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Detection Vapour of Nitrate Fertiliser Based Explosives on Transportation of Nitrates during Shipping using Diphenylamine-Calorimeter Optic Device

(Pengesanan Wap Bahan Letupan Berasaskan Baja Nitrat pada Pengangkutan Nitrat semasa Penghantaran menggunakan Peranti Optik Difenilamina-Kalorimeter)

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ABSTRACT

This study examines the ability of a Diphenylamine-Calorimeter Optical Device (DCOD) to detect the presence of nitrate in shipping containers. Fifteen selected inorganic fertilisers that potentially can be turned into an Improvised Explosive Device (IED) were analysed using UPLC-PDA. Results showed that only ammonium nitrate is suitable for turning into an IED and causing an explosion. A container model placed onboard a Malaysian Maritime vessel was used to determine the temperature and humidity experienced by nitrate during the voyage and at port. During the sea voyage (wet conditions), temperature and humidity were between 25-40.5 °C and 51.5-93.0%, respectively. In ports (dry conditions), the temperature ranged from 26.5-38.5 °C and 46-91% humidity. Using conventional tests in wet conditions, nitrous oxide was detectable with low reproducibility between 48-50 °C and vapour exposure duration of 850.0 to 895.0 s. While in dry conditions, nitrate oxide was detected regularly between 722.0 and 731.0 s and temperature between 44-50 °C. The sensitivity of the conventional and DCOD methods were evaluated and found to be similar. Field tests on DCOD were then conducted on nitrate stored in a container for 30 min, 1 h, 3 h and 2 days. Reading for positive results obtained were 67, 67, 11 and 0%, correspondingly. We conclude that DCOD can detect nitrate vapour in containers, but further modifications are required to increase its sensitivity.

Keywords: Container vessel; diphenylamine; IED; nitrate

ABSTRAK

Penyelidikan ini dijalankan untuk menguji kemampuan Alat Optik Kalorimeter Difenilamina (DCOD) bagi mengesan kehadiran nitrat dalam kontena. Lima belas baja tak organik yang berpotensi untuk dijadikan IED telah dianalisis menggunakan UPLC-PDA. Keputusan menunjukkan hanya IED berasaskan ammonium nitrat sahaja boleh menghasilkan letupan. Model kontena diletakkan di atas kapal Maritim Malaysia bagi menganalisis suhu dan kelembapan yang dialami oleh nitrat semasa pelayaran dan di pelabuhan. Semasa pelayaran (keadaan lembap), suhu dan kelembapan masing-masing adalah antara julat 25-40.5 °C dan 51.5-93.0%. Semasa di pelabuhan (keadaan kering), julat suhu dan kelembapan adalah antara 26.5-38.5 °C dan 46-91%. Ujian konvensional keadaan lembap menunjukkan gas nitros oksida dikesan pada suhu 48 °C hingga 50 °C apabila udara dialirkan pada tempoh masa 850.0 hingga 895.0 s manakala keadaan kering, nitros oksida telah dikesan secara seragam pada tempoh masa 722.0 hingga 731.0 s dan suhu antara 44-50 °C. Kesensitifan kaedah konvensional dan kaedah DCOD telah dinilai dan mempunyai persamaan. Ujian lapangan terhadap DCOD iaitu mengesan kehadiran wap nitrat dalam model kontena telah diuji pada selang masa 30 min, 1 jam, 3 jam dan 2 hari dan data bacaan keputusan positif yang diperoleh ialah 67, 67, 11 dan 0%. Kami membuat kesimpulan DCOD mempunyai potensi untuk mengesan wap nitrat dalam kontena tetapi pengubahsuaian perlu dilakukan untuk meningkatkan kesensitifan alat ini.

Kata kunci: Difenilamina; IED; kontena kapal; nitrat

INTRODUCTION

An improvised explosive device (IED) is a homemade bomb constructed from military or nonmilitary components. Due to the relative ease of obtaining IED components, its use in war-torn countries is prevalent (Moulton 2009). Although IED has a much lower relative air displacement strength per weight than military-grade explosives, its simplicity of construction allows the size of IED to be scaled up relatively quickly (Wilkinson 2019). IED has been reported to be able to destroy large installations. A good example is a destruction of U.S. Marines and French Paratroopers barracks in Beirut in 1983 (Staff 1983).

A major component of IED is Ammonium Nitrate (AN). Detection of this compound is possible due to the low vapour pressure and thermal decomposition of AN. Hence, numerous analytical trace explosives vapour detection methods have been developed under laboratory conditions for pre-blast and post-blast analysis. Offenders usually obtain nitrate in large quantities as fertilisers. Thus, creating a large-scale IED is a real possibility. Owing to this, identifying large illegal nitrate shipments would be beneficial to avoid a catastrophe.

IED comprises of six components - power switch, switch, detonator/initiator, wires, containers, and explosives (Howell 2017). The explosive components contain fuels and oxidisers, which provide a sufficient and rapid supply of oxygen needed to sustain an exothermic reaction. A commonly known IED is an ammonium nitrate-fuel oil mixture (ANFO). The effectiveness of this mixture to create an explosion is evident with the vast destruction seen in the Oklahoma City bombing (Marshall & Oxley 2011).

