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A solid colorimetric sensor for the analysis of amphetamine-like street samples

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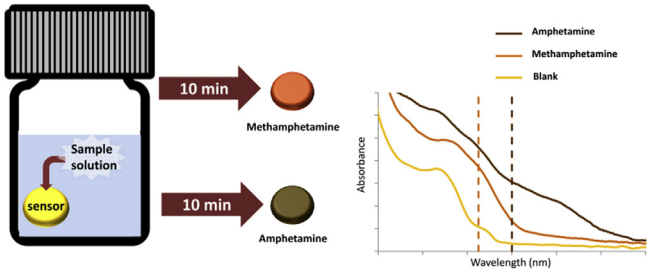
HIGHLIGHTS

- Kit for in-situ analysis of amphetamine drugs in street samples.
- A solid colorimetric sensor with the reagent embedded in a PDMS-TEOS-SiO_2 matrix.
- Validation for ecstasy street samples.
- Simplicity, portability and rapidity at a very low cost.

GRAPHICAL ABSTRACT



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ABSTRACT

A solid sensor obtained by embedding 1,2-naphthoquinone-4-sulfonate (NQS) into polydimethylsiloxane/tetraethylortosilicate/silicon dioxide nanoparticles composite has been developed to identify and determine amphetamine (AMP), methamphetamine (MAMP), 3,4-methylenedioxymetamphetamine (MDMA) and 3,4-methylenedioxyamphetamine (MDA). The analytes are derivatized inside the composite for 10 min to create a colored product which can be then quantified by measuring the diffuse reflectance or the color intensity after processing the digitalized image. Satisfactory limits of detection (0.002–0.005 g mL^{-1}) and relative standard deviations (<10%) have been achieved. The proposed kit has been successfully validated and applied to the analysis of amphetamine-like drugs street samples. The kit allows the *in-situ* screening of the mentioned illicit drugs owing to its simplicity, rapidity and portability, with excellent sensor stability and at a very low-cost.

1. Introduction

The consumption, production and commercialization of illicit drugs remain as a serious problem in many countries. In terms of production and use three synthetic drugs dominate the market: amphetamine (AMP), methamphetamine (MAMP), and ecstasy-type drugs especially 3,4-methylenedioxymetamphetamine (MDMA). Although AMP has been traditionally the most used compound, there are recent signs of the increasing availability of MAMP. Under the generic name “ecstasy” a wide variety of illicit tablets are sold in which MDMA is usually the active substance, but they may also contain other methylendioxylated amphetamines such as 3,4-methylenedioxyamphetamine (MDA) and 3,4-methylenedioxyethylamphetamine (MDEA) [1]. According to official investigations, the confiscated amounts of amphetamines and ecstasy samples have increased in recent years, and higher contents

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of MDMA in these seizures have been observed [2,3].

The identification and quantification of amphetamine-like drugs in illicit tablets have been described using several methods such as capillary electrophoresis [4], near infrared spectroscopy [5,6], gas chromatography [7,8] and liquid chromatography [9–11]. However, these methods require strict laboratory conditions and trained personnel. The development of suitable assays for instant detection of the most frequently used drugs in roadside drug testing would facilitate to take legal actions quickly. Uncertainty and delay times could be also minimized through the development of workplace screening tests. Therefore, there is an increasing interest in the development of affordable, easy-to-use and handheld devices for the detection and identification of these illicit substances in the field.

Fast detection of illicit drugs has been reported using portable ion mobility spectrometers (IMS) [12,13]. An alternative method based on surface ionization gas detection has been proposed to overcome the disadvantage of IMS of using radioactive sources for the ionization process [14]. For on-site screening purposes, portable Fourier transform infrared (FTIR) [15] and Raman spectrometers [16–18] have also been proposed. These spectrometers enable the rapid *in-situ* screening of the active principle, as well as the characterization of several excipients, without sample treatment. Nevertheless, street drugs are usually modified with excipients (i.e. adulterants or diluents) because they are typically sold by weight. Adulterants are added to mimic the effects of the active substance in order to increase its perceived quality, whereas diluents are simply added to increase the bulk and, consequently, the profits of the drug dealer. The utility of spectral libraries available is limited, owing to the wide range of excipients and their proportions in illicit preparations, which may hinder the characterization of some street samples. Moreover, these spectrometers are expensive and trained personnel may be required to interpret the results.

The employment of colorimetric tests such as the Marquis, Mandelin, Mecke and Simon's tests can be an inexpensive and fast alternative for on-site screening of suspected illicit substances. However, some of the reagents typically used for amphetamine-like compounds are hazardous; for example, the Marquis and the Mandelin reagents involve concentrated sulfuric acid. Also the reagent solutions may be instable. This is the case of the reagent 1,2-naphthoquinone-4-sulfonate (NQS); thus, tests with NQS are tedious because the reagent solutions have to be prepared daily. For on-site tests the employment of solid sensors (or solid reagents) is generally considered a more convenient alternative, mainly because risks associated with spillage are minimized [19].

