Full Paper

Propellants, Explosives, Pyrotechnics

DOI: 10.1002/prep.202000173

Optimization of Synthesis Parameters and Characterization of Green Primary Explosive Copper(I) 5-nitrotetrazolate (DBX-1)

Wen-Hsiang Li,[a] Kai-Chun Tseng,[b] Tsung-Mao Yang,[c] Jin-Shuh Li,*[c] and Kai-Tai Lu[c]

Abstract: Since the early 20th century, lead azide (LA) has been commonly used as a primary explosive. However, lead pollution in the air and soil has attracted more and more attention, particularly in military training grounds and shooting ranges. Copper(I) 5-nitrotetrazolate (DBX-1) is considered as one of the most promising alternatives to LA. DBX-1 is typically prepared from sodium 5-nitrotetrazolate dihydrate [$NaNT(H_2O)_2$] and copper(I) chloride (CuCl). But little is known about its optimal synthesis parameters. In addition, $NaNT(H_2O)_2$ is not commercially available. In this study, $NaNT(H_2O)_2$ was prepared by ourselves. Taguchi's experimental design method was used to determine the optimal experimental conditions for obtaining the maximum yield of DBX-1. The synthesized $NaNT(H_2O)_2$ and DBX-1 were identified by means of SEM, NMR, FTIR, EA, UV-Vis and STA TG-DSC, and the sensitivity of DBX-1 was determined using BAM fallhammer, BAM friction tester and electrostatic spark sensitivity tester. The experimental results indicated that the optimal synthesis parameters of DBX-1 were as follows: the reaction temperature was 100 °C, the reaction time was 30 min, the concentration of $NaNT(H_2O)_2$ was 0.075 wt.% and the molar ratio of $NaNT(H_2O)_2$ to CuCl was 1.15, and then the maximum yield after purification could reach 72.2 %. The decomposition activation energies of DBX-1 calculated by Kissinger and Ozawa methods were 178.6 and 179.0 kJ/mol, respectively. In addition, the impact sensitivity, friction sensitivity and electrostatic spark sensitivity of DBX-1 were 51 mJ, 0.4 N and 7.3 mJ, respectively, which were almost the same as those for LA.

Keywords: Green primary explosive · DBX-1 · Yield · Optimal synthesis parameters · Taguchi experimental design method

1 Introduction

Primary explosives are very sensitive materials and can easily be triggered by external stimuli (such as fire, sparks, impact and friction). Therefore, they are used to initiate main (secondary) explosives, propellants, and pyrotechnics, and are usually charged in devices such as primers, detonators, boosters, igniters, percussion caps and blasters. Two of the most widely used primary explosives are lead azide (LA) and lead styphnate (LS). In recent years, lead pollution in the air and soil has attracted more and more attention, particularly in military training grounds and shooting ranges. Therefore, a clear need exists for the successful development and replacement of these two aforementioned primary explosives [1, 2, 3, 4]. Although the various existing and new energetic materials have been studied as substitutes for LA, including silver azide (SA), diazodinitrophenol (DDNP), calcium 5-nitriminotetrazolate [5], copper(II) 5-chlorotetrazolate (CuClT) [6], copper(II) coordination complexes of the 5-nitrotetrazolate anion [7], all of them have some limitations that make them difficult to use widely [8]. Copper(I) 5-nitrotetrazolate [DBX-1, $Cu_2(NT)_2$, $NT{=}CN_5O_2^-$] is one of the most promising alternatives to LA to date, because it is similar to LA in terms of initiating ability, impact, friction and electrostatic spark sensitivity, and high thermal stability [9]. In addition, LA is not compatible with copper and some other metals used in the fabrication of ordnance components, however DBX-1 is compatible with these metals. DBX-1 also has high thermal stability and appears to be more resistant to oxidation under thermal cycling conditions [9]. However, DBX-1 has made little progress in replacing LA. The main factor slowing down the adoption of DBX-1 is related to its production. For DBX-1 to be widely used in commercial blasting products, a highly repeatable procedure for preparing DBX-1 will be necessary [10].

DBX-1 was first made by Dr. Walter Friederich and patented in 1960 [11]. It is typically prepared from sodium 5-

---

[a] *W.-H. Li*
School of Defense Science, Chung Cheng Institute of Technology, National Defense University, Taoyuan, Taiwan, ROC
[b] *K.-C. Tseng*
Master Program of Chemical Engineering, Chung Cheng Institute of Technology, National Defense University, Taoyuan, Taiwan, ROC
[c] *T.-M. Yang, J.-S. Li, K.-T. Lu*
Department of Chemical and Materials Engineering, Chung Cheng Institute of Technology, National Defense University, Taoyuan, Taiwan, ROC
886-3-3891716
Fax: +886-3-3892494
**e-mail: lijinshuh@gmail.com*

nitrotetrazolate dihydrate [$NaNT(H_2O)_2$, $NT{=}CN_5O_2^-$] and copper(I) chloride (CuCl) [12,13,14,15]. The procedure for the preparation of DBX-1 is as follows: the aqueous solution of CuCl is slowly dropped into the aqueous solution of $NaNT(H_2O)_2$ maintained at a temperature of 90–100 °C, after the dropwise addition is completed, the reaction is continued at the same temperature for about 2 hours, and then the red crystalline product of DBX-1 is obtained. Fronabarger et al. [16] also reported another synthesis method by using $NaNT(H_2O)_2$, copper(II) chloride ($CuCl_2$) and sodium ascorbate ($C_6H_7NaO_6$). The sodium ascorbate was used as the reducing agent to reduce copper (II) to copper (I) in the reaction process. However, non-repeatability has always been a major challenge in the synthesis of DBX-1 [10]. In addition, the purity of $NaNT(H_2O)_2$ is an important factor affecting the synthesis of DBX-1, but $NaNT(H_2O)_2$ is currently not commercially available [8].