In Malaysia, ammonium nitrate is easily obtained from either a hardware store, plant nurseries or agriculture suppliers as chemical fertilisers. They are commonly produced as small porous pellets called prills, which are usually identified as pink crystals. During an ANFO based explosion, fuel will heat the ammonium nitrate and cause the nitrate to decompose into ammonia quickly, as well as forming nitrogen oxides (N_2O, NO, NO_2 and HNO) and water vapour. The resulting nitrogen oxide will assist combustion even when there is a lack of oxygen (Yang et al. 2017). Heat and pressure from the decomposition of ammonium nitrate will further increase internal heat and, in turn, further accelerate decomposition. As this cascading reaction occurs within an IED high-pressure capable container, a pressure build-up will eventually cause a massive explosion (Babrauskas & Leggett 2020).

Explosions related to nitrate can occur intentionally (IED) or unintentionally. Storage of nitrate with improper ventilation and continuous exposure to heat will cause the nitrate to decompose. The first step of nitrate decomposition is usually endothermic, but subsequent decomposition is mainly exothermic (Willey 2020). When this occurs, in the case of low oxygen - H_2O, NH_3, NO, and HNO_3 will be created. For subsequent discussion, these molecules will be addressed as nitrate vapours. Although the decomposition temperature of ammonium nitrate is 170 °C, a study by Djerdjev et al. (2018) has indicated that ammonium nitrate can explode at temperatures as low as 50 °C. This explosion occurs if transition metal ions are present in the mixture. In the field, detonations at low ambient temperatures occur due to the heat flow exothermic process that leads to an explosion. Both of the oxidation reactions above are relatively slow, but as they proceed and the acidity increases, some of the transition metal like $Fe(OH)_3$ begins to dissolve. It turns out that the oxidation of pyrite by Fe(III) is a lot faster than by oxygen. As fertilisers also contain metal ions, an explosion is even more likely.

A heat spike will occur when a localised explosive happens, resulting in the surrounding temperature reaching above 200 °C. As the atmospheric heat reaches 132 °C, ammonia in the air will ignite flash. The temperature will then increase further to higher levels, reaching 651 °C. At this point, auto-ignition of ammonia will occur, resulting in the sudden expansion of air and eventually an explosion if kept in a closed compartment (Yang et al. 2021). Similar chain reactions described above were seen on the Beirut blast on 4 August 2020 (El Sayed 2020).

Generally, nitrate is imported into Malaysia in large quantities as fertilisers. These nitrate-based fertilisers are commonly packed in 25 kg fertiliser bags and imported into the country using metal container vessels. The containers are usually stored at docks that experience extreme temperatures during midday (Suhaila & Yusop 2018). As the nitrates are kept in enclosed space and exposed to temperatures reaching above 40 °C, nitrate vapours in the form of nitrous oxide will be produced and slowly accumulate. The transition of solid nitrate into the gas state is likely due to the transition of polymorphic phase IV to phase III - a condition known as minor vaporisation or thermal decomposition (Fabin & Jarosz 2021). There are five polymorphic phases represent such as Phase I cubic 170 °C to 125 °C, Phase II tetragonal 125 °C to 84 °C, Phase III orthorhombic 84 °C to 32 °C, Phase IV orthorhombic 32 °C to 16 °C and Phase V tetragonal below 16 °C.

The potential of nitrate vaporisation is influenced by nitrate powdered conditions, particularly the outer nitrate layers exposed to the environment. Three factors influence nitrate condition - temperature, relative humidity, and dew point temperature. The relative humidity is inversely proportional to temperature, and when the surrounding temperature reaches the dew point, fog is formed within the container (Lawrence 2005). The formation of water droplets will also develop inside the ceiling of container vessels. Dripping dews and high humidity will cause a phenomenon known as caking (Gezerman 2020). The presence of caking on the surface of nitrate will result in a reduction in nitrate vapour release.

There are currently several methods to detect nitrate ions in solution. Commonly used tests are Ring, Devarda's, Diphenylamine and Copper Turning test. The Ring test is a colourimetric test that can visually detect nitrate ions in a solution. The test is performed by adding ferrous (II) sulfate into a solution suspected of containing nitrate. 78% sulphuric acid is added slowly until two different layers are formed. The presence of nitrate ions will cause the formation of a brown ring between the two layers of the solution.

Devarda's test is a method that uses Devarda alloys (aluminium, zink, copper) as a reducing agent. When this alloy reacts with nitrate in sodium hydroxide solution, the liberated ammonia can be identified by ammonia odour or a colour change of litmus paper from red to blue (Sahrawat & Burford 1982).

Diphenylamine test is used to detect the presence of nitrate. The solution is prepared by dissolving 0.5 g of diphenylamine salt in 20 mL of distilled water. Then, 98% concentrated sulfuric acid is added to a volume of 100 mL. One drop of diphenylamine solution on any substance containing nitrate is sufficient to discolour the substance into blackish-blue within five s of reaction. The Diphenylamine test was chosen because the test solution is easily soluble in water, chemically stable, and easy to handle outside a laboratory environment (Hofer & Wyss 2017).