An alternative to avoid the employment of liquid reagents is the entrapment of the reagents into polymeric matrices in order to develop sensors. In this respect, polydimethylsiloxane (PDMS) has been employed for chemosensor fabrication in many recent works [20–26] due to its properties such as non-toxicity, inertness, stability, ease of processing and cost effectiveness [27,28]. However, the hydrophobicity of PDMS makes difficult its use in sensors aimed at the detection of polar compounds. Tetraethylorthosilicate (TEOS) can be added to PDMS for obtaining organic/inorganic hybrid materials with lower hydrophobicity. Silica nanoparticles (SiO_2-NPs) can also be added to increase the matrix porosity, and to reduce the cracking of the sensor during the drying phase, as reported by some authors [29,30].

In the present work, we have developed a kit based on a device of PDMS/TEOS/SiO_2 NPs doped with NQS reagent for the analysis of AMP, MAMP, MDMA and MDA. The non-hazard reagent NQS has been selected for derivatization because it forms colored derivatives with amines. Brown-grey and orange derivatives are obtained with primary and secondary amines in alkaline medium, respectively, making possible their colorimetric determination [31–33]. As demonstrated in previous works, the reagent can be immobilized into PDMS, which has been exploited for the measurement of amines of interest in environmental matrices such casein and in effluents and volatile amines in air, as well as biocides in industrial products [34–36]. In the present study, a solid sensor has been developed for the analysis of amphetamine-like compounds. In-situ screening is possible through the observation of color of the sensor after its introduction into a solution of the sample. After reaction, quantitative analysis has been carried out in the lab by direct measurement of the diffuse reflectance and also by measurement of color intensity after processing its digitalized image. The kit has been applied to ecstasy street samples and the accuracy has been validated by comparing the results with those obtained by liquid chromatography (LC). The tested samples have been also characterized by Fourier transform infrared-attenuated total reflectance (FTIR-ATR) spectroscopy.

2. Materials and methods

2.1. Reagents

All the reagents were of analytical grade. Acetonitrile (HPLC grade) and ethanol were purchased from Romil (Cambridge, UK). AMP sulfate, MAMP hydrochloride, MDMA hydrochloride, MDA hydrochloride, TEOS, SiO_2-NPs (5–15 nm spherical particle size), NQS, ibuprofen, acetylsalicylic acid, levamisol hydrochloride, procaine hydrochloride, ephedrine hydrochloride, scopolamine hydrobromide, cocaine hydrochloride, cannabinol, cannabidiol and Δ^9-tetrahidrocannabinol (THC) were obtained from Sigma-Aldrich (St. Louis, MO, USA). 9-Fluorenylmethyl chloroformate (FMOC) was purchased from Aldrich (Steinheim, Germany). Sodium hydrogencarbonate, starch and magnesium sulfate were from Probus, (Badalona, Spain). Sodium hydroxide and maltose-1-hydrate were supplied from Panreac (Barcelona, Spain). Paracetamol, caffeine, saccharose and D-lactose monohydrate were obtained from Guinama (Alboraya, Spain). Hydrochloric acid, mannitol and glucose anhydrous were purchased from Scharlau (Barcelona, Spain). PDMS Sylgard® 184 Silicone Elastomer Kit (Sylgard® 184 silicone elastomer base and Sylgard® 184 silicone elastomer curing agent) was provided by Dow Corning (Midland, MI, USA). Ultrapure water was obtained from a Nanopure II system (Sybron, Barnstead).

All solutions were stored in the dark at 4 °C to avoid possible decomposition.

2.2. Apparatus and conditions

Spectrophotometric measurements were carried out using a Cary 60 Fiber Optic UV–Vis spectrophotometer (Agilent Technologies), fitted with a remote fiber optic diffuse reflectance accessory from Harrick Scientific Products (Mulgrave, Victoria, Australia). Data were recorded and processed using a Cary WinUV software (Agilent Technologies). The spectral range measured was from 200 to 800 nm. The absorbance spectra were registered in diffuse reflectance mode. The working wavelength for measurement of the NQS derivatives formed for primary amines was 600 nm, and for secondary amines was 525 nm.

Photographic images of the sensors were taken with a Nikon CoolPix S2600 digital camera with 14 megapixels and 5× wide optical zoom. The camera was programmed without flashlight. The object distance was 10 cm. The images were imported into a computer, and their color differences were analyzed by free image editor software GIMP (version 2.8). The color intensity was assessed using the color picker tool of GIMP with an average of 35 × 35 pixels close to the center of the circular device. An area of 100 × 100 pixels was selected using the ellipse select tool. The red-green-blue