Short Communication

Reflectance-based detection of oxidizers in ambient air

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A B S T R A C T

This study used two types of paper supported materials with a prototype, reflectance-based detector for indication of hydrogen peroxide vapor under ambient laboratory conditions. Titanyl based indicators provide detection through reaction of the indicator resulting in a dosimeter type sensor, while porphyrin based indicators provide a reversible interaction more suitable to continuous monitoring applications. These indicators provide the basis for discussion of characteristics important to design of a sensor system including the application environment and duration, desired reporting frequency, and target specificity.

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1. Introduction

Peroxide-based homemade explosives have been identified as a threat by the US Department of Homeland Security and the US Department of Defense. Numerous online articles warn first responders of the threat these materials present, the ease of their synthesis, and their inherently unstable nature. Preparation can be as simple as mixing household chemicals, such as acetone, acid, and peroxide, making the materials favored for incorporation into improvised explosive devices (IEDs). Triacetone triperoxide (TATP), hexamethylene triperoxide diamine (HMTD), tetramethylene diperoxide dicarbamide (TMDD) and related cyclic organic peroxides are examples of specific compounds, but peroxide-based explosives can be used in either liquid or solid forms. Liquids, for example, have been used in terrorist incidents, including the 2005 attacks on transit systems in London and the foiled airline attacks of 2009.

The threat posed by these compounds has resulted in development of a wide range of detection approaches for single compounds (i.e., TATP) utilizing techniques from mass spectrometry through portable electrochemical approaches [1–3]. A more general method could target the hydrogen peroxide present in the liquid explosive materials and often found as an impurity and/or degradation product remaining in the solids utilized. While colorimetric detection methods for hydrogen peroxide in solution are widely available [4–12], those available for gas phase detection are more limited [3]. A paper-based material has been reported for detection of hydrogen peroxide vapor [13]. The material relies on the interaction of peroxide with ammonium titanyl oxalate resulting in a change from white to yellow (Scheme 1). Titanium based indicators have been used by a number of groups for detection of hydrogen peroxide [7–12]. The recent report, however, utilizes a paper support, providing a large surface area for interaction of target with the indicator as well as an open pore network for ease of diffusion throughout the material [13]. Selectivity for hydrogen peroxide was demonstrated with no response to ethanol, methanol, acetone, tetrahydrofuran, hexane, toluene, ethyl acetate, or chloroform.

In the current study, the paper supported titanyl indicator is used with a prototype chemical sensor. The sensor hardware has previously been described for use with paper supported porphyrin indicators for the detection of alcohol vapor [14]. It relies on an array of commercially available color sensors and provides data output consisting of white, red, green, and blue color values. Data is collected in five second intervals, allowing for rapid determination of target presence. While the previous work characterized the titanium indicators under highly controlled conditions, the prototype

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[1] At NRL Summer 2015 through SEAP internship.
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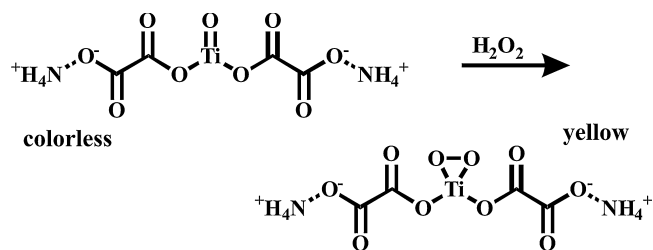
Scheme 1. Modification of titanyl indicator by peroxide resulting in yellow color.

sensor of this study provided the opportunity to look at indicator performance in the ambient environment with conditions changing in real-time.

2. Experimental

For synthesis of peroxide specific indicators, ammonium titanyl oxalate monohydrate was purchased from Sigma Aldrich and used as received. The paper support materials were purchased from Whatman (Cat No. 1001 150). Loading of the paper support was accomplished using 100 μL of 20 μM ammonium titanyl oxalate monohydrate in water which was drop-cast onto a 2.5 cm × 2.5 cm swatch [13]. This was followed by drying under vacuum at room temperature for 1 h. Cobalt (CoDIX), copper (CuDIX), and nickel (NiDIX) variants of Deuteroporphyrin IX bis ethyleneglycol (CAS 6239456-72-5) were prepared by reflux as previously reported [14,15]. Paper supported porphyrin indicators were prepared using a dip and dry technique. For a 5 cm × 33 cm swatch, 0.4 mM porphyrin in water (total volume 6 mL) was used. The paper support (WypAll X60) was pulled through this solution and allowed to dry slightly before being pulled through the solution again. This was repeated until all porphyrin solution had been deposited (typically three cycles). Samples were then dried at 100 °C before storing in the dark in sealed plastic bags. This is a modification of the procedure described previously for preparation of the indicator materials [14].