Identification of containers carrying nitrate is essential to reduce the risk of terrorists converting its content into a large IED. As nitrate is transported on large containers ship with sizes ranging from Feedermax, Panamax, Post-Panamax, New Panamax to ultra-large; searching a single container carry nitrate among 1,000 to 14,000 TEU would be like be looking for a needle in a haystack. Henceforth, equipment is required to detect nitrate fumes (N_2O) emitted by shipping containers quickly and accurately (Khadasevich & Ladutska 2018). This study looked at the possibility of developing a Diphenylamine-Calorimeter Optical Device (DCOD) capable of detecting nitrate oxide vapour from Ammonium Nitrate fertiliser stored in a shipping container.

METHODS

The first objective was to identify 15 common inorganic nitrate fertilisers in the Malaysian market that could potentially be used as an Improvised Explosives Device (IED). All fertiliser samples were obtained from the Department of Agriculture Malaysia or various agricultural shops in Klang Valley, Malaysia. NPK Fertilisers brands selected from the local manufacturer were as follows: Ammonium Nitrate 34% (Odorata Enterprise), Foliar (EDM TEE Sdn Bhd.), Calcium Nitrate Ecohydro (Norgessalter Norwegian), *Daun Hijau* (Fertiland Trading Co.), Green Gro 63Q (Fertiland Trading Co.), *Sebatian Padi 1* (Department of Agriculture Malaysia), *Sebatian Padi 2* (Department of Agriculture Malaysia), *Sebatian Padi 3* (Department of Agriculture Malaysia), *Nitrophoska Biru* (Department of Agriculture Malaysia), *Urea Kuning* (Department of Agriculture Malaysia), *Urea Putih* (Department of Agriculture Malaysia), *Sebatian* Hi Ray Plus (Department of Agriculture Malaysia), Potassium Nitrate Ecohydro (Arab fertilizers & Chemicals Industries Ltd.), Yara Mila (Department of Agriculture Malaysia) and Vitagreen (Vitapro (M) Sdn Bhd.). The experiment was done in two phases, first to determine the percentage of actual nitrate in each product and the second to determine if the selected nitrate could be used to turn into an IED and explode.

DETECTION OF NITRATE COMPOSITIONS BY UPLC-PDA

The quantity of nitrate present in each product was determined based on the modification method by Burhan et al. (2016). A Waters® Acquity™ Ultra Performance Liquid Chromatography-Photodiode Array Detector (UPLC-PDA) equipped with Acquity™ Binary Solvent Manager (pump system), Acquity™ Sample Manager (autosampler system), Acquity™ Photodiode Array Detector and Waters® Empower Pro Chromatography software was used. The UPLC was configured with an ACQUITY™ UPLC BEH C18 (2.1 × 150 mm, 1.7 µm particle size). PDA was set on scanning mode between 200 and 400 nm. Mobile phase consisted of filtered acetonitrile/water (70/30 v/v), pH = 3 with a flow rate of 0.1 mL/min. Ultrapure water was obtained from Sartorius Arium® Pro Water Purification System. The mobile phase solution was filtered using SunSri Titan 47 mm PTFE membrane (0.20 µm pore size).

Samples were injected into the UPLC system using a Waters Acquity autosampler at a volume of 1.0 µL. Sample preparation of fertiliser samples involved dissolving 23 gm of fertiliser powder with ultrapure water in a volumetric flask of 100 mL. The fertiliser solution was left to be dissolved for 10 min. Then, 1 mL of the previous solution was pipetted into a 100 mL volumetric flask and dissolved again with ultrapure water.

A total of five different concentrations series of standard Potassium Nitrate solutions were prepared using a potassium nitrate stock solution. This standard stock solution of 500 mg/L was prepared by mixing 0.125 g of 99% Potassium Nitrate (Acros Organics, Spain) with ultrapure water into a 250 mL volumetric flask. Then, the stock solution was diluted to standard solutions of 10, 20, 50, 70, and 100 mg/L. Calibration of nitrate was based on a potassium nitrate standard curve of the concentration mentioned above. All samples, external standard and calibration standards injection volume was 1 µL, and triplicate analysis was done for each sample. The concentration of nitrate was taken as an average of 3 injections.

DETERMINATION OF EXPLOSIVE CAPABILITY OF NITRATE PRODUCTS

The explosive capability of the nitrate as an IED was determined by packing Ammonium Nitrate 24.4%, Calcium Nitrate 22%, Potassium Nitrate 19.3%, Green Gro 63Q 9.3%, and Vitagreen 8.9% in a pressure releasing pipe. Twenty-three grams of each previously mentioned fertiliser were packed into individual 10 × 1.5 cm polyvinyl chloride (PVC) pipes. A further 2 g of grey sulphur was used to act as a primer. A roll of iron wool was packed within the sulphur powder to act as an initiator. A pair of black and red copper wire was then connected to the ends of the iron wool. Each end of the pipe was sealed with a pressure release PVC nipple and glued together with PVC cement. A small opening at one end of the pipe nipple was drilled to allow the paired wire to be connected to a safety switch and a 12V battery. The gap present in the opening was further sealed using PVC cement (Gregory et al. 2010).

