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Preparation of novel optical fibre-based Cocaine sensors using a molecular imprinted polymer approach

Stephen P. Wren[a,*], T. Hien Nguyen[a], Paul Gascoine[b], Richard Lacey[c], Tong Sun[a], Kenneth T.V. Grattan[a,d]

[a] School of Engineering and Mathematical Sciences, City University London, London EC1V 0HB, UK
[b] Smiths Detection, Bushey, Watford, Hertfordshire WD23 2BW, UK
[c] Centre for Applied Science and Technology, Home Office, Hertfordshire AL4 9HQ, UK
[d] City Graduate School, City University London, London EC1V 0HB, UK

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ABSTRACT

Novel chemical sensors using fibre optic-based techniques for the detection of Cocaine have been developed, utilising molecularly imprinted polymers (MIPs) containing fluorescein moieties as the signalling groups. The fluorescent MIPs were formed and covalently attached to the distal end of specially chosen optical fibres to create fibre optic probe-based sensors. These sensors exhibited are producible and quantifiable change in the intensity of the fluorescence signal received from the sensor in response to Cocaine in aqueous acetonitrile mixtures. High selectivity for Cocaine over Codeine and a range of known Cocaine interferants has been demonstrated for one of the sensors developed in this work.

1. Introduction

Illicit use of Cocaine is a global problem with world-wide annual Cocaine consumption currently standing at around 600 tonnes. The United Nation's 2010 World Drug Report concluded that the North American Cocaine market alone was valued at $38 billion in 2008 and has been rising since. The World Health Organisation estimated that 0.7% of the global burden of disease in 2004 was due to Cocaine and opioid use, with the social cost of illicit substance use nearly 2% of Gross Domestic Product in those countries that have measured it. Consequently, sensitive and accurate detection of Cocaine is critically important for law enforcement and clinical diagnostics across the world. In 2010, for example, the UK Border Agency made more than 1200 individual seizures of Class A drugs totalling 3000 kg.

The detection of Cocaine has been extensively investigated due to the adverse health effects and related dangers associated with its use [1,2] and *highly sensitive* detection of Cocaine is critically important, as discussed above. Existing technologies for drug detection include manual handling, a method that is rendered less effective as it is easy to miss concealed items during searches and its operation is very time-consuming and resource-intensive. Employment of sniffer dogs involves a high cost (due to the need for specially trained handlers) and is complicated by limited duty cycles and false alarms. Other competing technologies are encumbered by issues such as low sensitivity and poor selectivity and the use of either bulky or fragile systems. These options include Raman Spectrometry [3] (involving the use of sophisticated lasers with high associated expense), Ion Mobility Spectrometry [4] (often gives false alarms), Fourier Transform Infrared Spectroscopy (high false alarm rate), Gas Chromatography–Mass Spectrometry [5] and Liquid Chromatography–Mass Spectrometry (where samples require testing at remote sites and systems are bulky and expensive). In addition, field ID Kits (e.g. drug wipes) make use of expensive consumables and require delicate equipment. Also, many biosensors [6,7] are fragile and costly. Floor standing systems are non-portable and operate over short ranges. Their disadvantages include poor

* Corresponding author at: School of Engineering and Mathematical Science, City University London, Northampton Square, London EC1V 0HB, UK.
Tel.: +44 02070403641.
E-mail addresses: stephen.wren.1@city.ac.uk, wrens@lineone.net (S.P. Wren).

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effectiveness when moisture is present in air; specific inspection and identification of materials being non-straight forward using Terahertz imaging; high cost and safety concerns (X-ray, Z Backscatter scanning). There is thus a need for new, more reliable and more cost-effective solutions.

Optical fibre sensors can, however, offer many advantages over other sensing technologies. These include their small size, lightweight nature, low cost, the potential for multiplexing multiple sensors on a single fibre network and their remote sensing capability. Such sensors are chemically and physically robust and are particularly suitable for working in harsh environments due to their immunity to electromagnetic interference. In addition, utilising the molecularly imprinted polymer (MIP) technique is a key strength because preparation of synthetic molecular receptors allows recognition of any given target molecule. Other advantages of such sensors are their durability, thermal and chemical stability, low cost and long shelf-life plus MIP-based sensing, provides a more stable alternative to biological receptors. Limited sensing solutions for Cocaine detection (e.g. aptamer-based biosensors [8–11]) are in existence but a compact, hand-held monitor utilising stable synthetic molecular receptors does not exist. This set of technologies includes aptamer-based electrochemical detection [8,9], aptamer-coated, piezoresistive, microcantilever-based biosensing [10] and an electrogenerated chemiluminescence aptamer-based approach [11]. In addition, Hans and Sigrist [12] are developing a sensor for detecting Cocaine in saliva and high affinity MIP nanoparticles [13] and extraction MIPs [14] for Cocaine have been reported.

