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Selective pre and post blast trinitrotoluene detection with a novel ethylenediamine entrapped thin polymer film and digital image colorimetry

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ABSTRACT

A novel test kit was developed for the selective detection of trinitrotoluene (TNT). A thin film of ethylenediamine (EDA)-entrapped polyvinyl chloride was fabricated within a small tube which made the kit easily portable. A red-brown complex was obtained from a selective reaction of released EDA with TNT. The test kit was used in conjunction with digital image colorimetry for rapid quantitative analysis of TNT. The Red-Green-Blue (RGB) values from digital photos of the colorimetric products were used as the analytical data to establish calibration curves of TNT. A wide linear range (0–100 $\mathrm{mgL^{-1}}$) with good linearity ($R^2 > 0.99$) and low limit of detection (1.00 ± 0.02 $\mathrm{mgL^{-1}}$–5.4 ± 0.3 $\mathrm{mgL^{-1}}$) was obtained for quantification of TNT. Good precision was obtained in both intra- and inter-day tests (2.18–5.59%RSD and 4.00–8.83%RSD, respectively). The method showed good accuracy with control and spiked soil samples: TNT readings were 8.0–12.2 $\mathrm{mgL^{-1}}$ with 10 $\mathrm{mgL^{-1}}$ known concentration. The test kit could be stored in both desiccator and freezer for 2 months (only +0.6% and +5.0% change in the blue channel intensity). The test kit was able to detect trace residues of TNT from an actual bombing crime scene (Ratchaprasong intersection, Bangkok) one week after the bombing.

1. Introduction

2,4,6-Trinitrotoluene (TNT) is one of the most widely used explosive materials. It has been reported to contaminate the environment especially after military activities, operational deployment of land mines, and other industrial and mining activities [1–3]. Because TNT is highly toxic for many macro- and microorganisms [4–6], a rapid low cost method for the detection of TNT is desired for use at potential contaminated sites, to assess improvised explosive devices and post blast sites, and in land mine detection.

Various types of sensor such as electrochemical sensors, mass sensors, and optical sensors have been reported for the field detection of explosive materials [7,8]. Optical sensors are flexible in their ability to detect a wide variety of explosives, and can be miniaturized. Among the optical sensors, fluorescence sensors provide the highest sensitivity (possibly with some loss of selectivity), while the colorimetric sensors are simple and could be easily applied in rapid on-site detection. The latter are commonly based on specific reagents entrapped within a solid support [1,9,10]. When TNT reacts with the entrapped reagents, the reaction products absorb light at specific visible wavelengths, so they appear colored to the naked eye. Mutual solubility of the colorimetric reagent and the solid support is important in the fabrication of colorimetric sensors. A non-polar TNT-selective reagent such as dicyclohexylamine

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(DCHA) [1] is commonly entrapped within a poly vinyl chloride (PVC) matrix, while the polar tetramethylammonium hydroxide reagent has been entrapped within poly vinyl alcohol (PVA) cryogel [11].

TNT is known to form a charge transfer complex with various amines, including DCHA [1,12], isopropylamine, tetraethylenepentamine, and bis(3-aminopropyl)amine) [13]. Among these, ethylenediamine (EDA) was found to provide the most stable complex with the largest association constant [13]. Hence, it was selected here as the selective colorimetric reagent for the determination of TNT. PVC, a non-polar polymer matrix, was then used as a polymer support to develop a selective thin film, to be used in a novel TNT test kit.

Most colorimetric sensors are combined with spectrophotometric detection for quantitative analysis, so a transparent homogeneous sensor film is required [1]. Suitable elasticity is also desired since the sensor film needs to properly fit in the optical cuvette. In this work, an easy-to-prepare selective thin sensing film was combined with digital image technology for the first time, to avoid the limitations from need of an actual spectrophotometric measurement. Rapid quantitative analysis is instead pursued using a common digital camera or a smartphone camera. This would make on-site TNT detection convenient, removing the need of a spectrophotometer in sample quantification.

Digital image colorimetry is the analysis of digital color images of colorimetric products, from reactions between the analyte of interest and an appropriate reagent [11,12,14]. During imaging, the light reflected from the colored product passes through an RGB filter in the camera. The filter separates the light to three different spectral ranges, which are each detected and recorded by the image sensor located behind the filter. Combining the image layers from all three filters generates the common fully colored digital image, at least for the subjective human perception. On the other hand, a common digital color image can be separated to its component color layers, *e.g.* by using Matlab [15,16], Kylix [17,18], Visual basic [19,20], or Adobe Photoshop [12,14,21,22], and individual RGB values are obtained for each image pixel. These color layer intensity values are the analytical data for quantification of the target analyte.