The distance between the IED and bomb switch was 5 m. A safety barrier was built, separating the user and the IED. The explosion experiment was conducted at a shooting range in Mantin, Negeri Sembilan. A weapon and explosive expert officer from the Malaysian Maritime Enforcement Agency (MMEA) was present throughout the experiment to ensure all Safety Standard Operating Procedure (SOP) was followed. The test was done in triplicate, and all experiments were video-recorded at two different angles.

DETERMINATION OF TEMPERATURE VARIATIONS IN SHIPPING CONTAINERS

The second objective was to determine the temperature variation a shipping container would experience when sailing on a cargo ship plying through the Straits of Malacca. An MMEA ship - KM Bagan Datok patrol vessel was used. The ship had sailed along the straits for seven days. Temperature and humidity variation in a metal 20-foot container model was fabricated and put on the ship's deck. A temperature sensor data logger (EL-USB-TC-LCD) had recorded temperature and humidity data changes within the model every 5 min. Two voyages four months apart were made by KM Bagan Datok patrol vessel, allowing us to collect two sets of data. Collected data were analysed to identify maximum and minimum temperature and humidity variation. This information was classified as a 'wet environment'. A similar protocol was also conducted while the ship was at the dock. Maximum and minimum temperature and humidity variations were noted. This set of data was classified as a 'dry environment'. Data from the two environments were later used for the next objective of the study.

DETECTION OF NITRATE VAPOURS BY DIPHENYLAMINE TEST

The third objective was conducted to determine if the selected nitrate fertiliser could produce nitrate vapours (N_2O, NO, NO_2, and HNO) and later be detected visually using Diphenylamine solution. Nitrate ion in vapour, possibly nitrous oxide gas (N_2O) in dry environment analysis was conducted by heating Ammonium Nitrate over a hot plate. The hot plate had a rotating knob to set the plate temperature and create our desired dry environment. A new aluminium container was heated between 26 °C and 50 °C as per data obtained in the previous objective. As mentioned above, the heating of the container was done using a heating plate. A temperature electrode (FLUKE 51 II Thermometer) was used to determine the actual temperature within the container. Air from the container was continuously pumped at the rate of 1047 cm^3/s into a Diphenylamine solution. Diphenylamine solution is a standard test to detect nitrate. Time taken for the Diphenylamine solution to change from translucent to blue was noted. If no changes were detected in 30 min, we concluded that nitrate vapour was not detectable. A negative control test consists of heating a new empty aluminium container. To ensure minimal chance of sample carryover, all equipments - aluminium cans, Diphenylamine solution container, and pipes connecting to DCOD were cleaned frequently. Aluminium tin containers were cleaned and washed with soap and distilled water. All inlet and outlet air pipelines are frequently replaced. All tests were done in triplicate.

Detection of nitrous oxide in a wet environment was done similar to the above protocol. The wet environment was created by heating the container in a water bath instead of the heating plate. We selected this form of heating because heating this way produced heat and humidity similar to what was seen in the second objective but much more controllable. As the water bath has a temperature regulator control, the wet environment was easy to handle. A temperature probe was inserted into the aluminium tin to ensure a more accurate temperature reading.

DETECTION OF NITRATE VAPOUR BY DCOD

The fourth objectives were to determine if a Diphenylamine-Calorimeter Optical Device (DCODTM) can detect the presence of nitrate in the vapour much better than using the conventional method with visually. DCOD sensitivity was tested in dry condition by heating an aluminium container containing Ammonium Nitrate (AN) to a temperature of 26 °C. The experiment was repeated at every 2 °C until reaching 50 °C. Temperature range was selected based on the previous data collected while the ship was in port. The experiment was tested at each temperature in triplicate. How quickly the device detected nitrate was also noted and compared against the time taken to detect the vapour visually (Detection of nitrate vapours by diphenylamine test in objective 3). The mini charged-coupled device (CCD) was chosen as an alternative way to detect colour changes in the diphenylamine solution as it is more sensitive, durable acid-resistant. Interpretation of the camera colour signal of the Diphenylamine solution was made based on RGB (Red Green Blue) colour code. As the camera has a wide focus, detecting blue colour spots resulting from the reaction of Diphenylamine solution with nitrate was simple and easy. A similar experiment was also done for wet conditions. Instead of using a heating plate, the aluminium container was heated using a water bath.

FIELD VALIDATION STUDY

A field validation study on the dry condition was then conducted at UKM Forensic Science Simulation Site. The wet condition study was not studied after the next step due to the low repeatability of positive results on previous tests. The validation study consisted of three model containers measuring 24 × 18 × 14.5 cm. Four ventilation holes 0.5 × 0.5 cm located at each upper corner were made on every model container. This was to create neutral pressure between the outside and inside of the container as per an actual shipping container. A Data Logger electrode wire was inserted into the model container through a ventilation hole for 24 h to obtain the temperature variation. Data recorded determined the temperature and humidity faced by materials stored in containers.

