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Determination of As(III) and As(V) ions by chemiluminescence method

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Abstract

A new chemiluminescence (CL) method for the selective determination of As(III) and As(V) ions in aqueous solution has been studied using a FIA system. The method is based on the increased CL intensity with the addition of As(V) ion into a solution of lucigenin and hydrogen peroxide. The addition of As(III) ion into the solution did not change the CL intensity. Total concentration of As ions was determined after pre-oxidation of As(III) to As(V) with hydrogen peroxide in basic solution. The As(III) content was estimated by subtracting the content of As(V) ion from total As concentration. The effects of concentrations of KOH and H_2O_2, and flow rates of reagents on CL intensity have been investigated. The calibration curve for As(V) ion was linear over the range from 1.0×10^{-2} to 10 μg/g, the coefficient of correlation was 0.997 and the detection limit was 5.0×10^{-3} μg/g under the optimal experimental conditions.

Keywords: Arsenic; Chemiluminescence; Lucigenin

1. Introduction

An accurate determination of arsenic species in environmental and biological samples is of importance due to the toxicity of this heavy metal and its related compounds [1]. Arsenic exists in the environment in a number of valent states. The valence state of arsenic plays an important role for its behavior and toxicity in the aqueous systems [2]. Organic arsenic compounds are not toxic as are inorganic arsenic. Regarding inorganic arsenic, trivalent species are considered to be more toxic and generally are found at ultra-trace levels. Since the degree of toxicity for As(III) and As(V) are so different, it is not sufficient enough to determine the total content of arsenic in a given sample, in order to estimate its physiological or environmental risks. Some previous papers described experimental procedures for the speciation of As(III) and As(V) by using ion-exchange chromatography or liquid chromatography. In a subsequent step, atomic absorption spectrometry [3,4], atomic fluorescence spectrometry [5,6], hydride generation [7,8] or inductively coupled plasma mass spectrometry [9,10] were usually used as detection techniques. Electrochemical techniques, especially stripping voltammetry, have also been used [11,12]. Reactions involving complexating agents such as dithiocarbamates (DTC) and dithiophosphates (DTP) are simple and provide an alternative means for the separation of different oxidation states of arsenic [13]. The reduction agents, such as potassium iodide or cysteine, are applied to convert As(V) to As(III) in order to specify As(V) and As(III) [14]. Recently, chemiluminescence (CL) method was used for speciation of Cr(III) and Cr(VI), based on the chromium(III)-catalysed oxidation of luminol by hydrogen peroxide in a basic aqueous solution [15].

In this paper, the selective determination of As(III) and As(V) were based on the increased CL intensity with the addition of As(V) in a solution of lucigenin and hydrogen peroxide. The concentration of As(V) was obtained by direct measurement, and the concentration of As(III) involved a previous oxidation of As(III) to As(V) with hydrogen peroxide in a basic solution [16]. The As(III) content was estimated by subtracting the content of As(V) from the total As concentration. The effects of lucigenin, hydrogen peroxide and KOH on CL intensity were investigated.

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2. Experimental

2.1. Reagents

Lucigenin (bis-*N*-methylacridium nitrate) and $Na_2HAsO_4 \cdot H_2O$ were obtained from Aldrich (Milwaukee, WI, USA). Hydrogen peroxide (30%) and potassium hydroxide were purchased from Sigma (St. Louis, MO, USA). An As(V) ion stock solution was prepared by dissolving an appropriate amount of $Na_2HAsO_4 \cdot H_2O$ in deionized water, which was diluted with deionized water to give a concentration of 1000 ppm. 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.

