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A new chemiluminescence method for determination of dicyandiamide based on the N-bromosuccinimide–merbromin–cetyltrimethylammonium bromide system

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ABSTRACT

A novel and highly sensitive chemiluminescence (CL) method for the determination of dicyandiamide (DCD) has been developed based on the new CL system of N-bromosuccinimide–merbromin–cetyltrimethylammonium bromide in alkaline solution. Experiment conditions were optimized using central composite design-response surface methodology. Under the optimal conditions, the relative CL intensity was linear with the concentration of DCD ranging from 5.0×10^{-8} g mL^{-1} to 3.0×10^{-6} g mL^{-1}. The detection limit, at the signal-to-noise ratio of 3, was 3.0×10^{-9} g mL^{-1}. The relative standard deviation was 1.9% for 11 repeated determinations of 1.0×10^{-6} g mL^{-1} DCD. The proposed method was successfully applied to the analyses of DCD in tap water and milk products. And the recoveries were in the range of 87.0–102.3% with relative standard deviation values of 1.2–2.9%. Moreover, the minimum sampling rate was 120 samples h^{-1}. The possible mechanism of the CL reaction was also discussed.

1. Introduction

Dicyandiamide (DCD), the dimer of cyanamide, is a widely used chemical intermediate (Fig. 1A). It has been broadly used in the production of melamine and as a curing agent for epoxy resins [1]. In the agricultural industry, DCD is applied as a nitrification inhibitor to prevent nitrogen loss in the soil and keep them in the ammoniacal form [2,3]. However, DCD can result in some diseases, such as methemoglobinemia and eczema [4]. In January 2013, dicyandiamide residue was found in some milk produced in New Zealand, a big exporter of dairy products, which captured the attention from all over the world. Therefore, it is of great importance to develop a simple and sensitive method to monitor DCD in food and environment. Several analytical methods for the determination of DCD have been proposed, including liquid chromatography–tandem mass spectrometry (LC-MS) [5–8], high-performance liquid chromatography (HPLC) [9–11], hydrophilic interaction liquid chromatography (HILIC) [12], ion exclusion chromatography (IEC) [13], ultraviolet (UV) spectroscopy [14], and colorimetric method [15]. Although most of these assay methodologies are specific, they all have one or more drawbacks, such as high cost, time-consuming, lack of sensitivity, and inconvenience.

In recent years, chemiluminescence (CL) combined with a flow-injection method has been paid much attention for the analysis of inorganic and organic species in many different fields [16–18]. It provides unique advantages such as simplicity, rapidity, high sensitivity, wide working range, and low cost of instrumentation and maintenance. To the best of our knowledge, there is no report on the determination of DCD using the FI-CL method.

Merbromin is a green crystalline organic compound that forms a red aqueous solution, used as germicide and antiseptic (Fig. 1B) [19]. It could emit fluorescence at appropriate concentration [20]. In this work, it was firstly found that merbromin could be oxidized by N-bromosuccinimide (NBS) in an alkaline medium to produce CL, and the introduction of DCD could obviously enhance the CL intensity in the presence of cetyltrimethylammonium bromide (CTAB). Therefore, a novel CL system of NBS–merbromin–CTAB was proposed for the determination of DCD.

The instrumental and chemical parameters were respectively optimized by using a univariate procedure and central composite design-response surface methodology (CCD-RSM) which allowed the simultaneous establishment of the variables and evaluation of the interactions among them [21,22]. The results from two optimization methods were compared and the best parameters were chosen to detect DCD. Under the optimal conditions, the proposed FI-CL system was applied to the determination of DCD in tap water and milk products with satisfactory results. Furthermore, the possible CL emission mechanism was also discussed.

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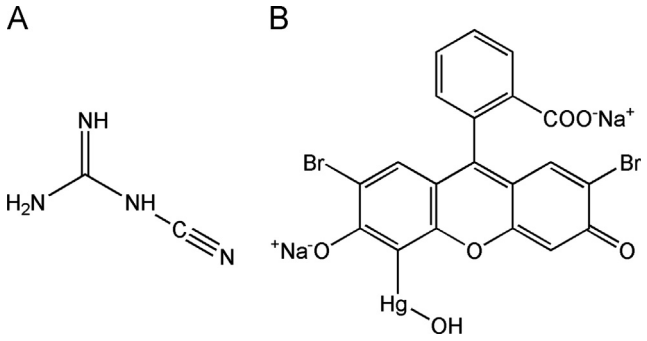

Fig. 1. Chemical structures of dicyandiamide (A) and merbromin (B).

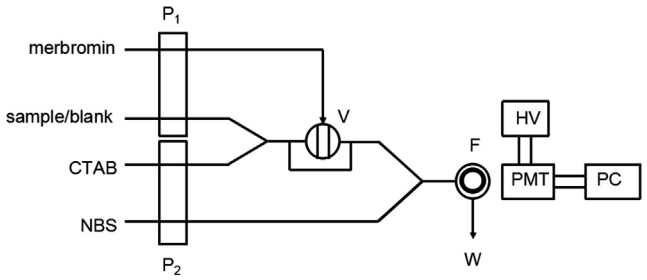

Fig. 2. Schematic diagram of the FI-CL system. P1 and P2, peristaltic pump; V, injection valve; F, flow cell; W, waste water; HV, negative voltage; PMT, photomultiplier tube; PC, personal computer.