The validation study looked at the ability of DCOD to detect nitrate vapour present in the air of a model container filled with nitrate. The model container was exposed to the environment for 30 min, 1 h, 3 h, and two days. Each experiment was done in triplicate. Time taken to detect nitrate was noted. If DCOD could not detect nitrate vapour after 30 min, the outcome was classified as Non-Detectable (N/D). Negative control consisting of an empty model container was also used.

RESULTS

PERCENTAGE OF NITRATE

The nitrate concentration of 15 brands of fertilisers was determined using Ultra-Performance Liquid Chromatography-Photodiode Array Detector (UPLC-PDA). Nitrate peak was detected at 204 nm and retention time (RT) of 0.547 min. No interfering peaks originating from other compositions within the fertiliser were detected at 204 nm (Figure 3). Results (Table 1) indicated that all brands had different nitrate concentrations. Five brands with the highest percentage of nitrate were Ammonium Nitrate, Potassium Nitrate, Calcium Nitrate, Green Gro 63Q, and Vitagreen. Of the five, Ammonium Nitrate fertiliser had recorded the highest percentage of nitrate at 24.4% of total weight. Calcium Nitrate, Potassium Nitrate, Green Gro 63Q, and Vitagreen had a total percentage weight of 22.0, 19.3, 9.3, and 8.9%, respectively. The concentration levels detected by the UPLC did not tally with the composition printed on the label.

IED EXPLOSION TEST

Five brands with the highest nitrate content were then used to create an IED. The manufacturing of pipe bombs was as mentioned earlier. IED explosion test on the five brands was conducted in triplicate. The result (Figure 1) indicated only Ammonium nitrate could explode successfully. Potassium nitrate was the only one to produce fire sparks during the test that lasted less than 5 s. Other brands were not even able to make any noticeable reaction.

TEMPERATURE AND HUMIDITY RANGE

Temperature and humidity data were collected using a data logger that was put in a model ship container. The container was then put on a Malaysian Maritime vessel plying the Straits of Malacca for 20 days (10 days × 2 journeys). A total of 2883 data sets were collected. The recorded temperature was between 25-40.5 ℃ with a humidity range (RH) of 51.5-93.0% (Figure 2). This set of data was classified as data from a wet environment.

Data for a dry environment was obtained using the protocol above, but this protocol requires the vessel to be docked at port for four days. A total of 370 data sets were collected. The temperature (26.5-38.5 ℃) and humidity (46-91%) variations were much lower than the data sets seen from the wet environment.

The temperature and humidity data between the two voyages were found consistent. The confounding factors were kept at a minimum as we had used the same vessel - KM Bagan Datok, and model container. The collection of data points in a dry environment had resulted in an additional 2095 data sets. A paired t-test on humidity and temperature with time as the matching variable was conducted between the humidity and temperature data of the first journey to the second journey. Statistical results indicated no significant difference between the humidity and the temperature data from the two journeys for both environments (wet and dry). The outcome of this result indicates that the humidity and temperature variation experienced by KM Bagan Datok in the two journeys (at the port and sea) was similar. Hence, we can confidently speculate that the temperature range that we had used in the later experiment is suitable for simulating conditions that a container would experience at sea and the docks.

WET NITRATE VAPOUR TEST (CONVENTIONAL METHOD)

Diphenylamine test was performed in a wet condition using a water bath. The temperature variable was set at a temperature range of 26.0 to 50.0 °C with a 2.0 °C step. These values were derived from the previously mentioned experiment. Regulation of humidity was made by air ventilation and water bath. During the investigation, the humidity within the lab was between 70 and 85%. To achieve higher levels of humidity, the water bath was set at 100 °C. In general, humidity for the experiment was between 52% and 93%, and this range affected the outcome of the result. Detection of nitrate was done visually in which a presence of nitrate would change the colour of the Diphenylamine solution from translucent to dark blue. The result of wet nitrate vapour detection using the Diphenylamine test was mixed. Nitrate was detected at 48 °C to 50 °C but with low reproducibility (Table 2). The time taken for Diphenylamine solution to detect nitrate from Ammonium Nitrate fertiliser›s vapour was 850.0+0.5 to 895.0+8.2 s.

DRY NITRATE VAPOUR TEST (CONVENTIONAL METHOD)

A similar experiment was conducted in a dry environment. The heat from a dry condition was achieved using a hot plate. The temperature experiment was set at a temperature range of 26.0 ℃ to 40.5 ℃. The humidity range was between 51.5% and 93%. Nitrate was detected at temperatures between 44 °C and 50 °C. The time for Diphenylamine solution to react with nitrate vapour from Ammonium Nitrate fertiliser was 722.0+0.8 to 731.0+3.7 s (Table 3).

COMPARISON DIPHENYLAMINE-CALORIMETER OPTICAL DEVICES (DCOD) AND DRY TEST (CONVENTIONAL METHOD)

Comparison detectability of Diphenylamine-Calorimeter Optical Devices (DCOD) versus a conventional method was only conducted for a dry environment. Experiment for a wet environment was not undertaken beyond this point due to the inconsistent results.

A total of 39 tests were conducted in a dry environment. Results from the experiment indicated that there were no significant differences in time taken to detect nitrate using dry condition conventional method 726.6+4.0 s and DCOD 7245.0+4.9 s, respectively, (Paired t-test: t(39) = -3.989, p = 0.399) (Table 4).

