Determination of As(V) ion by Chemiluminescence Method

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A method to determine As(V) ions in aqueous solution by chemiluminescence method has been studied using a stopped flow system. The method is based on the increased chemiluminescence intensity with the addition of As(V) ion to a solution of lucigenin and hydrogen peroxide. The effects of KOH concentration, H_2O_2 concentration and flow rate of reagents on the chemiluminescence intensity have been investigated. The calibration curve for As(V) was linear over the range from 1.0×10^{-6} M to 1.0×10^{-4} M, the coefficient of correlation was 0.997 and the detection limit was 3.3×10^{-7} M under the optimal experimental conditions.

Key words : Chemiluminescence, Lucigenin, Determination, As(V) ion

1. Introduction

Chemiluminescence method based upon the difference of chemiluminescence signal due to the change of analyte contents is a very active area of current research in analytical chemistry[1-3]. The chemiluminogenic reagents commonly used are luminol(3-aminophthalhydrazide)[4], lucigenin[5], potassium permanganate[6], acridinium esters[7], peroxyoxalates[8], dioxetanes[9] and Ru(II) ion[10]. Luminol which is the most widely used for chemiluminogenic reagent reacts with oxidizing agents such as oxygen and hydrogen peroxide to produce chemiluminescing product. The chemiluminescence spectrum for this reaction shows a broad band whose maximum intensity appears at 425 nm[11].

The chemiluminescence intensity from luminogenic reagent is directly proportional within certain limits to the concentration of hydrogen peroxide, the catalyst, or luminogenic reagent itself. Metal ions such as Co^{2+}, Cu^{2+}, Fe^{3+} and Eu^{3+} or various metal complexes used for the catalyst for the chemiluminescence reaction have been determined by measuring the difference in chemiluminescence intensity due to the change of concentration[12]. The chemiluminescence analysis has several advantages such as the low detection limit, the high sensitivity, the high selectivity, the ease of manipulation and the inexpensive instrumentation[3].

This paper describes a method for the determination of As(V) ion by chemiluminescence method by using a stopped flow injection system. In the present work, lucigenin has been used for the chemiluminogenic reagent and hydrogen peroxide for the oxidizing agent. The optimum analytical conditions for the determination of As(V) ion were obtained on the basis of the results of the effects of pH of the chemiluminogenic solution, concentrations of reagents and flow rate on the chemiluminescence intensity.

2. Experimental Methods

2.1 Reagent

Lucigenin (Bis-N-methylacridium nitrate) and $Na_2HAsO_4H_2O$ were obtained from Aldrich (Milwaukee, WI, USA). Hydrogen peroxide (30%) and potassium hydroxide were purchased from Sigma (St. Louis, MO, USA). All the other chemicals were of analytical reagent grade and were used as received. Deionized water was obtained by means of a Millipore (Bedford, MA, USA) Milli-Q water system and used throughout the whole experiment. A stock solution of As(V) ion(1.0×10^{-2} M) was prepared by dissolving an appropriate amount of $Na_2HAsO_4H_2O$ in deionized water.

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2.2 Instrumentation

A schematic diagram of an automated stopped flow injection analyzer used in the chemiluminescence measurements is shown in Fig. 1. The flow system employed in this work consisted of two peristaltic pumps (Ismatec Model MS-4 Reglo/6-100, Glattbrugg-Zürich, Switzerland). One (P1) delivered a chemiluminogenic reagent solution (R1) and a sample solution (R2). The other (P2) delivered a hydrogen peroxide solution and potassium hydroxide solution (R3). The sample solution was mixed with the mixture of P1 stream in a Y-shaped element positioned at 5 mm before the flow cell inlet. PTFE tubing (0.8 mm i.d.) was used to connect all the components of this system. A bifurcated optical fiber bundle (Model 77533, Oriel, Stratford, CT, USA) was screwed to the flow cell for the position of the sensing tip of the optical fiber to be the same for each measurement. The flow cell was housed in a laboratory made light tight chamber to remove all the unnecessary stray light. One end of the fiber bundle was fixed at 10 mm before the emission port and the other end at 10 mm before the excitation port of the cell component of a spectrofluorometer (Model FL111, Spex, Edison, NJ, USA). To record emission and excitation spectra, a 450 W Xe lamp was used. To measure chemiluminescence intensity, the Xe lamp was shut off and the luminescence emitted from the cell was fed to a photomultiplier tube (Model R928, Hamamatsu, USA). The voltage used for the photomultiplier tube was 900 V. The acquisition mode used was signal/reference (S/R) for the excitation and emission spectra and signal (S) for the chemiluminescence measurements. The chemiluminescence intensity at 473 nm was monitored for the determination of As(V) ion. For the chemiluminescence measurements the integration time and slit width was 1 s and 5 mm, respectively.