This work discusses a solution developed in the laboratory which combines the advantages of the use of MIPs with those of employing optical fibre sensing. The focus of this research is aimed at the development of a stable, compact and portable sensing system capable of real time drug detection for use, for example, by security staff, e.g. police forces or airport customs staff in situ to provide a quantitative indication that suspicious materials do contain Cocaine. A rapid method that helps to distinguish between illicit substances and legal impurities (interferants) is also a desirable aim of the sensors developed. Furthermore, the findings disclosed herein do include positive examples of sensor selectivity for Cocaine over Codeine and a range of other masking agents.

2. Technical approach

This research builds on and takes forward previous work by some of the authors [15,16] by enhancement and further optimisation of an approach using a fluorescein-based scaffold interacting with Cocaine. A combination of molecular imprinting, as a method

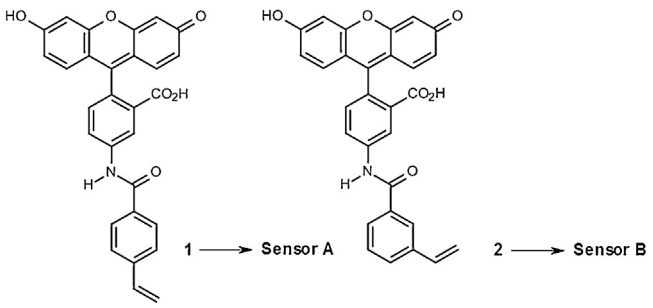

Fig. 2. Chemical structures of fluorophore monomers **1** and **2**.

for generating chemically selective binding sites, and fluorescence modulation (as a means of signalling the presence and concentration of the analyte) was used in the sensor material design. The MIP receptor which is selective for Cocaine was covalently bonded to the distal end surface of an optical fibre, as illustrated in Fig. 1. The optical fibre itself facilitated the guidance of excitation light to the sensor material and the collection of the fluorescence signal generated when the sensor material interacts with the target molecules. This imprinting and sensing approach is also illustrated in Fig. 1. A complex is formed between the carboxyl group on the fluorophore and the amine group present in Cocaine (analyte). The complex is copolymerised with cross-linking monomer on the end surface of the fibre, which has been functionalised with polymerisable groups. Then the analyte is extracted from the polymer and the resultant MIP formed on the end surface of the fibre contains recognition sites incorporating the fluorophore and thus exhibits an increase of fluorescence intensity selectively in the presence of the analyte.

The strategy employed in this research is designed to enhance the selectivity of the sensor for Cocaine over that reported previously and in relation to other chemical agents – the approach taken thus was two-pronged. Firstly, it was anticipated that additional interactions between the fluorophore and the drug would be achieved through subtle monomer design; however it was recognised that this may not be facile, in light of the distance between the amine group and the two ester groups present in the Cocaine (Fig. 1). A second option involved targeting monomers that bore different functional groups to acrylamidofluorescein [16]. Thus herein, the fabrication of sensors derived from vinylphenyl fluorophores **1** and **2**, as shown in Fig. 2, and labelled sensor **A** and sensor **B** respectively was undertaken and the approach used is described below. Compound **2** was chosen because it is a close analogue of **1** (regioisomer) and could be prepared swiftly.

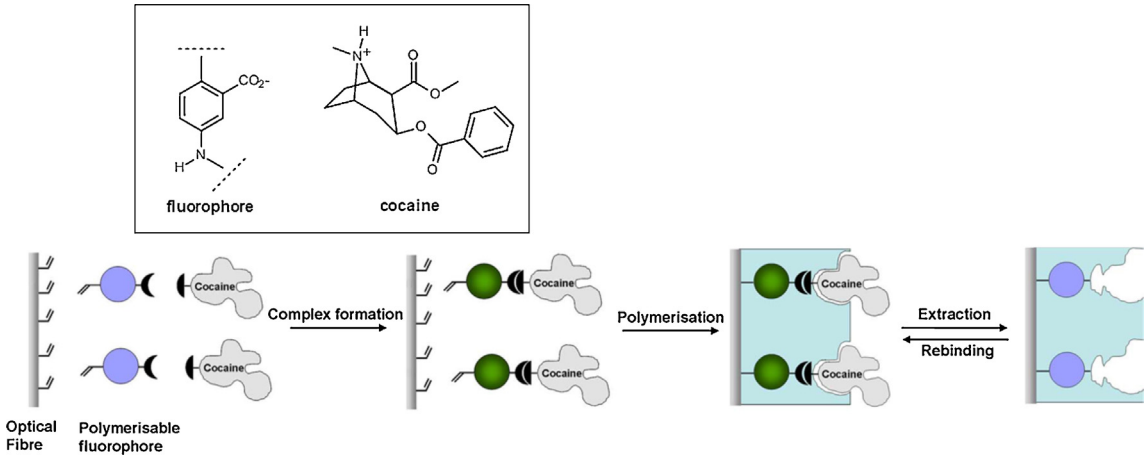

Fig. 1. Fluorescent MIP sensor approach for Cocaine sensing.