FIELD VALIDATION OF DCOD

Given the minor differences between the conventional and DCOD, the experiment continued with field validation of DCOD. A model container vessel filled with Ammonium Nitrate fertiliser was left at the UKM Forensic Science Simulation field. Air from the container was sucked and pumped into DCOD after nitrate was stored into the model container for 30 min, 1 h, 3 h, and two days. DCOD was then used to detect the presence of nitrate vapour. The positive results from the DCOD for nitrate stored for 30 min, 1 h, 3 h, and two days were at 67, 67, 11, and 0%, respectively. Low positive validation test results were probably due to Ammonium Nitrate's caking, thus, creating a barrier restricting the nitrate vapour to escape from the powder (Table 5).

DISCUSSION

Malaysian Intensive Agriculture Policy is based on the wide use of agricultural supplements such as fertilisers and pesticides to increase output. Due to a lack of sufficient supply of local fertilisers and pesticides, both the agriculture and plantation sectors rely heavily on imported fertilisers. In 2013 alone, the fertiliser and pesticides imported were 3.95 million and 122,885 tonnes, respectively (Krishnen et al. 2016). Mineral fertilisers accounted for more than 90% of fertilisers used by all types of farming operations in Malaysia (Ahmad 2001). Most imported mineral fertilisers are urea, ammonium sulfate, calcium ammonium nitrate, phosphate rock, superphosphates, ammonium phosphate, potassium chloride, potassium sulfate, NPK, NP, and PK compound fertilisers.

In Malaysia, 3.8 million tonnes of N, P, K fertilisers were imported in 2004, valued at USD 529 million (Zakaria 2006). The Malaysian Government has enforced Act 514 and Control of Supplies Act 1961 to regulate these fertilisers' sale, distribution, and storage (Hassan 2001; Nurhayati 2000). Despite this, enforcement of the Act is lacking due to the numerous unregistered suppliers of fertilisers, either as wholesalers, hardware shops or nurseries and lack of enforcement officers.

A preliminary investigation of fertilisers offered by these establishments and from the Ministry of Agriculture indicated that most of them are selling fertilisers under the brand names of Agro Foliar™, *Ammonium Nitrat*, *Kalsium Nitrat, Daun Hijau*™, Green Gro™, *Nitrophoska Biru*™, *Sebatian Padi 1*™, *Sebatian Padi 2*™, *Sebatian Padi 3*™, *Potassium Nitrat*], *Sebatian* Hi Ray Plus™, *Urea Putih*™, *Urea Kuning*™, Vitagreen™, and Yara Mila™. Hence the selection of these fertilisers for this study.

Nitrogen composition determines the explosive potential of the fertilisers. Therefore, a nitrogen composition analysis of the fertilisers was conducted using UPLC. Results indicated that every brand had a different nitrate concentration, and its concentration was not reflected by the composition list printed on the fertilisers package (Table 4). Three brands of fertilisers had a very high percentage of nitrate - Ammonium nitrate (24.4%/g), Potassium Nitrate (19.3%/g), and Calcium Nitrate (22.0%/g). A study had indicated that a nitrate concentration above 16%/g would increase the risk of the fertilisers exploding (Fraga et al. 2017). Concentration at this level also allows a terrorist to quickly create an IED without the need to concentrate the nitrate chemically (Westrol et al. 2017).

During the IED explosion test, only two fertilisers could produce some reaction. Ammonium nitrate IED was able to create an explosion, Potassium nitrate IED created fire sparks, and the rest had not made any observable reaction. Although Ammonium nitrate and Potassium nitrate have been well documented as significant substrates for an IED, the inability of Potassium nitrate to produce an explosion could be due to how the IED was constructed (Kavický et al. 2014; Menning & Östmark 2008). Due to safety reasons, the material used to create all the IEDs was made from PVC pipes. At the end of every pipe, a PVC nipple was used. PVC cement was used to secure the nipple to the pipe. This type of pipe has an inverse operating temperature to pipe derating factor and maximum psi. For example, at 27 °C, PVC has a derating factor of 0.88 and a maximum psi of 202 psi. When the temperature within the pipe increases, the derating factor decreases sharply - at 60 °C, the pipe derating factor is only 0.22. At this level, the PVC pipe can only withhold a maximum pressure of 51 psi before failing (American Water Works Association 2002).

Ammonium nitrate has a much higher reaction rate compared to Potassium nitrate. So, it is suspected that pressure generated by the production of gases nitrous oxide and water vapour was fast enough to overwhelm the declining maximum pressure of the pipe, thus causing an explosion. On the other hand, as potassium nitrate has a much lower reaction rate, the temperature within the pipe could reach above 210 °C before the pressure within the pipe had reached its maximum pressure (Ballard et al. 1987). During this condition, liquefaction of the pipe occurred, resulting in holes in the pipe. These holes caused pressure within the pipe to suddenly drop. Exposure of reacting potassium nitrate to the environment causes fire sparks - that can be seen coming out from the pipes (Figure 1- middle picture).

