Forensic Science International 264 (2016) 1–6

Contents lists available at ScienceDirect

Forensic Science International

journal homepage: www.elsevier.com/locate/forsciint

Electrochemiluminescent detection of methamphetamine and amphetamine

Jonathan McGeehan, Lynn Dennany *

WestCHEM, Department of Pure and Applied Chemistry, University of Strathclyde, Centre for Forensic Sciences, Technology and Innovation Centre, 99 George Street, Glasgow, G1 1RD, UK

ARTICLE INFO

Article history:
Available online 5 March 2016

Keywords:
Methylamphetamine
Electrochemical sensors
ECL
Drug analysis

ABSTRACT

Direct detection of amphetamine type stimulants (ATSs) including methylamphetamine (MA) in street samples and biological matrices without the need for pretreatment or extraction is a great challenge for forensic drug analysis. Electrochemical techniques, such as electrochemiluminescence (ECL), are promising tools for this area of analysis. This contribution focuses on the electrochemical and photochemical properties of $[Ru(bpy)_3]^{2+}$ Nafion composite films and their subsequent use for the detection of ATS in particular MA. Under optimised conditions, the response linearly increased with the concentration over the concentration range 50 pM $\leq$ [MA] $\leq$ 1 mM while an equivalent dynamic range was obtained for amphetamine with a correlation coefficient of 0.9903 and 0.9948 respectively. The ECL signal was monitored at ~620 nm, representing the λ_{max} for the $[Ru(bpy)_3]^{2+}$ Nafion composite films. This wavelength is shifted by approximately 15 nm compared to the photoexcited λ_{max} for the same system. The modified films were formed by direct interaction with the electrode surface without the need for surface modification or chain linkers. This is a major advantage for the fabrication of any sensor as it reduces the synthesis times resulting in more economically and cheaper production costs. This technique is simple, rapid, selective and sensitive, and shows potential for the high-throughput quantitation of ATS as well as possibilities for adaptation with other techniques such as FIA or LC systems.

© 2016 Elsevier Ireland Ltd. All rights reserved.

1. Introduction

Methamphetamine (MA) has received much attention as an amphetamine type stimulant (ATS) drug that, even in small amounts, has a strong impact on the central nervous system causing mental alertness and other symptoms [1,2]. It has been used to treat obesity and alcoholism, but it can cause physiological and psychological effects such as increased heart rate and blood pressure, affecting body temperature, attention and mood. It has also been reported as a widely abused drug in many areas of the world [3,4]. As a result, the determination of MA has attracted much attention. Many chromatographic methods have been utilised for the identification and quantification of MA including gas chromatography (GC) [5], HPLC [6], GC–MS [7], LC–MS [8], solid phase microextraction capillary electrophoresis [9] and capillary electrophoresis electrochemical/ECL [10]. The demand for portable, rapid and quantitative methods for the determination and analysis of illicit substances has been highlighted as the concerns over methamphetamine and amphetamine usage [11] increase with growing concern over the situation within Europe [12]. Techniques which have the ability to street samples and biological matrices without the need for pre-treatment or extraction is a great challenge for forensic drug analysis and this contribution will try to address this need through the application of ECL to the analysis of amphetamine and methampethamine. Current chromatographic methods generally involve time consuming derivatisation steps [13–15] and/or extraction methods for biological samples [16]. In this study, we present a simple and rapid ECL method as proof of concept for the detection and analysis of amphetamine and methamphetamine [17].

ECL has been the subject of extensive study for the past three decades [18–22]. The production of light from intermediates generated during electrolysis occurs when the energy liberated by reaction between the electrogenerated precursors is sufficient to generate a product in an electronically excited form [23]. Studies of inorganic ECL have been dominated by transition metal complexes [24,25], particularly ruthenium poly(pyridyl) species, e.g., those of the general formula $Ru(L)_3^{2+}$, e.g., where L = 2,2′-bipyridine [26], or

* Corresponding author. Tel.: +44 0141 548 4322; fax: +44 0141 548 2532.
E-mail address: lynn.dennany@strath.ac.uk (L. Dennany).

http://dx.doi.org/10.1016/j.forsciint.2016.02.048
0379-0738/© 2016 Elsevier Ireland Ltd. All rights reserved.

4,7-diphenyl-1,10-phenanthroline [27]. This is due to the attractive photophysical and electrochemical properties that these compounds typically exhibit.

ECL combines the inherent sensitivity, selectivity and linear range advantages of chemiluminescence methods with increased temporal and spatial control over the chemiluminescent reaction making ECL a powerful analytical tool, particularly when the surface may be modified to tune the ECL properties. Systems utilising both organic and inorganic complexes have been developed [18,28,29]. ECL usually involves the reaction of electrogenerated species that react to form excited states, usually via an energetic redox reaction [18]. Thus, ECL can also be utilised to probe electron and energy transfer processes at electrified interfaces [30,31]. As such it has been used for the detection of alkylamines, NADH, hydrazine, amino acids, biomolecules and a variety of pharmaceutical compounds [24,32,37].

For example, one of the many applications of $[Ru(bpy)_3]^{2+}$ ECL is the detection of amino acids [34], and amine containing substances [2,35]. A key advantage of ECL is that is offers the possibility of detecting very low concentrations of amino acids, i.e., sub-nM, with good reproducibility by detecting both the current and light responses. Most detection systems involve the solution phase detection of amino acids or amine containing substances by ECL and flow injection analysis (FIA) [36]. However, changes in the micro environment of solution based analysis, including changes in viscosity, temperature, ion strength and pH, can influence the resultant ECL. For example, Jackson et al. [36] demonstrated that $[Ru(bpy)_3]^{3+}$ generated in situ undergoes a chemiluminescent reaction with free amino acids. In agreement with previous studies, the chemiluminescence was maximised at pH values near the pK_a of the N-terminal amine site [34]. Similar results were obtained for ATS when electrochemically analysed in solution phase approaches [2,35].

