Sensors and Actuators B 136 (2009) 105–112

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

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

An optical fibre reflectance sensor for *p*-aminophenol determination based on tetrahydroxycalix[4]arene as sensing reagent

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ARTICLE INFO

Article history:
Received 16 June 2008
Received in revised form 2 November 2008
Accepted 13 November 2008
Available online 24 November 2008

Keywords:
p-Aminophenol
Optical fibre
Reflectance sensor
Tetrahydroxycalix[4]arene

ABSTRACT

A fibre-optic sensor for *p*-aminophenol (PAP) based on the use of 25,26,27,28-tetrahydroxycalix[4]arene (CAL4) immobilised onto Amberlite XAD-16 and reflectance spectrometry has been developed. The sensor is based on the reaction of PAP with CAL4 in presence of an oxidant to produce an indophenol dye. The reflectance measurements were carried out at a wavelength of 620 nm since it yielded the largest divergence different in reflectance spectra before and after reaction with the analyte. A highly linear calibration curve ($r^2 = 0.992$) was observed in the PAP concentration range of 0.5–35 ppm (linear within 0.5–5.5 ppm) with a calculated limit of detection (LOD), defined as the lowest concentration level of analyte that the proposed method can detect to be statistically different from an analytical blank (i.e., yielding an analytical response greater than three times the standard deviation of a blank), of 0.109 ppm. The sensor response from different probes ($n = 5$) gave an RSD of 1.8% at 10.9 ppm PAP concentration. The response time of the optical one-shot sensor was 5 min for a stirred solution. The intra- and inter-assay variability (as relative standard deviation: RSD) was approximately 2 and 4%, respectively. The lifetime of the blank sensor (CAL4 adsorbed onto XAD-16) was at the order of weeks–months when protected from light, while of the analyte sensor (XAD-16 + CAL4, to which the oxidation product of PAP is coupled) was at the order of days when protected from air and light. Using the optical sensing probe, PAP in urine, pharmaceutical and pharmaceutical wastewater was determined. Although aminophenols showed serious interference, the method was not affected from common ions and from various important drug active constituents present in urine and pharmaceutical effluents such as acetaminophen, acetylsalicylic acid, sorbitol, and caffeine. The proposed technique was tested by replicate analysis of several complex samples with spiked PAP, with recoveries ranging between 97 and 102%.

1. Introduction

p-Aminophenol (PAP) is a commercially important intermediate for the manufacture of analgesic and antipyretic drugs [1]. It is also used as a developer in photography under trade names activol and azol and in chemical dye industries [2]. As a result, large amounts of PAP may enter the environment as a pollutant. *p*-Aminophenol is very harmful for human body due to its structural similarity to aniline and phenol. *p*-Aminophenol readily autoxidizes in solution and the rate increases with the pH. It is in redox equilibrium with quinimine under aerobic conditions, and its potential is close to that of the quinhydrone system [3]. There may be cases in real life when rapid on-site determination of *p*-aminophenol is of vital importance, such as indirect detection of organo-phosphorus nerve agents and pesticides by measuring inhibition of acetylcholine esterase-catalyzed hydrolysis of *p*-aminophenyl acetate to PAP [4] or fast urinary screening and antidote administration for paracetamol which may cause lethal hepatic necrosis and renal failure at high doses [5]. Although a maximum contaminant level goal (MCLG) set by US-EPA for drinking water does not exist for *p*-aminophenol, acetaminophen (the pain relieving drug which yields PAP upon hydrolysis) was one of the most frequently encountered organic pollutant in 127 surface water samples – found in the 1–100 ng/L range – analyzed by Minnesota Ground Water Association [6]. Therefore, it is of great importance to develop a simple and rapid method for the field measurement of trace levels PAP.

A review of the literature revealed that many methods have been reported for the analysis of PAP. These include an automated analysis derivatisation approach and several alternative HPLC methods with electrochemical, spectrophotometric, or flu-

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doi:10.1016/j.snb.2008.11.011

orescence detection. Methods utilising GC, CE and titration with electrochemical detection have been reported, alongside other electrochemical approaches including differential pulse polarography. Spectrophotometric and fluorescence methods have also been reported, utilising derivative UV or reactions to produce a coloured derivative. A popular subset of this methodology was papers describing the formation of different PAP indophenol derivatives, using a variety of reagents [7–11]. However, conventional methods of determining PAP are found to be tedious and time-consuming using sophisticated instruments. In addition, classical analytical procedures cannot be used for the field determination of PAP.

Optical chemical sensors (optodes) have played an important role in industrial, environmental and clinical monitoring since their introduction more than two decades ago as a result of their low cost, possibility for miniaturisation, and great flexibility [12]. Optical sensors offer a wide field of application and are of potential utility in all kinds of analytical sciences. Optical sensors can also be coupled to the fast growing fibre optics technology, leading to the fabrication of fibre-optic chemical sensors (FOCSs). Optical fibre technology is used to transmit electromagnetic radiation to and from a sensing region that is in direct contact with the sample. The chemical changes that occur as a result of interactions between analyte and immobilised reagents are measured spectroscopically by analyzing the radiation that returns from the sensing region [13–15]. In optical sensors, such indicators are chemically immobilised in a solid support, and spread as a thin layer or coating [16,17]. In recent years, special attention has been devoted to the direct quantification of coloured species retained on the surface of a solid support by diffuse reflectance spectroscopy [12,15,18]. Reflectance spectroscopy is the investigation of the spectral composition of surface-reflected optical radiation with respect to its angularly dependent intensity and the composition of the incident radiation [4].