Nitrate vapour tests in wet and dry conditions had produced different results. The constant variable during the experiment was flow rate. The temperature was comparable between the two conditions. The variability factor between the conditions was the humidity. The heat from the water bath and the hot plate slowly decompose ammonium nitrate, producing gases of nitrous oxide and water vapour. During wet conditions, the existing high amount of water vapour (high humidity) in the air is further increased with the additional water vapour produced by nitrate decomposition. This causes relative humidity (RH) to increase closer to nitrous oxide's specific humidity (SH). The dynamic between SH and RH will eventually cause less nitrate vapour in the air. Hence, fewer are being sucked by the pump and transferred to the Diphenylamine solution. During dry conditions, the effect of additional water vapour from nitrate decomposition in a low humidity environment is negligible as the margin between RH and SH is quite far apart. The outcome is that nitrate vapour is produced sufficiently to be detected by the Diphenylamine solution (Ridhi et al. 2021).

Diphenylamine-Calorimeter Optical Devices (DCOD) to detect products from nitrate degradation/decomposition in the vapour was comparable to the conventional method. Before starting the experiment, it was hypothesised that the DCOD would have higher sensitivity to detect early colour changes of the Diphenylamine solution as it changes from transparent to blue in nitrate. We suspect that the reduced sensitivity of DCOD could be due to the deficiencies of the container material holding the Diphenylamine solution. The container was made from thick transparent glass. It was selected as the glass was sufficiently thick and resistant to shatter if the detection device was accidentally dropped and resistant to the acidity of the Diphenylamine solution. Unfortunately, transparent glass is created from light green and blue hues. Due to this, baseline sensitivity to blue for the detector needed to be increased, making it less sensitive to early changes of the solution. A sensitive solid-state nitrate detector might be a better choice in the future, although the development of this form of sensor is very much in the early stage (Chen et al. 2020).

Despite the relative similar sensitivity of conventional and DCOD to detect nitrate vapour, DCOD field studies were done as having multiple DCOD deployed on a large vessel would still be beneficial. It would reduce human resources during the screening of large container ships.

A field validation study indicated that DCOD could correctly detect the presence of nitrate vapour from a model container 67% of the time. This is reflected in Table 5 for analysis of 30 min and 1 h. The sensitivity of the DCOD has seen a dramatic decline at 3 h and two days. It was noticed that 2 h after the experiment started, rain fell. The rain had increased the humidity of the surrounding temperature. Rain was also present on the second day.

TABLE 1. Comparison of nitrate percentage concentrate in mg/L for branded NPK fertiliser as analysed by UPLC and advertised on the label

Type of fertilisers (brand)	Nitrate concentration (mg/L)	Percentage nitrate to weight	Percentage nitrate based on label (NPK)
UPLC result			
Agro Foliar	125.97±1.25	5.2%	20:20:20+micro
Ammonium Nitrat	122.46±2.40	24.4%	33.5% N
Kalsium Nitrat	111.77±7.30	22.0%	15.5:0:0+26.3% CaO
Daun Hijau	6.97±0.88	1.4%	15:15:15
GRO 63Q	46.78±6.60	9.3%	21:21:21+TE & VIT B1
Nitrophoska Biru	126.00±0.57	5.1%	12:12:17:2+8S
Sebatian Padi 1	4.52±0.20	0.9%	17.5:15.5:10
Sebatian Padi 2	3.94±0.17	0.8%	17:20:10
Sebatian Padi 3	3.28±0.26	0.6%	17:3:25:2
Potassium Nitrat	96.65±5.32	19.3%	13:0:46
Sebatian Hi Ray Plus	2.75±0.18	0.5%	No information
Urea Putih	2.39±0.11	0.5%	No information
Urea Kuning	5.91±0.79	1.2%	No information
Vitagreen	45.10±1.54	8.9%	No information
Yara Mila	36.78±3.52	7.3%	12:12:17:2 MgO

