction is decreased and hence, the CL intensity is reduced. Higher concentrations can cause the aggregating or demolishing the NPs and therefore, CL signal is again decreased.

**Table 2** Interference of different ions on the CL intensity of alkaline RhoB –  $\text{KMnO}_4$  – Au-NPs in optimum condition with 50 nM  $\text{CN}^-$ 

| Potentially interfering substance   | Tolerance limit (interference to analyte ratio) |
|---|---|
| $\text{Na}^+$ , $\text{K}^+$ , $\text{F}^-$ , $\text{Cl}^-$ , $\text{Br}^-$ , $\text{I}^-$ , $\text{CO}_3^{2-}$ , $\text{NO}_2^-$ , $\text{NO}_3^-$ , $\text{SO}_4^{2-}$ , $\text{CH}_3\text{COO}^-$ , $\text{IO}_3^-$ , $\text{PO}_4^{3-}$ , $\text{Ca}^{2+}$ , $\text{Mn}^{2+}$ , $\text{Ni}^{2+}$ , $\text{Mg}^{2+}$ , $\text{Pb}^{2+}$ , $\text{Cd}^{2+}$ | 4,000   |
| $\text{Zn}^{2+}$ , $\text{Ag}^+$ , Vitamins B <sub>1</sub> , B <sub>2</sub> , Oxalate, Glucose, Cysteine, Ascorbic acid, Glutathione, Alanine, Lactose, Uric Acid, Citrate  | 2,000   |
| $\text{SO}_3^{2-}$ , $\text{S}^{2-}$ , $\text{SCN}^-$   | 200   |
| $\text{Cu}^{2+}$ , $\text{Hg}^{2+}$   | 15  |



The effect of RhoB concentration over the range of 8 to 36  $\mu\text{M}$  was also examined. According to the results (Fig. S1-c, ESM), increasing RhoB concentration up to 20  $\mu\text{M}$  enhanced the CL intensity because the reaction proceeds and more excited-state RhoB are produced. Excess RhoB, however, decreased the CL emission probably as a result of self-absorption. The maximum CL intensity was obtained at 20  $\mu\text{M}$  RhoB, and this amount was used as the optimum concentration.

The effect of Au-NP (~22 nm) concentration on the CL response was examined. It can be seen from the results (Fig. S1-d, ESM) that optimum CL response is achieved by the addition of  $3.67 \times 10^{-10}$  M of Au-NP solution.

Finally, in order to investigate the effect of permanganate concentration, solutions with concentration of  $\text{KMnO}_4$  in the range of  $5 \times 10^{-5}$  to  $3 \times 10^{-4}$  M were prepared. As shown in Fig. S1-e (ESM), the CL signal increased with increasing permanganate concentration up to  $1.5 \times 10^{-4}$  M and then decreased at its higher concentrations. At lower  $\text{KMnO}_4$  concentrations the number of excited-state species is decreased and the response is diminished. The decrease at higher  $\text{KMnO}_4$  concentrations is probably due to the interaction of NPs by excess  $\text{KMnO}_4$ .

#### Analytical application of the chemiluminescence system

We found that ultra-trace amounts of cyanide have a considerable diminishing effect on the CL intensity of alkaline  $\text{KMnO}_4$ -RhoB-Au-NPs CL system. Cyanide is well known to be capable of dissolving gold in the presence of oxygen and in alkaline aerated solutions. It is related to  $\text{CN}^-$  extreme ability to form  $\text{Au}(\text{CN})_4^-$  complex with Au atoms on Au-NPs [22, 23, 25]. So, etching of Au-NPs might be happened in the presence of  $\text{CN}^-$  and the NPs are decreased in size, thus RhoB molecules leave their surfaces. The free RhoB molecules do not emit considerably and the CL intensity of the system is decreased (Fig. 3). The kinetic study showed that the CL intensity decreased rapidly in the first 8 min after addition of  $\text{CN}^-$  and then remained constant.

The decrease in CL intensity is proportional to the  $\text{CN}^-$  concentration and based on this phenomenon a sensitive method was developed for the determination of  $\text{CN}^-$ . In optimum condition, the difference between CL intensity ( $\Delta I = I_0 - I$ ) in the absence ( $I_0$ ) and presence of  $\text{CN}^-$  ( $I$ ) was plotted versus the concentration of  $\text{CN}^-$  in M. The calibration graph and corresponding CL profiles are shown in Fig. 4 and Fig S2 (ESM), respectively. The linear dynamic range was 0.01–0.50  $\mu\text{M}$ , with a detection limit (3 s) of 2.8 nM. The relative standard deviations (RSD %) for five replicate determinations of 20, 80 and 300 nM  $\text{CN}^-$  were 3.1, 1.4 and 0.47 %, respectively. These results indicate that this CL system has a good linearity, relatively high sensitivity and suitable precision. Comparison between the developed method and some other reported analytical methods for the  $\text{CN}^-$  quantification is shown in Table 1. As can be seen, the

linear dynamic range and sensitivity of the developed method are better than most of other CL or NP-based methods.

It should also be noted that alkaline  $\text{KMnO}_4$ -RhoB-Au-NPs is a novel CL system which can have potential applications in the determination of some other important compounds.

#### Study of interferences

In order to test the interference effect of some potentially interfering substances, increasing amounts of these species were added into a solution of 50 nM cyanide and determination was performed. The tolerable concentration ratios for interferences in relative error of <5 % are shown in Table 2. As can be seen, the amounts of most of the potentially interfering species in biological fluids are below their tolerable levels, so there would be no interferences from these species in cyanide determination.

#### Analysis of real samples

The procedure was easily applied to the determination of cyanide in environmental and human biological samples (Table S3, ESM). In order to validate the method, known quantities of cyanide were added into the samples before pretreatment step, and then the samples were prepared and analyzed according to the general procedure. Statistical analysis of these results using Student *t*-test showed that there are no significant differences between the added and found values.

#### Conclusion

Alkaline  $\text{KMnO}_4$ -RhoB system was described as a new reaction that generates a weak CL emission. The CL intensity of this system is considerably enhanced in the presence of Au and Ag-NPs. The size effect of NPs was investigated and possible mechanism was discussed for the reaction. In addition, a sensitive method was developed for the determination of cyanide that is based on the inhibiting effect of cyanide on the action of Au-NPs due to their complex formation. The method has good linearity, high sensitivity and appropriate precision, and is suitable for the determination of cyanide in environmental and biological samples.

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