Enhanced electrogenerated chemiluminescence of tris(2,2’-bipyridyl) ruthenium(II) system by L-cysteine-capped CdTe quantum dots and its application for the determination of nitrofuran antibiotics

Narin Taokaenchan, Tanin Tangkuaram, Pusit Pookmanee, Sirirat Phaisansuthichol, Surasak Kuimalee, Sakchai Satienperakul

Department of Chemistry, Faculty of Science, Maejo University, Chiang Mai 50290, Thailand

Article info
Article history:
Received 18 August 2014
Received in revised form 6 November 2014
Accepted 17 November 2014
Available online 20 November 2014

Keywords:
Nitrofurans
CdTe quantum dots
Electrogenerated chemiluminescence

ABSTRACT
This paper reports a new approach to enhance the electrogenerated chemiluminescence (ECL) of the tris(2,2’-bipyridyl)ruthenium(II) (Ru(bpy)₃²⁺) system using resonance energy transfer with L-cysteine-capped cadmium telluride quantum dots (CdTe-QDs) in aqueous solution. The oxidative peak signal of Ru(bpy)₃²⁺ occurred at a voltage of 1.10 V when the potential was cycled between 0.4 and 1.6 V using cyclic voltammetry with a carbon screen-printed electrode (SPE) in a 0.11 M phosphate buffer at pH 7.50. The L-cysteine-capped CdTe-QDs were synthesized and added into the solution of Ru(bpy)₃²⁺ to magnify the ECL signal. The ECL emission signal was investigated and the extreme enhancement of the ECL intensity was achieved due to the energy transfer by the L-cysteine-capped CdTe-QDs. It was found that the induced ECL from the Ru(bpy)₃²⁺ CdTe-QDs system was inhibited by the presence of selected nitrofurans. This quenching effect of nitrofuran antibiotics on the anodic ECL of Ru(bpy)₃²⁺ CdTe-QDs was found to be selective and concentration dependent and was observed to have a linear relationship over the concentration range 10⁻¹⁰⁻¹⁰⁻⁶ M. The detection limits were found to be 0.40, 0.73 and 0.60 μM for furaltadone (FTD), furazolidone (FZD) and nitrofurantoin (NFT). In addition, the proposed ECL method was successfully applied to detect the total residuals of selected nitrofuran residues in animal feed samples with satisfactory results.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction
Nitrofurans (NFs) are antibiotic drugs, which have been widely used in the dairy, livestock, poultry and aquaculture production industries in past decades. The nitrofuran derivatives in which there exists the greatest possibility of contamination are furaltadone (FTD), furazolidone (FZD), nitrofurazone (NFZ) and nitrofurantoin (NFT). Due to concerns of their carcinogenicity and mutagenicity, these antibiotics have been banned in the EU (Regulation (EC) No. 1442/1995) and in many countries overseas. Therefore the use of nitrofurans for livestock has also been prohibited in countries such as Australia, USA, Philippines, Thailand and Brazil (Vass et al., 2008). Unfortunately, nitrofurantoin antibiotics are still available and in use in a number of third world countries including Thailand. Several analytical methods have been described for the determination of nitrofuran residues in food and animal tissues, such as liquid chromatography (LC), in combination with different detection techniques, for example photodiode array (DAD) (Chumanee et al., 2009), fluorescence (Sheng et al., 2013) and mass spectrometry (MS) (Barbosa et al., 2007). These methods are time-consuming and require expensive instrumentation, hence, there is now an urgent need for a rapid, low cost, high-capacity and sensitive method to screen NF residue-contaminated feed, stored grain and agricultural products in order to control the quality of exported foods to the EU.

In recent years, chemical sensors and biosensors have played an essential role in the fields of environmental (Prakash et al., 2013), medical diagnostics (Yu et al., 2014) and pharmaceutical analysis (Khorshid and Issa, 2014). Many analytical methods and techniques have improved chemical sensors and biosensors in sensitivity and miniaturization. There is also a need to determine analytes at increasingly lower levels with lower detection limits, and to improve the accuracy and precision at those limits.

In addition to photochemiluminescence (CL), electrogenerated chemiluminescence (ECL) has also recently been developed for chemical sensors based on an optical reaction and electrochemical potential control. In ECL, electrochemically-generated intermediates undergo a highly exergonic reaction to produce an
Specific speciation of As(III) and As(V) in aqueous solution by a split microfluidic chemiluminescence system

N. Taokaenchans, R. Puntharod, T. Tangkuaram, P. Pookmanee, S. Phaisansuthichol, S. Sangsrichan and S. Satienperakul*

Department of Chemistry, Faculty of Science, Maejo University, Chiang Mai 50290, Thailand, e-mail: sakchais@mju.ac.th