FIGURE 1. Explosion test at shooting range

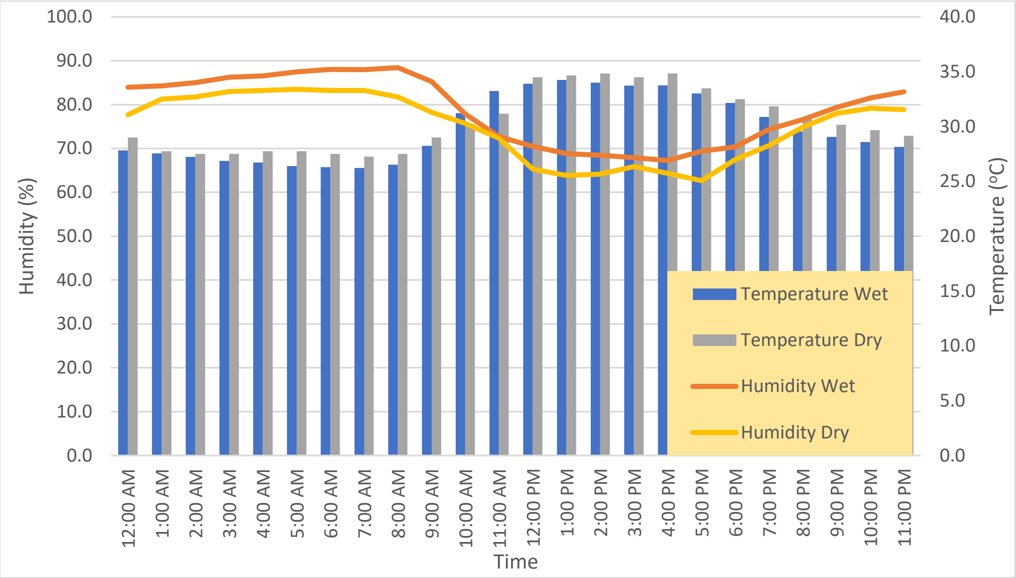

FIGURE 2. Temperature and humidity between wet and dry conditions. Data was collected using a model shipping container place on a ship

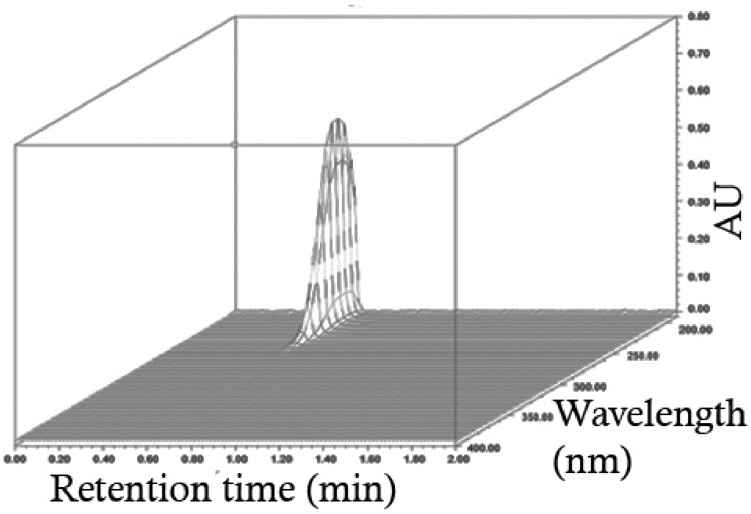

FIGURE 3. A 3D Chromatogram of nitrate peak detected at wavelength 204.3 nm at retention time 55 s

TABLE 2. Result for wet test using a conventional method

Temperature (°C)	Repeat (s)			Average+SD (s)	Diphenylamine results
	1	2	3		
26.0	890	880	890	886.7+4.7	Negative
28.0	885	882	886	884.3+1.7	Negative
30.0	889	890	888	889.0+0.8	Negative
32.0	880	885	895	886.7+6.2	Negative
34.0	884	884	886	884.7+0.9	Negative
36.0	886	889	890	888.3+1.7	Negative
38.0	886	884	889	886.3+2.0	Negative
40.0	887	887	886	886.7+0.5	Negative
42.0	890	889	887	888.7+1.2	Negative
44.0	892	886	887	888.3+2.6	Negative
46.0	889	882	885	885.3+2.9	Positive
48.0	880	875	873	876.0+2.9	Positive
50.0	850	860	870	860.0+8.2	Positive

TABLE 3. Result for dry test using a conventional method

Temperature (°C)	Repeat (s)			Average+SD (s)	Diphenylamine result
	1	2	3		
26.0	729	730	727	728.7+1.2	Negative
28.0	729	730	734	731.0+2.2	Negative
30.0	730	725	729	728.0+2.2	Negative
32.0	725	730	734	729.7+3.7	Negative
34.0	720	725	722	722.3+2.0	Negative
36.0	725	730	734	729.7+3.7	Negative
38.0	720	725	722	722.3+3.7	Negative
40.0	725	730	734	729.7+3.7	Negative
42.0	720	725	722	722.3+2.0	Negative
44.0	729	726	726	727.0+1.4	Positive
46.0	727	728	725	726.7+1.6	Positive
48.0	725	727	726	726.0+0.8	Positive
50.0	720	722	724	722.0+1.6	Positive

TABLE 4. Comparison between DCOD and Conventional method in dry condition to detect the presence of nitrate vapour based on time (s) and Temperature. Means and SD values represent the average value that test was done in triplicate reading

Temperature(°C)	DCOD		Conventional method	
	N (repeats)	Mean+SD (s)	N (repeats)	Mean+SD (s)
44.0	3	722.3±1.4	3	727.0±1.6
48.0	3	723.0±2.1	3	726.7±1.3
46.0	3	721.0±0.1	3	726.0±0.6
50.0	3	717.3±3.6	3	722.0±3.4

TABLE 5. Validation of DCOD in the field using a model container filled with ammonium nitrate. The number of successful detections out of three instances

Incubation of nitrate in model container	Result	
	Positive	Negative
30 min	2	1
1 h	2	1
3 h	1	2
2 days	0	3

CONCLUSIONS

DCOD can detect nitrate vapour from cargo containers containing Ammonium Nitrate. Despite this, its sensitivity is mainly dependent on the humidity of the surrounding temperature. The best location to use this device would be at the ship docks and not while the containers are at sea.

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