



On-site semi-quantitative analysis for ammonium nitrate detection using digital image colourimetry



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ABSTRACT

Digital image colourimetry was successfully applied in the semi-quantitative analysis of ammonium nitrate using Griess's test with zinc reduction. A custom-built detection box was developed to enable reproducible lighting of samples, and was used with the built-in webcams of a netbook and an ultrabook for on-site detection. The webcams were used for colour imaging of chemical reaction products in the samples, while the netbook was used for on-site colour analysis. The analytical performance was compared to a commercial external webcam and a digital single-lens reflex (DSLR) camera. The relationship between Red-Green-Blue intensities and ammonium nitrate concentration was investigated. The green channel intensity (I_G) was the most sensitive for the pink-violet products from ammonium nitrate that revealed a spectrometric absorption peak at 546 nm. A wide linear range (5 to 250mgL^{-1}) with a high sensitivity was obtained with the built-in webcam of the ultrabook. A considerably lower detection limit ($1.34 \pm 0.05\text{mgL}^{-1}$) was also obtained using the ultrabook, in comparison with the netbook ($2.6 \pm 0.2\text{mgL}^{-1}$), the external web cam ($3.4 \pm 0.1\text{mgL}^{-1}$) and the DSLR ($8.0 \pm 0.5\text{mgL}^{-1}$). The best inter-day precision (over 3 days) was obtained with the external webcam (0.40 to 1.34% RSD), while the netbook and the ultrabook had 0.52 to 3.62% and 1.25 to 4.99% RSDs, respectively. The relative errors were $+3.6$, $+5.6$ and -7.1% , on analysing standard ammonium nitrate solutions of known concentration using I_G , for the ultrabook, the external webcam, and the netbook, respectively, while the DSLR gave -4.4% relative error. However, the I_G of the pink-violet reaction product suffers from interference by soil, so that blank subtraction ($|I_G - I_{G\text{blank}}|$ or $|A_G - A_{G\text{blank}}|$) is recommended for soil sample analysis. This method also gave very good accuracies of -0.11 to -5.61% for spiked soil samples and the results presented for five seized samples showed good correlations between the various imaging devices and spectrophotometer used to determine ammonium nitrate concentrations. Five post-blast soil samples were also analysed and pink-violet product were observed using Griess's test without zinc reduction indicating the absence of ammonium nitrate. This demonstrates significant potential for practical and accurate on-site semi-quantitative determinations of ammonium nitrate concentration.

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1. Introduction

Ammonium nitrate is a powerful oxidizer, commercially available as hygroscopic crystals or white granules that are odorless, colourless, and transparent [1,2]. It is a salt of nitric acid, and was first used as blasting agent in 1867 [3]. It is currently available in three grades for use as explosive, fertilizer or chemical [2,4]. The explosive grade can be mixed with fuel oil to produce an explosive mixture known as ammonium nitrate fuel oil (ANFO), commonly used in construction work. Such a mixture can be improvised (homemade) or commercially obtained.

Ammonium nitrate was first used to replace the potassium nitrate in black powder by Grindel and Robin in the beginning of the 19th century [2,5]. It was reported in the Delhi bombing [6], and was also used to destroy the Alfred P. Murrah Federal Building in the United States, in 1995 (Oklahoma City Bombing) [7]. The Irish Republican Army (IRA) has also used crushed ammonium nitrate in their bombs in Northern Ireland and London [4]. The governments in Pakistan and Afghanistan have banned the use of this fertilizer due to its diversion from farming to the production of ANFO [8]. The Council of Australian Government and various other countries have also restricted access to ammonium nitrate [4]. Due to its low cost and availability in bulk quantities, ammonium nitrate and ANFO as an improvised explosive still remain a significant threat.

Ammonium nitrate can be detected using positive ionization mode electrospray ionization-mass spectrometry (ESI-MS) [3,9,10],

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inductively coupled plasma mass spectrometry (ICP-MS) [11], and isotope ratio mass spectrometry [4]. Although, clearly mass spectrometry (MS) has great potential for detection of the compound, the high cost and size of equipment generally prevent portable applications. Ammonium and nitrate ions are also detectable using ion chromatography (IC) [12] and capillary electrophoresis (CE) [13], however, these instrumental techniques are, for the most part, both laboratory based and time consuming.

Nitrate ions are also presumptively detected using the diphenylamine test and the Griess's reagent, while Nessler's reagent is commonly used for ammonium ions [3,14], however, currently there is no colourimetric test for the ammonium nitrate ion pair [3]. Such colourimetric methods could provide valuable and cost effective tools for on-site screenings, with confirmatory analysis being undertaken using instrumental methods within the laboratory [15,16]. Explosion investigators need a reliable triage mechanism so that effective decision making and use of available resources can be made, especially when large numbers of samples are recovered, such as in the case of the Bali bombing [17].

In recent years, colourimetric methods have been extended to various fast and direct quantitative determinations by coupling with the analysis of digital images [18–22]. Such methods have been used for rapid quantitative analysis of trinitrotoluene [18,21], as well as other analytical applications [19,20,22–27]. A digital image provides basic red green blue (RGB) colour data for colourimetry. During imaging, the reflected light from a colourimetric product passes through three filters, the RGB filters, which allow the image to be decomposed into three components representing different spectral ranges. These components are detected and recorded by image sensors within the digital camera. The final colour of a digital image is formed additively from the three RGB component images. The RGB values of pixels in a colour image can be used to generate calibration equations for quantitative image analysis. In practice the colourimetric products from known concentration standards would be imaged for such calibration. Then the calibrated image analysis would be used to quantify unknown samples, to estimate their analyte concentrations.