Calix[*n*]arenes (*n* = 4, 6, 8), the well-known family of macrocyclic ligands, frequently serve as molecular scaffold for the construction of more elaborate supramolecular systems, such as various receptors possessing interesting complexation abilities towards target molecules or ions [19,20]. Many calixarenes and their derivatives can be used as specific ligands for analytical chemistry, sensor techniques, medical diagnostics, and for the synthesis of new materials [21]. Different types of calixarene sensors have been reported in the literature. Optical sensors based on calixarenes have been designed to detect various metal ions [19–25], gaseous ammonia [26,27] and organic amines [28]. Piezoelectric quartz crystal calixarene sensors have been designed to monitor volatile organic pollutants in the gas phase and in aqueous solution [29–32]. Electrochemical sensors based on calixarenes have been demonstrated for various metal ions [33,34].

Although quartz crystal microbalance [35] and electrochemical [36] sensors have previously been used for PAP detection, the only reflectometric sensor in literature for the same assay was developed by Filik et al. [37] using immobilised bis-8-hydroxyquinoline as the sensing element. In this work, an optochemical sensor used to determine PAP is proposed. 25,26,27,28-Tetrahydroxycalix[4]arene (CAL4) is a known reagent and used as a coupling agent for the detection of PAP by a spectrophotometric method [5]. The mechanism of *p*-aminophenol (i.e., hydrolysis product of acetaminophen or paracetamol) reaction with CAL4 in the liquid phase (without utilising a sensor) has been indicated – with formulae of related reactants and products – in a previous work of the authors [5]. The proposed reaction scheme is as follows: PAP produces a reactive benzoquinoneimine in the presence of KIO_4 in alkaline medium, which is then coupled to CAL4 to produce a blue derivative (indophenol dye; see Fig. 1). Naturally this chromophore, in adsorbed form onto the XAD copolymer, may have shown a bathochromic shift in absorption maximum relative to that in liquid solution [5]. The objective of this work is to develop a simple and rapid sensing method for the field determination of PAP by making use of the above reaction mechanism. Solid phase microextraction (SPME) technique combined with portable UV–vis reflectance spectroscopy was used for monitoring and analyzing of PAP. The performance of the immobilised CAL4 on XAD-16 as a reagent in the development of optical reflectance sensor for PAP determination has been demonstrated. The recovery of the proposed method was tested by replicate analysis of several samples with spiked PAP. The method was validated with the use of a comparative spectrophotometric method.

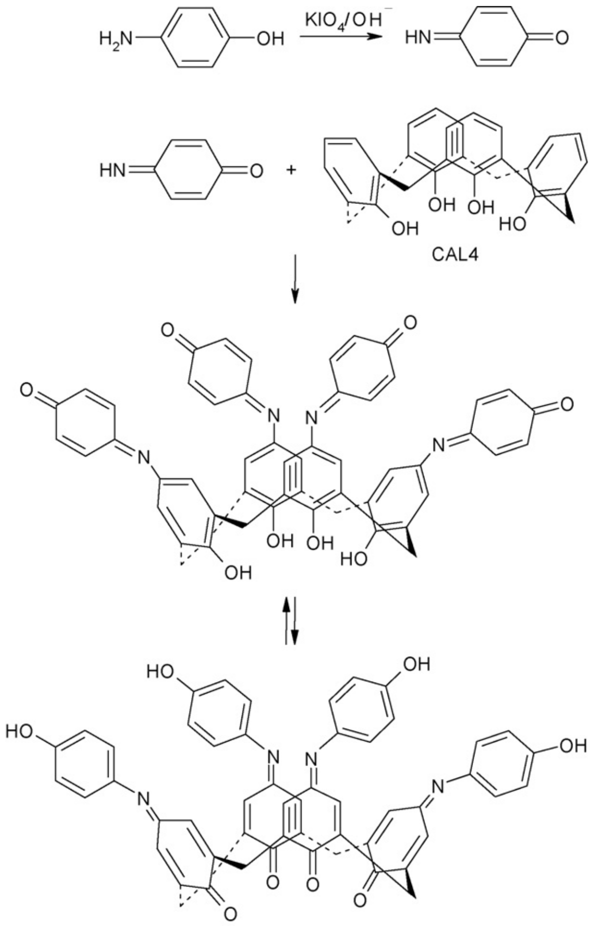

Fig. 1. Structural formulae of the sensing layer constituent; 25,26,27,28-tetrahydroxycalix[4]arene (CAL4) and its coupling product with the quinoneimine derived from periodate oxidation of *p*-aminophenol (PAP).

2. Experimental

2.1. Apparatus

The instrumentation set-up used for this experiment is as shown in Fig. 2. Experiments were carried out using a commercially available miniature fibre-optic based spectrometer (Ocean Optics Inc., HG4000CG-UV-NIR) which utilises a small tungsten halogen lamp (Ocean Optics Inc.) as the light source and a charge-coupled device (CCD) based detector for reflectance measurements. Light reflected from the flow cell was transmitted by a bundle of optical fibres to a miniature fibre-optic spectrophotometer (Ocean Optic HG4000CG-UV-NIR) which was connected to a PC (Dell-compatible) and also a printer. For optical isolation, the flow cell and the detector were kept in a black box to minimise any interference from ambient light. The spectral deconvolution was performed after smoothing