In this work, a polymer film based colorimetric test kit was developed for the determination of TNT. The test kit is based on entrapped colorimetric reagent, EDA, within a thin film of PVC. The developed colorimetric test kit is intended for use with digital RGB imaging, *i.e.*, ordinary color photography, to quantify TNT. The photography was done with a box isolating the sample and the camera from the surroundings, fixing their positions, and providing reproducible lighting. The thin film test kit was applied to both pre- and post-blast detection, including also trace explosive residues at the crime scene of Bangkok bombing, which took place in 2015.

2. Materials and methods

2.1. Materials

2,4,6-Trinitrotoluene in acetonitrile (1 mg mL^{-1}) was purchased from Supelco (Bellefonte, PA). EDA solution, dioctylphthalate (DOP, 99%), tetrahydrofuran (THF), and PVC (high molecular weight) were purchased from Sigma-Aldrich Ltd. Acetone was purchased from Merck (Darmstadt, Germany). Ultrapure water was obtained from Barnstead EasyPure II laboratory water purification system (Barnstead EasyPure II, Thermo Fisher Scientific, OH).

2.2. Preparation of the TNT test kit

The high molecular weight PVC (1 g) was dissolved in THF (11 mL) for 3 h with magnetic stirrer, to obtain a clear viscous solution. A plasticizer (DOP, 150 μL) was then directly added into the clear PVC solution before adding the colorimetric reagent (2.5 mL EDA). The mixture was stirred until it appeared homogeneous. Fifty microliters of the mixture was transferred into a small plastic tube (200 μL) and left at ambient conditions for an hour to allow the excess THF solvent to evaporate. When a thin film containing EDA appeared at the bottom of the tube, the lid of the tube was closed. These TNT test kits were kept in a desiccator until further use. Blank test kits were also prepared using otherwise the same procedure but without adding EDA.

2.3. Characterization of the polymer film

The morphology of the polymer film was investigated using scanning electron microscopy (SEM) (Quanta400, FEI, Czech Republic). The functional group of the TNT test kit was characterized by Fourier transform infrared spectroscopy (FTIR) (Equinox55, Bruker, Germany). Spectral analysis was performed over a range of 4000–400 cm^{-1} at a resolution of 4 cm^{-1} using KBr pellet samples.

2.4. Stability of the TNT test kit

The stability of the TNT test kit was evaluated by preparing 70 TNT test kits using the same ingredients and at the same time. Three test kits were used to detect TNT on the day of preparation, and the remaining test kits were divided and stored in a freezer and a desiccator until required. Three test kits were subsequently removed from the storage for TNT detection each day over a one week period and then on a weekly basis for a further 3 weeks and finally after 2 months.

2.5. Color test of TNT

A range of TNT standards (0.5–100 mgL^{-1}) was prepared by diluting a stock solution (1 $mgmL^{-1}$ in acetonitrile) with acetone. One hundred microliters of each TNT standard solution was transferred to a test kit and mixed by shaking. The resultant colored products were photographed using the built-in digital camera of an iPhone 4.0 at 1 min of reaction, as well as at 2 min of reaction. Each test was repeated using three test kits, while the resultant products were photographed six times. The average intensities of the red, green and blue color layers (the RGB values) across the 6 images for each test kit were investigated, using an in-house RGB analysis program.

2.6. Photographic system and digital image analysis procedure

The photographic system and digital image analysis procedure were the same as in our previous work [11]. Briefly, a designed photographic box (13.5cm × 15.5cm × 7.5 cm) was used for all imaging done with the built-in digital camera of an iPhone 4.0. Each image was 1.05 MB size (2592 × 1936-pixel) and was saved as a JPEG (24-bit) file in the iPhone's memory. An in-house RGB analysis program was used to analyze all images. A single data point for each standard concentration was obtained from the average RGB values of all six images of the three test kits (18 values in total), and these were used to determine the calibration curves.

2.7. Color test of TNT in post-blast samples

Post-blast soil samples were prepared and analyzed using the same procedure as in our previous study [11,12,14]. One gram of soil sample was extracted with 2.5 mL of acetone using a sonicator for 15 min. After filtering through Whatman No.1 filter paper, the filtrate of extract in acetone was analyzed using the TNT test kit. Cardboard post-blast samples were also analyzed by extracting the