The various types of digital cameras for colour imaging include digital single-lens reflex (DSLR) cameras [18–20,28], digital compact cameras [26,27,29], built-in cameras in mobile phones [21,22], and webcams [30–35]. The use of such cameras as colourimetric detectors lowers the cost of quantitative analysis by avoiding the costs of an expensive spectrophotometer, and webcams in particular are inexpensive and readily accessible.

In this study, on-site quantitative colourimetric tests were developed for the determination of ammonium nitrate. A webcam was used as a cost effective colourimetric detector, while a netbook and an ultrabook were selected to process the colour images. These devices were selected because they are small, lightweight, legacy-free, and inexpensive. The performance of this detection system using both the external and the built-in webcams in the netbook and the ultrabook was investigated, and compared against a comparatively expensive DSLR camera for imaging.

2. Materials and methods

2.1. Materials

Ammonium nitrate (grade A, 99.99%) was supplied by S.M. chemical supplies Co. Ltd. (Bangkok, Thailand). Sulphanilamide was obtained from Panreac (Barcelona, Spain), while *N*-(1-naphthyl)ethylenediamine dihydrochloride (NED) and zinc powder were obtained from Sigma-Aldrich (USA). Mercury chloride, potassium iodide and sodium hydroxide were obtained from Ajax Finechem, (Australia). Reagent grade potassium nitrate was obtained from Carlo Erba (Milan). All standard solutions were prepared with ultrapure water (Barnstead EasyPure II, Thermo Fisher Scientific, OH).

2.2. Colourimetric test for ammonium nitrate.

A Griess's test with zinc powder was used to determine the presence of the nitrate ion of ammonium nitrate. The Griess's reagent was prepared by dissolving sulphanilamide (0.5 g) and NED (0.01 g) in 1.25 mL of 85% phosphoric acid and 10 mL of ultrapure water. The nitrate ions in an ammonium nitrate standard solution (10 mL) were first reduced to nitrite by zinc powder (2.5 mg) for 15 minutes and the resulting powder collected gravity filtration. The test was performed by combining the filtrate (100 μ L) with Griess's reagent (25 μ L).

Nessler's test was also used for determination of ammonium ion. Nessler's reagent was prepared by dissolving mercuric chloride (2.3 g) and potassium iodide (1.6 g) in 10 mL of distilled water. Then, 10 mL of 6 M NaOH was added and allowed to stand overnight and finally, the solution was decanted before use. The test was performed by adding ammonium nitrate solution (100 μ L) to Nessler's reagent (100 μ L).

The solutions from both tests were mixed by shaking, and left to stand for 2.5 minutes prior to observation of the resultant colour. Each experiment was repeated 3 times.

2.3. RGB imaging system and procedure

Two RGB imaging systems were developed, one for the webcams and another for the DSLR camera. For webcams, a custom-built colour detection box was used to block external light. The 3 × 2 × 2-inch box was made of opaque black corrugated plastic board with a white interior. Three flat cap PCR micro-tubes were hung from the top of the box, holding the samples to be imaged. Three white high intensity light emitting diodes (LEDs) were placed at the top of the box as light sources, 1 inch distance from each micro-tube. The front wall had a slot for the camera or webcam so that the samples could be imaged under reproducible illumination.

Three types of webcam camera were investigated, namely the built-in webcam in a netbook (1.3MP CMOS Acer Crystal Eye high-def webcam, Acer Aspire One), the built-in webcam in an ultrabook (0.9MP CMOS built in HD webcam, Asus VivoBook S400CA), and a commercial external webcam (5MP CMOS Lifecam Cinema HD, Microsoft). The chemical tests were performed within the micro-tubes and the colourimetric products were imaged using an automatic mode setting for each camera. Six images of each test result for each samples were captured. The images were saved as JPEG compressed files of sizes 12.3 KB (Acer, 640 × 480 pixels), 93.5 KB (Asus, 1280 × 720 pixels), and 16.6 KB (external webcam, 640 × 480 pixels).

For the DSLR camera, the simple photographic system described in previous work [21] was used. It was set up in a 25 × 22 × 22-inch opaque safety cabinet with a white interior. A Nikon D5200 digital camera (23.5 × 15.6 mm, 24MP DX RGB CMOS sensor) was placed at an optimal 9.5 in distance from the sample stand. Six images of the three micro-tubes were captured for each set of tests with the camera set to the default exposure using automatic focus, automatic white balance, automatic sensitivity, and single image mode. Each image was 3.65 MB (6,000 × 4,000 pixels) when saved as a JPEG.

The RGB values of the digital images were analysed with a custom-built RGB analysis program installed on the Acer Aspire One. For each of the three sample tubes a 20 × 20 pixel image patch was initially selected, manually for colour analysis using the mouse. This image patch was then automatically selected on all subsequent images. The average of RGB intensity values ($n = 6$) for each of the three micro-tubes in each image were transferred in an Excel spreadsheet for subsequent data analysis. The average RGB values were used as a single data point when establishing calibration curves, one curve for each colour layer providing a total of three curves.

2.4. System performance

Ammonium nitrate standard solutions from 1 to 10000mgL⁻¹ were investigated. Precision was expressed as a percentage relative standard

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