The prototype reflectance instrument utilized low cost, commercially available color sensing breakout boards from Parallax, Inc. (model TCS3200-DB, Rocklin, CA), providing a color light-to-frequency integrated circuit from AMS (model TCS3200, Plano, TX), a pair of white LEDs, and an adjustable lens. The device was previously described in detail [14]. Briefly, six of the breakout boards were used with a customized multiplex platform in which the boards were mounted using in-house developed holders made from chemically resistant Delrin plastic (McMaster-Carr, Princeton, NJ). The indicator support provides a lip on the bottom that can sit on top of a Petri dish or bottle (Fig. 1). The device output consists of a stream of digital pulses proportional to the intensity of the color being measured. A custom printed circuit board (PCB) interfaces with and controls the six sensors. The PCB uses an Atmel ATMega microcontroller (Atmel Corporation, San Jose, CA) to regulate the timing of events, count pulses, and report the results to a computer. Communications between the instrument and the computer are via USB; power is supplied through a dc barrel jack. A LabWindows developed software-based graphical user interface (GUI) communicates with the PCB firmware through simple ASCII commands.

Target exposure was completed using 200 mL Nalgene bottles containing a solution volume of 30 mL. Target solutions consisted of deionized water; dilutions of 30% hydrogen peroxide; dilutions of sulfuric, hydrochloric, and nitric acid; and solvents such as ethanol and acetone. H_2O_2 solutions of 3%, 1.2%, 0.3%, 0.15%, and 0.06% in water provided maximum initial headspace concentrations of 8.45,
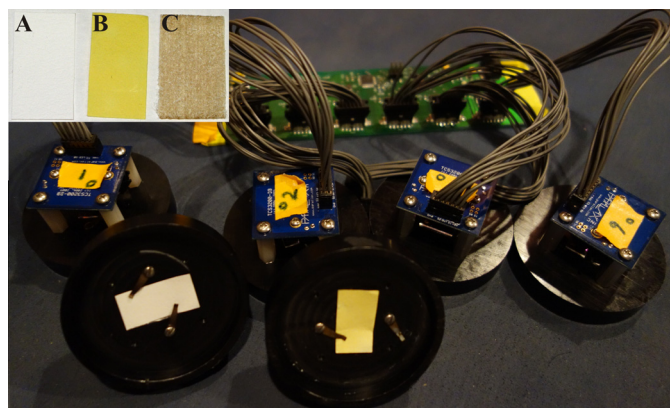

Fig. 1. Photograph of the prototype sensor system with fresh (A) and exposed (B) titanyl indicators and (C) the CoDIX indicator.

3.38, 0.84, 0.42, and 0.17 ppm, respectively. Solutions were prepared and capped for 2–4 h to allow for headspace equilibration prior to exposure of indicators. Data was collected for a minimum of five minutes prior to target exposure to establish a baseline for the indicators. For this measurement, bottles containing 30 mL of water were used as the control solutions. Exposure was initiated by exchanging water containing bottles for those containing target. An alternative approach accomplished target exposure by placing the indicator supports over empty Petri dishes for pre- and post-exposure measurements. The exposure measurements were completed by placing the holder over a Petri dish (60 mm; total volume 57 mL) containing 1 mL of warmed target solution (10 min in oven at 60 °C).

3. Results and discussion

The titanyl indicators were evaluated using the prototype reflectance sensor with target (30 mL) in 200 mL Nalgene bottles. This experiment is significantly different from those described in the original report [13]. Initial characterization utilized a sealed 9 L headspace over 1 L of target solution with a fan generating impacting air flow. Under these conditions, the target content at even the lowest utilized concentrations (0.1 ppm vapor) would not change over the course of the measurement. The experiments of the current study were not conducted in a sealed headspace nor did they utilize a large target excess; concentrations of target were expected to change over time. Ambient temperatures were between 24 and 27 °C with relative humidity between 43% and 55%. Though the prototype device reports red, green, and blue (RGB) color values (Fig. 2, Panel A), changes observed for the titanyl indicators were much more dramatic for the blue channel than for the red or green. The data has been normalized using the average value from the pre-exposure measurement to account for sensor to sensor variation in the data. In Fig. 2 (Panel B), we report the changes in the blue channel over time following exposure of indicators to various concentrations of hydrogen peroxide. The rates of change in reflectance for the titanyl indicators (blue and green values only) were found to be concentration dependent with saturation of the indicator occurring at ~9.5 h for the 3% target solution and ~15.5 h for the 1.2% target solution. Measurements were continued to 66.5 h; none of the lower target concentrations resulted in indicator saturation. (Additional results provided in the Supplementary Material.)

Previous work with the prototype sensor utilized porphyrin indicators and focused on chemosorptive interactions [14,16], often of a reversible nature. The titanyl compounds utilize a reactive interaction (non-reversible) with the peroxide vapor.