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Real time quantitative colourimetric test for methamphetamine detection using digital and mobile phone technology

Aree Choodum [a,b,*], Kaewalee Parabun [a], Nantikan Klawach [a], Niamh Nic Daeid [c], Proespichaya Kanatharana [b,d], Worawit Wongniramaikul [b,e]

[a] Department of Applied Science, Faculty of Science, Prince of Songkla University, Hat Yai, Songkhla 90112, Thailand
[b] Trace Analysis and Biosensor Research Center, Prince of Songkla University, Hat Yai, Songkhla 90112, Thailand
[c] Centre for Forensic Science, Department of Pure and Applied Chemistry, WestCHEM, University of Strathclyde, 204 George Street, Glasgow G1 1WX, UK
[d] Department of Chemistry and Center of Excellence for Innovation in Chemistry, Faculty of Science, Prince of Songkla University, Hat Yai, Songkhla 90112, Thailand
[e] Faculty of Technology and Environment, Prince of Songkla University, Phuket Campus, Phuket 83120, Thailand

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ABSTRACT

The Simon presumptive color test was used in combination with the built-in digital camera on a mobile phone to detect methamphetamine. The real-time Red-Green-Blue (RGB) basic color data was obtained using an application installed on the mobile phone and the relationship profile between RGB intensity, including other calculated values, and the colourimetric product was investigated. A wide linear range (0.1–2.5 mg mL^{-1}) and a low detection limit (0.0110 ± 0.0001–0.044 ± 0.002 mg mL^{-1}) were achieved. The method also required a small sample size (20 μL). The results obtained from the analysis of illicit methamphetamine tablets were comparable to values obtained from gas chromatograph-flame ionization detector (GC-FID) analysis. Method validation indicated good intra- and inter-day precision (2.27–4.49%RSD and 2.65–5.62%RSD, respectively). The results suggest that this is a powerful real-time mobile method with the potential to be applied in field tests.

1. Introduction

Methamphetamine is a synthetic stimulant which affects the central nervous system [1]. It is increasingly abused and has caused serious health and social problems. It is usually called "crank" if in the form of the powder hydrochloride salt, "Yaba" in Thai when in the form of tablets, and "Ice" in its clear crystal form. This illegal drug has been classified as a Category I narcotic under the Narcotic Act B.E. 2522 of Thailand, while it has been reclassified from a Class B to a Class A Schedule 2 drug under The Misuse of Drugs Act 1971 (UK) in 2007 [2].

Colourimetric presumptive tests are common methods used for field test. The Marquis and Simon presumptive chemical tests are recommended for methamphetamine by the United Nations International Drug Control Programme [1]. The Marquis test produces an orange-brown reaction, while a blue reaction is obtained from the Simon test. The latter test can be used to differentiate this drug from amphetamine *via* the selective reaction of the Simon's reagents with the secondary amine within methamphetamine. These tests are currently widely used as the presumptive tests for methamphetamine in most forensic laboratories because they are rapid, simple, and reliable. However they are currently only used to produce qualitative results. Quantitative analysis of methamphetamine is generally achieved within a forensic science laboratory using gas chromatography which may coupled with flame ionization detector (GC-FID) and/or mass spectrometry (GC–MS) [3–9].

Our previous work has shown a great potential for digital image-based analysis to be used to develop fast and direct quantitative determinations [10–12] which extend the potential value of colourimetric presumptive test methods. The method has been used for rapid quantitative analysis by color test for amphetamine and methamphetamine [10], opiates [12], and the explosive trinitrotoluene [11]. It has also been reported in other analytical applications [13–19]. These applications have been based on the analysis of basic red green blue (RGB) color data obtained from digital images [12,14] generated by a digital camera. During image processing, the reflected light from the colored products of a colourimetric test pass through three different filters, red, green, and blue, and is detected and recorded by image sensors

* Corresponding author at: Department of Applied Science, Faculty of Science, Prince of Songkla University, Hat Yai, Songkhla 90112, Thailand.
Tel.: +66 0 7428 8102; fax: +66 0 7444 6681.
E-mail addresses: choodum@gmail.com, aree.c@psu.ac.th (A. Choodum).

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such as charge-coupled devices (CCD) [14,19] or complementary metal oxide semiconductors (CMOS). The final color of the digital image is composed from the additive data of the three RGB filters after scaling and adjustment to compensate for variations in the conditions of capture. The RGB values of digital images can be measured for example using the image processing tool box in Matlab [15,20], Kylix [17,21], Visual basic [16,18], or Adobe Photoshop [10–12] and can be used to calibrate the images, concentrating on the analytes of interest. This method, thus, provides a basis on which quantitative colourimetric analysis of samples containing an unknown quantity of analyte can be undertaken.

In previous studies, standard digital cameras *e.g.* digital single-lens reflex (DSLR) cameras have been used to produce the color images. However, images can also be conveniently produced using built-in digital cameras in commonly available smart phones.

This study used the built-in digital camera of an iPhone and an iPhone application (app) for color analysis instead of any other image processing programs. This resulted in a more convenient analysis. The RGB values from the color products were also immediately available without the necessity to connect to an external computer as reported in previous studies. The rapid, portable, and accurate quantitative analysis of methamphetamine was achieved by using a simple colourimetric test only.