2. Experimental

2.1. Apparatus

The flow-injection system employed for CL was an IFFM-E analysis system (Xi'an Remex Electronic Instrument High-Tech Ltd., China) consisting of two peristaltic pumps, a six-way injection valve with a sample loop, a flow cell and a photomultiplier (PMT). All the components of the flow system were connected with polytetrafluoroethylene (PTFE) tubes (0.8 mm i.d.). UV spectra were recorded on a UV-1800 spectrophotometer (Shimadzu, Japan) and fluorescence spectra were detected with an RF-5301 spectrophotometer (Shimadzu, Japan). A TGL-16M centrifuge (Xiangyi Centrifuge Co., Hunan, China) was used in sample treatment.

2.2. Reagents

All chemicals were of analytical reagent grade and double distilled water was used throughout. The standard solution of DCD (0.1 mg mL^{-1}) was prepared by dissolving 0.0100 g DCD (National Institute for the Control of Pharmaceutical and Biological Products, Beijing, China) in water and diluting to 100 mL. Stock solutions of merbromin (0.01 mol L^{-1}) and sodium hydroxide (1.0 mol L^{-1}) were prepared by dissolving 0.7560 g merbromin (Shanghai Baoman Biological Technology Co., Ltd., Shanghai, China) and 4.0000 g NaOH (Xi'an Chemical Reagent Factory, Xi'an, China) in 100 mL water. The working solutions of merbromin and NaOH were prepared by mixing appropriate amount of their stock solutions and diluting to 100 mL. Dissolving 0.1780 g of NBS (Xi'an Chemical Reagent Factory, Xi'an, China) in 100 mL water, stock solution of NBS (0.01 mol L^{-1}) was obtained. The CTAB stock solution (0.01 mol L^{-1}) was obtained by dissolving 0.3645 g CTAB (Xi'an Chemical Reagent Factory, Xi'an, China) in water and diluting to 100 mL. The stock solutions were stored in a refrigerator at 4 °C and kept in dark. The working solutions of NBS and CTAB were prepared from the stock solutions by appropriate dilution with distilled water. Acetonitrile, n-hexane and methanol (Xi'an Chemical Reagent Factory, Xi'an, China) were used in sample treatment.

2.3. Sample treatment

Tap water samples were obtained from local tap water. The samples were at first filtered through a 0.22 μm membrane. Then ions were eliminated by adding an exchange resin [23].

Milk and milk powder were purchased from local supermarket. 1 mL of milk or 1.0 g of milk powder and 3 mL of double-distilled water were added into a 10 mL centrifuge tube and ultrasonically shaken for 5 min. In order to remove protein, 7 mL of acetonitrile was added and the mixture was ultrasonically shaken for 20 min. After centrifugation at 4000 rpm for 20 min, the supernatant was collected. Fat contained in supernatant was removed by adding 5 mL n-hexane. The lower layer was further purified by solid phase extraction on a Sep-Pak Plus AC-2 cartridge [5]. Firstly, the cartridge was preconditioned with 10 mL of acetonitrile and then 10 mL of double-distilled water, after which 5 mL of the extraction solution was applied and left to flow through the cartridge. Secondly, the cartridge was washed with 10 mL of double-distilled water and the analytes were eluted with 30 mL of acetonitrile–methanol solution (3/2, v/v). Finally, the eluate was evaporated to dryness under nitrogen at 45 °C. The dried extract was dissolved into 10 mL of double-distilled water and then appropriately diluted for FI-CL analysis. The recoveries were carried out in the same way but adding known amounts of DCD to the samples before any pretreatment.

2.4. Procedure

The FI-CL system procedure is shown in Fig. 2. All the solutions were delivered to the flow cell by two peristaltic pumps. CTAB solution was premixed with blank or sample solution followed by a certain amount of the mixed solution of merbromin and NaOH injected into the emerging stream by the six-way injection valve. And then the mixture merged with NBS solution in the flow cell. The CL emission produced was detected and amplified by a PMT and a luminometer automatically. The signal was exported to an IBM-compatible computer for data acquisition. The concentration of DCD was quantified based on the enhancement of CL intensity, $\Delta I = I - I_0$, where I and I_0 were the CL signals in the presence and absence of DCD, respectively.

2.5. Central composite design

Central composite design (CCD) consists of 2^k factorial points, $2k$ star points and m replications of center points. It is applied in the study of the chemical variables. The factor domains were selected according to the results obtained by the single-factor-at-a-time method.

In order to describe the way in which the variables were related and in which they influenced the response, response surface methodology (RSM) was employed to assemble the model. Therefore, the response data from the CCD were analyzed by multiple regressions to fit to the following parametric equation (full second order polynomial):

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_4X_4 + b_5X_1^2 + b_6X_2^2 + b_7X_3^2 + b_8X_4^2 + b_9X_1X_2 + b_{10}X_1X_3 + b_{11}X_1X_4 + b_{12}X_2X_3 + b_{13}X_2X_4 + b_{14}X_3X_4 \quad (1)$$

where Y represented the experimental response, X_1, X_2, X_3 and X_4 were the four independent variables, b_0 was the intercept, b_1–b_4