2.3 Procedure

A chemiluminogenic reagent solution containing 1.0×10^{-5} M luciginen was used for calibration. The chemiluminogenic reagent solution was not stable under ambient conditions, and a fresh solution was made daily. The As(V)

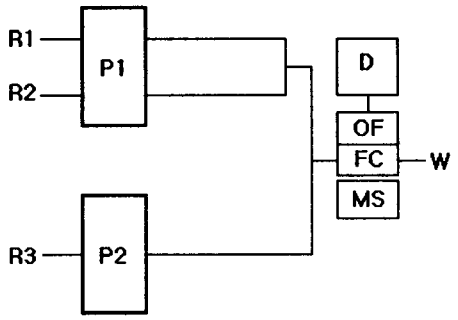

Fig. 1. Schematic diagram of a stopped flow analyser for chemiluminescent determination of As(V) ion in aqueous medium: R1, lucigenin solution; R2, sample stream; R3, H_2O_2 solution and KOH; P1 and P2, peristaltic pump; FC, flow cell; Ms, magnetic stirrer; OF, bifureated optical fiber bundle; D, detector, W, waste.

standard solutions were freshly prepared by appropriate dilution of the 1.0×10^{-2} M stock solution. The volume of chemiluminogenic reagent, potassium hydroxide solution, hydrogen peroxide and sample solution injected for the stopped flow analysis was 0.9 mL for each measurement. The flow rate flowing through the flow cell was programmed to be 5.0 mL min^{-1}. Calibration plots of chemiluminescence intensity measured at 473 nm versus concentration of AS(V) standard solution were carried out. For each standard solution, 3 successive measurements were conducted.

3. Results and Discussion

3.1 Effect of concentration of H_2O_2

Fig. 2 shows the chemiluminescence intensity as a function of H_2O_2 concentration in the presence of 1.0×10^{-5} M lucigenin. The chemiluminescence intensity is increasing on increasing the concentration of H_2O_2 up to about 1.2. Further increases in peroxide concentration reduce light emission, and a H_2O_2 concentration of 1.2 M was selected for the present analysis. To obtain the optimum concentration of luminol, we measured chemiluminescence intensity as a function of luminol concentration in the presence of 1.2 M H_2O_2. Up to 1.0×10^{-5} M of lucigenin, chemiluminescence was proportional to lucigenin concentration, but at higher concentration chemiluminescence signal decreased.

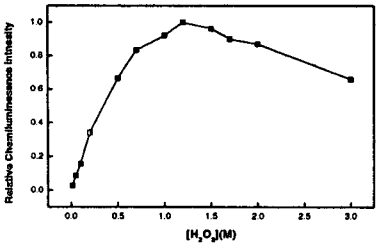

Fig. 2. Effect of H_2O_2 concentration on chemiluminescence intensity: [As(V)], 1.0×10^{-5} M; [lucigenin], 1.0×10^{-5} M; [KOH], 1.7 M; flow rate, 5.0 mL/min.