2. Materials and methods

2.1. Materials

Crystal methamphetamine standard (Ice; purity ~98.5%) and Yaba (as samples seized by law enforcement agencies) were obtained from the Drug Control Division, Food and Drug Administration Thailand (license number: 1003.2/790). Methamphetamine standard solutions were prepared with ultrapure water (Barnstead EasyPure II, Thermo fisher scientific, OH). Acetaldehyde was purchased from Aldrich Chemical Co. Ltd. (Dorset, England), and anhydrous sodium carbonate was purchased from Fisher Chemicals, Fisher Scientific UK Limited (Loughborough, UK). Sodium nitroprusside dihydrate (>98.0%) was purchased from Fluka (Sigma–Aldrich Chemie, Steinheim, Germany).

2.2. Colourimetric presumptive test (Simon test).

Two reagents were required for the Simon test, 10% (v/v) acetaldehyde in aqueous sodium nitroprusside solution (1%, w/v) (reagent 1) and 2% (w/v) sodium carbonate in water (reagent 2) [1]. The reagents were prepared under optimized conditions as follows: 10 μL of reagent 1 was added to 20 μL of the methamphetamine solution in a micro-tube. This was followed by 80 μL of reagent 2. The solution was then mixed by shaking and left to stand for 2 min prior to detecting its color intensities.

Each experiment was repeated 3 times. The linear range was investigated from 0.05 to 10 mg mL^{-1}. The average intensities of the red, green and blue colors from 3 replications were used to establish a calibration graph for each color. The limit of detection was calculated using standard methods (limit of detection = $y_B + 3S_B$ where y_B is the intercept of the calibration curve and S_B is the standard deviation of the blank) [22]. Precision was expressed as the percentage relative standard deviation for each color from the 3 replicate analysis.

2.3. RGB capturing system and procedure

A custom-built color detection box (Fig. 1) was used to eliminate any effects from environmental light. The box (8.0 cm × 11.0 cm × 5.5 cm) was made of opaque black corrugated plastic board with an internal white background. A flat cap PCR micro-tube was hung at the top of the box as a reaction container. A 5 W cool daylight Philips light bulb was put at the top of the box as the upper light source, 2 cm from the micro-tube (this was found to be the optimal distance). The intensity of the color product inside the micro-tube was detected using the ColorAssist app (FTLapps, Inc.) for an iPhone 4.0 in the flash-off mode.

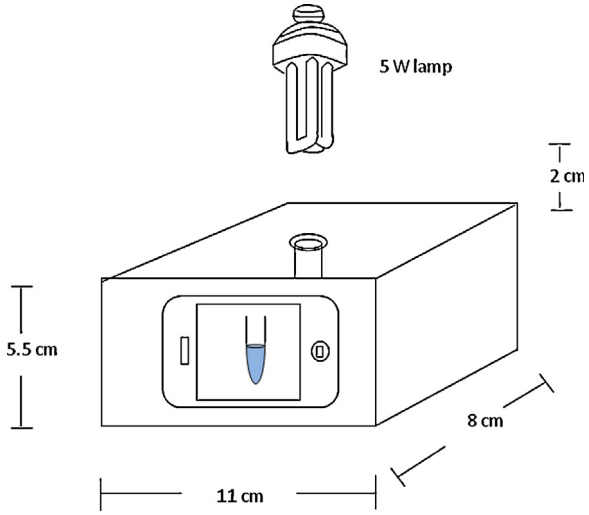

Fig. 1. Real time on-mobile color analysis system for methamphetamine detection.

2.4. Gas chromatography-flame ionization detector analysis

An Agilent 7980A gas chromatograph equipped with a flame ionization detector (Agilent Technologies, China) was used for sample quantification. Samples of 1 μL were injected and separated using a HP-5 capillary column (30 m length × 0.32 mm mm id × 0.25 μm film thickness). The column was kept at 100 °C for 1 min, increasing to 260 °C at a rate of 20 °C min^{-1} and held for 3 min [10]. A split ratio of 25 to 1 with a carrier gas (high-purity-grade helium) flow rate of 1.0 mL min^{-1} was used. The flow rate of fuel (hydrogen), oxidant (air zero), and make-up gas were 30, 300, and 25 mL min^{-1}, respectively. The inlet and detector were kept at 260 °C and 275 °C, respectively. The instrument was calibrated for methamphetamine in the range of 0.0025–2 mg mL^{-1} where $n = 6$ for each calibration standard injected.

2.5. Analysis of Yaba samples

Five seized Yaba samples obtained from the Drug Control Division of the Food and Drug Administration of Thailand. A sample of ten milligrams from each Yaba sample was extracted with 1 mL of water and sonicated for 5 min. The supernatant was analyzed using the Marquis and Simon test. Samples were also quantified using the iPhone method under test and using GC-FID. For gas chromatographic analysis, methanol was used to extract the methamphetamine from the Yaba.

3. Results and discussion

3.1. Simon test for methamphetamine

Methamphetamine reacts with acetaldehyde to produce an enamine intermediate which then reacts with sodium nitroprusside to produce an immonium salt. This salt can then be hydrolyzed to a Simon-Awe complex to give a blue colored product [10,23]. At high concentrations (>1 mg mL^{-1}) the blue product remains for 3–4 min before gradually changing to purple which becomes deeper