2.2. Apparatus

A schematic diagram of the flow injection system used for the speciation and determination of arsenic is shown in Fig. 1. All connecting lines and reaction coils were obtained from Bran+Luebbe (Roselle, IL, USA). An Ismatec Model 404 peristaltic pump was used to transfer carrier streams. Sample solutions were introduced into the flow-line by a Rheodyne (Cotati, CA, USA) Model 7125 six-way injection valve with a loop. A Spex (Edison, NJ, USA) Model FL111 spectrofluorimeter equipped with a coiled glass flow cell (1.0 mm i.d., 20 mm total diameter) was used for detecting and recording the CL intensity of the reaction product. The Spex DM3000 program was used for data acquisition and data analysis. For the CL measurement, the light source of the spectrofluorimeter was switched off. The slit width of the emission monochromator was 5.0 mm. The high voltage for the photomultiplier tube was set to 900 V. A Mettler Toledo (CH-8603 Schwerzenbach, Switzerland) MA235 pH/Ion analyzer was used for pH measurements.

2.3. Oxidation of As(III) to As(V)

In a 4-ml vial, 500 μl of a 5.0×10^{-2} M H_2O_2 solution and 1.0 ml of a 1.7 M KOH solution were added followed by the addition of an As(III) standard solution of different concentrations. After the addition of reagents, constant stirring was maintained for 30 min.

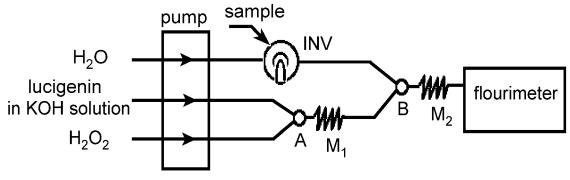

Fig. 1. A schematic diagram of the FIA system used for the determination of arsenic species: INV, injection valve; A and B, mixing tee; M1 and M2, mixing coil.

2.4. Extraction protocol of CRM for spike test

The NIST 1633b CRM (coal fly ash) was used for spike tests to validate the present method. Since the CRM used does not have the certified values for As(III) and As(V), the values obtained by Bendicho [17] of 0.15 and 0.42 μg/g for As(III) and As(V), respectively, were used. The following one-step extraction protocol to obtain water-soluble total As fraction was employed. Approximately, 2.0 g of the test material was placed in a 50-ml flask and 20 ml of water was added. The mixture was maintained at 55 °C for 10 h. The mixture was then centrifuged for 15 min at 1800 rpm. The extract was filtered through a 0.45-μm nylon syringe filter and transferred to a 25-ml flask.

2.5. Procedure

The aqueous 1.2 M H_2O_2 solution and the 1.0×10^{-5} M lucigenin solution in 1.7 M KOH were mixed in a mixer A. The sample containing As(V) was injected directly into the H_2O carrier stream using a six-way injection valve. The carrier solution containing analyte was mixed with the H_2O_2/lucigenin solution in a mixer B. The total flow rate of pump was fixed to 5 ml/min. The light produced in the course of the CL reaction was measured using a Hamamatsu R928 photomultiplier tube at 900 V. Each sample was injected in triplicate.

3. Results and discussion

3.1. Effects of H_2O_2 and lucigenin concentrations

Fig. 2 shows the CL intensity of the system as a function of the H_2O_2 concentration in the presence of 1.0×10^{-5} M lucigenin. The level of CL intensity rises with an increase in H_2O_2 concentration up to about 1.2 M. Further increases in hydrogen peroxide concentration reduce light emission, and thus 1.2 M was selected for H_2O_2 concentration in the present study. To obtain the optimum concentration of lucigenin, the CL intensity was measured as a function of the lucigenin concentration in the presence of 1.2 M of H_2O_2. Up to 1.0×10^{-5} M of lucigenin, CL intensity was in proportion to the lucigenin concentration, but, at a higher concentration, the CL signal decreased.

3.2. Effect of KOH concentration

The effect of the KOH concentration on the CL intensity was investigated. The CL was observed only in an alkaline medium. Fig. 3 shows the CL intensity as a function of the KOH concentration in the presence of 1.0×10^{-5} M lucigenin. The CL intensity increases with a rise in the level of KOH up to about 1.7 M. Further increases in the KOH concentration reduce the CL intensity, and thus 1.7 M was selected as the KOH concentration for the present work.