3.2 Effect of concentration of KOH

Fig. 3 shows the chemiluminescence intensity as a function of KOH concentration in the presence of 1.0×10^{-5} M lucigenin. The chemiluminescence intensity is increasing on increasing the concentration of KOH up to about 1.7. Further increases in KOH concentration reduce light emission, and a KOH concentration of 1.7 M was selected for the present analysis. To obtain the optimum concentration of lucigenin, we measured chemiluminescence intensity as a function of lucigenin concentration in the presence of 1.7 M KOH. Up to 1.0×10^{-5} M of lucigenin, chemiluminescence was proportional to luminol concentration, but at higher concentration chemiluminescence signal

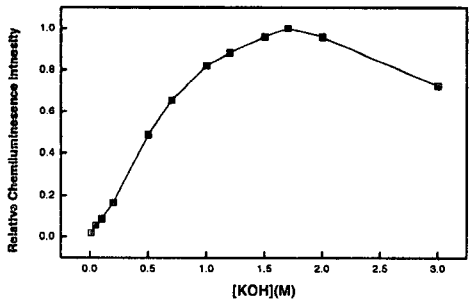

Fig. 3. Effect of KOH concentration on chemiluminescence intensity: [As(V)], 1.0×10^{-5} M; [lucigenin], 1.0×10^{-5} M; [H_2O_2], 1.2 M; flow rate, 5.0 mL/min.

decreased.

3.3 Effect of flow rate

The flow rate of reagents delivered to a flow cell is an essential factor for chemiluminescence measurements using a flow injection system because it determines the contact time between reactants and a sensing tip. It also controls, to some extent, the diffusion of reactants from the flowing solution to a sensing tip. Therefore, the influence of the flow rate of the chemiluminogenic reagent solution on the chemiluminescence response was investigated in the 1.0 - 6.5 mL min^{-1} range.

For this work, the volumes taken on the basis of the results of initial crude optimization were 0.9 mL for lucigenin, H_2O_2 and As(V) ion solution, respectively. The result is shown in Fig. 4. The lower flow rates resulted in higher contact time for the sensing tip of optical fiber but they were found to be unfavorable for the sensitivity because the chemiluminescence reaction is a very fast process. A flow rate of 5.0 mL min^{-1} was chosen in this work for optimum value to have a fast response as well as a high chemiluminescence intensity.

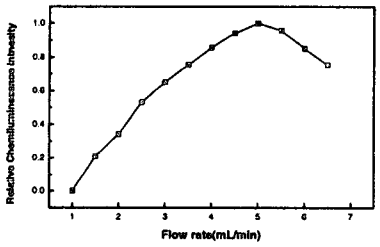

Fig. 4. Effect of flow rate on chemiluminescence intensity: [As(V)], 1.0×10^{-5} M; [lucigenin], 1.0×10^{-5} M; [H_2O_2], 1.2 M; [KOH], 1.7 M.

3.4 Calibration curve for As(V)

The average of peak heights of three successive chemiluminescence signals obtained under the optimum experimental conditions for each As(V) ion standard solution was used for calibration. Fig. 5 shows a typical calibration curve for different As(V) ion concentrations.

A linear response to As(V) ion concentration was established over the range of 1.0×10^{-6} - 1.0×10^{-4} M. The correlation coefficient in this range was 0.997. The detection limit (3σ) was found to be 3.3×10^{-7} M.

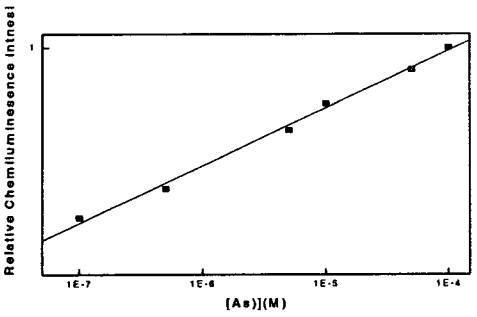

Fig. 5. Calibration curve for As(V) ion obtained by chemiluminescence method using a stopped flow system: [lucigenin], 1.0×10^{-5} M; [H_2O_2], 1.2 M; [KOH], 1.7 M; flow rate, 5.0 mL/min.

4. Conclusions

A method to determine As(V) ion in aqueous solution by chemiluminescence method using lucigenin as a chemiluminogenic reagent was developed. The chemiluminescence intensity was found to increase with the addition of As(V) ion. The proposed method demonstrated that chemiluminescence method is simple and sensitive, offering satisfactory linear dynamic range. Under the optimum experimental conditions the detection limit was 3.3×10^{-7} M.

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