The simultaneous determination of As(III) and As(V) in aqueous solution based on the acidic permanganate and luminol chemiluminescence (CL) detection systems have been applied to a split microfluidics flow injection (µFI) with dual-channel manifolds at rapid sampling rate. The µFI-CL system consisted of two halves of micro-conduit platforms, which ran on a simple device made from small pieces of the laser engraved polymethylmethacrylate (PMMA) and polydimethylsiloxane (PDMS). The specific CL reaction for As(III) was produced by the oxidation of acidic potassium permanganate in the presence of sodium hexametaphosphate media, while the CL reaction for As(V) was generated based on the oxidation of luminol with a vanadomolybdoarsenate heteropoly acid (AsVMo-HPA) complex in an alkaline solution. The µFI method involved the injection of the mixed standard solution into an acid carrier stream where it was then splitted and merged with the reagent solutions of each reaction systems on a spiral-designed microfluidic platform. The solution mixtures were passed through each spiral flow channel, where the CL intensity of both resulting reaction mixture were measured with two photomultiplier tubes. Linear calibrations for As(III) and As(V) were established over the concentration ranges of 20-60 µg L⁻¹. The limits of detection (signal-to-noise ratio of 3) of As(III) and As(V) were found to be 4 µg L⁻¹ and the limits of quantification (signal-to-noise ratio of 10) were found to be 10 µg L⁻¹, respectively. The proposed procedure was successfully applied for the determination of As(III) and As(V) in ground water samples.

Introduction
Arsenic is a naturally occurring element present in the environment in both organic and inorganic forms. Inorganic arsenic is considered to be the most toxic form of the element, and arsenic contamination of ground water is found in many countries throughout the world, including China, Bangladesh, Vietnam and Thailand. The presence of arsenic in natural water is of concern because of its toxicity and possible carcinogenic activity, and the biological effects of arsenic are significantly altered by its oxidation state as well as by its complexation with organic materials. Depending on the environment, inorganic arsenic can exist in two different oxidation states As(III) and As(V) in natural water, although As(V) is thermodynamically favored. Because of its ability to form complexes with certain co-enzymes, however, As(III) is more toxic to animal and plants than As(V). The USEPA reduces the maximum permissible level (MPL) of arsenic in drinking water from 50 to 10 µg L⁻¹ [1]. Current arsenic detection always relies on large apparatus including atomic absorption spectrometry (AAS) [2], hydride generation atomic fluorescence spectrometry (HGAFS) [3-6], inductively coupled plasma atomic emission spectrometry (ICP-AES) [7-9] and inductively coupled plasma mass spectrometry (ICP-MS) [10-12]. The USEPA approved spectrometric methods are all based on atomic spectrometry which can readily provide detection limits in the sub-microgram per liter range, but the instrumentations are bulky, expensive, and require large amounts of pure gas in addition to the high cost of consumables. Hence, the alternative, portable and sensitive equipment is continually demanded for on-site measurement.

Microfluidic devices currently present unique advantages for sample handling, reagent mixing, separation, and detection. Microfluidic channel dimensions typically range from 1 to 1000 µm in width and height and require between 100 nL and 10 µL of sample and reagents. In addition to obvious advantages that are associated with smaller samples, reagent and waste volumes required which is ideal for handling costly and difficult-to-obtain samples and reagents. The materials used to construct microfluidic devices vary, depending on the application; however, the vast majorities are constructed of glass, silicon, polymers or even filter paper using photolithography to define hydrophobic micro-channels. One particular polymer that has recently been used extensively is poly (dimethylsiloxane), or PDMS since PDMS is a transparent, elastomer polymer that can be fabricated rapidly by laser engraving with features having dimensions as small as 10 nm. The elastomeric nature of PDMS makes it a great sealant, since often the adhesion due to the conformational surface contact with a smooth, flat surface is enough to seal meso- or even microchannels for low pressure applications [13, 14].

During the past decades, there have been word-wide efforts to develop miniaturized instrumentation for chemical analysis. However, the utilization of microfluidics in the attempts for the determination of arsenic has rarely appeared. One attempt had been reported by Matusiewicz et al. [15]. Only few reports exploited the use of chemiluminescence (CL) detection to determine inorganic arsenic species and most of them were based on a flow injection (FI) system [16, 17].

In this present work, the integration of a microfluidic device with CL detection for the determination of As(III) and As(V) in aqueous samples is proposed. Since, CL provides high sensitivity and selectivity, while it is a simple and inexpensive optical instrumentation. The acidic permanganate and luminol chemiluminescence detections have been allocated for our system. The sandwich type microfluidics chip consisted of two halves of spiral conduit platforms where the CL reaction for As(V) was generated based on the oxidation of luminol with a vanadomolybdoarsenate heteropoly acid (AsVMo-HPA) complex in an alkaline solution. On the other hand the CL reaction for As(III) was produced by the oxidation of acidic potassium permanganate in the presence of a sodium hexametaphosphate media.

Experimental
Chemical and apparatus
All chemicals used are analytical reagent (AR) grade, and all standard and reagent solutions were prepared with deionized water. As(III) and As(V) stock solution (1,000 mg L⁻¹) were prepared by dissolving 0.1734 g of NaAsO₂ (Ajax, Australia) and 0.4160 g of Na₂HAsO₄·H₂O in 100 mL of deionized water, respectively. The As(III) and As(V) stock solutions were kept in a sealed container in a refrigerator at 4