There are several disadvantages to using solution phase reactants including loss of signal due to diffusion of the ECL reagent out of the detection zone, the limited ability to repeatedly electrochemically cycle an individual luminophore and high reagent consumption. To overcome these problems, considerable effort has been invested in immobilising the $[Ru(bpy)_3]^{2+}$ reagent on an electrode [34,2,35,36]. This kind of reagentless ECL sensor can avoid external addition of reagents and can also overcome the limitation of reagent consumption since the $[Ru(bpy)_3]^{3+}$ is regenerated in situ.

In this study, we report on the electrochemical, photophysical and electrochemiluminescent properties of $[Ru(bpy)_3]^{2+}$:Nafion composite films modified on glassy carbon electrodes. The surface coverage of the complex about 7.5×10^{-9} mol cm^{-1}, which is consistent with that expected for a composite film. The $Ru^{2+/3+}$ couple is electrochemically reversible and the surface coverage is very stable over extended periods under voltammetric cycling. Significantly, emission is observed from the modified electrodes following photoexcitation or reaction of the electrochemically generated Ru^{3+} species with MA. This work has shown that the ruthenium composite film is suitable for the use in ECL detection of MA and could be extremely helpful in the development of portable quantitative systems for the detection of ATS over a forensically relevant linear range, minimising the requirement for sample preparation. Ideally, this system could be used in combination to exploit this technology for a variety of illicit substances and this is an area in which future work would focus.

2. Experimental

2.1. Materials

All the materials were purchased from Sigma–Aldrich and were used as received, with the exception of the interferent starch (BDN Laboratory Supplies) and the high purity methanol (Fluka). The controlled substances, MA and amphetamine, were purchased from Sigma–Aldrich in their salt forms. All concentrations of these controlled ATS are quoted as free base concentrations.

2.2. Methods

Working electrodes were prepared by polishing with alumina (1.0–0.3 μm) on a felt pad, followed by sonication in distilled deionised water for 30 min. Where appropriate, working electrodes were modified by applying a drop (≈15 μL) of an ethanolic solution of the $[Ru(bpy)_3]^{2+}$:Nafion film to the electrode surface. Stock solutions of Nafion-$[Ru(bpy)_3]^{2+}$ were prepared by dissolving 1 mg of $[Ru(bpy)_3]^{2+}$ in 2 mL methanol. Then, 200 μL of this solution was diluted in 1.8 mL of methanol and 200 μL of Nafion (5% (w/v) mixture of low molecular weight alcohols) was added. The mediator was found to precipitate at higher concentrations. The modified electrodes were then allowed to dry in the dark for 10–12 h. The surface coverage, Γ, was determined by graphical integration of background corrected cyclic voltammograms (<5 mV s^{-1}). In all cases the surface coverage were typically ~7.5×10^{-9} mol cm^{-1}. All solutions were deoxygenated using nitrogen or argon prior to measurement.

Electrochemical experiments were performed in a standard electrochemical cell using a CH instruments (Memphis, TN) model 602E potentiostat. Cyclic Voltammetry experiments were carried out using a 3 mm diameter glassy carbon working electrode in a conventional three electrode assembly using a platinum flag as the counter electrode. Potentials were measured versus a standard Ag/AgCl aqueous reference electrode (3 M KCl). Measurements involving simultaneous detection of light and current utilised a CH instrument model 602E connected to a Hamamatsu H6780-20 PMT powered at −600 V. During the experiments, the cell was kept in a light-tight box in a specially designed holder where the working electrode was positioned directly opposite to the fibre optic bundle, the other end of which was coupled to the PMT. Emission spectra were recorded on a Cary Eclipse Fluorescence Spectrophotometer with an excitation and emission slits of 5 nm, 800 V PDA power and a scan rate of 120 nm/min. All other reagents used were of analytical grade, and all solutions were prepared in milli-Q water (18 mΩ cm).

3. Results and discussion

3.1. Electrochemical properties of the glassy carbon electrode modified with the composite film containing $[Ru(bpy)_3]^{3+}$ in Nafion

The electrochemical behaviour of the $[Ru(bpy)_3]^{2+}$ when surface confined within a Nafion film on a GC electrode was examined using cyclic voltammetry. Fig. 1 shows the typical voltammetric behaviour of the ruthenium modified electrode in 0.1 M H_2SO_4. The surface coverages were determined by graphical integration of background corrected cyclic voltammograms (<5 mV s^{-1}) and were typically about 7.5×10^{-9} mol cm^{-1}, which is consistent with that expected for a composite film [24,25,27]. The anodic and cathodic peaks corresponding to the $Ru^{2+/3+}$ couple are clearly visible at 1125 mV and 1075 mV respectively. The formal potential, $E^{\circ\prime}$, is within 25 mV of that found for the complex dissolved in acetonitrile where the working electrode is a platinum microdisk [17]. This observation indicates that the electron density of the metal centre does not change significantly upon surface immobilisation and that the composite film is highly solvated.

In addition, the peak to peak separation between anodic and cathodic waves is close to zero at low scan rates, the full width at half maximum (FWHM) is close to the theoretically value of 59 mV

Download English Version:

https://daneshyari.com/en/article/6551794

Download Persian Version:

https://daneshyari.com/article/6551794

Daneshyari.com