The synthesis of $NaNT(H_2O)_2$ was first reported by von Herz in 1937 [17]. In this synthesis procedure, 5-aminotetrazole (5-AT, HN_4CNH_2) is used as the starting material, which reacts with sodium nitrite ($NaNO_2$) and Copper(II) sulfate ($CuSO_4$) in sulfuric acid (H_2SO_4), the precipitated intermediate product is copper hydrogen nitrotetrazolate tetrahydrate [$Cu(H\text{-}NT)(NT)_2(H_2O)_4$], after filtering, this intermediate product reacts with the aqueous solution of sodium hydroxide (NaOH) to form the solution of NaNT $(H_2O)_2$ containing some copper oxide (CuO) precipitate, after removing CuO from the solution of $NaNT(H_2O)_2$, NaNT $(H_2O)_2$ crystals are obtained by evaporation of the solution and purified by recrystallization from water. However, $Cu(H\text{-}NT)(NT)_2(H_2O)_4$ is a gelatinous green solid. Therefore, it is very difficult to completely separate this intermediate product from the solution during the filtration process. Gilligan and Kamlet [18] also filed a patent related to the synthesis of $NaNT(H_2O)_2$ in 1978. It is found that nitric acid (HNO_3) instead of (H_2SO_4) can lead to a reduction in the amount of time required for the separation and washing of $Cu(H\text{-}NT)(NT)_2(H_2O)_4$. Furthermore, it should also be considered that the dry $Cu(H\text{-}NT)(NT)_2(H_2O)_4$ is a sensitive explosive and operating this compound can be dangerous to the operator, especially as the scale of the reaction increases. Klapötke et al. [8] developed a new procedure for preparing crystalline NaNT. This procedure avoids the filtration step of the intermediate product $Cu(H\text{-}NT)(NT)_2(H_2O)_4$ by adding the aqueous solution of NaOH directly to the reaction mixture. The resulting aqueous solution of $NaNT(H_2O)_2$ is then evaporated to dryness and extracted with acetone. Recently, Bottaro et al. [19] published a new patent for the preparation of NaNT $(H_2O)_2$ by reacting 5-AT, an acid (nitric acid, sulfuric acid, perchloric acid or hydrochloric acid) and $NaNO_2$ in water in a batch reaction at an elevated temperature. Using this procedure, the yield of pure $NaNT(H_2O)_2$ can be significantly increased to about 90 %.

This study mainly explored the optimal synthesis parameters to improve the yield of DBX-1. It was synthesized by reacting $NaNT(H_2O)_2$ with CuCl in water. Because NaNT $(H_2O)_2$ is not commercially available, it was prepared by reacting 5-AT, HNO_3 and $NaNO_2$ in water. Taguchi $L_9(3^4)$ orthogonal array with four control factors and three levels of each control factor was adopted to design the experimental conditions for the synthesis of DBX-1. The experimental data were used to analyze and evaluate the experimental optimal parameters combination for the maximum yield of DBX-1. Furthermore, the synthesized $NaNT(H_2O)_2$ and DBX-1 were characterized by means of scanning electron microscopy (SEM), nuclear magnetic resonance spectrometer (NMR), Fourier transform infrared spectrometer (FTIR), elemental analyzer (EA), ultraviolet-visible spectrometer (UV-Vis) and simultaneous thermogravimetry-differential scanning calorimetry (STA TG-DSC), and the sensitivity of DBX-1 was determined using BAM fallhammer, BAM friction tester and electrostatic spark sensitivity tester. The DSC data were also used to calculate the activation energies by the Kissinger and Ozawa methods and then to further assess the thermal stability of DBX-1.

2 Experimental

There are some cautionary statements regarding the synthesis experiments of DBX-1. DBX-1 and its synthetic raw material $NaNT(H_2O)_2$ are sensitive to impact, friction and electrostatic discharge, and must be handled with care during synthesis and analysis. In addition, nitric acid used for synthesizing $NaNT(H_2O)_2$ is corrosive and can cause irritation to the eyes, skin, and mucous membrane, and must be handled with care during synthesis.

2.1 Materials

Sodium 5-nitrotetrazolate dihydrate [$NaNT(H_2O)_2$] was used as the starting material, reacting with copper(I) chloride (CuCl) to synthesize Copper(I) 5-nitrotetrazolate (DBX-1). It was prepared by reacting 5-aminotetrazole (5-AT), nitric acid (HNO_3) and sodium nitrite ($NaNO_2$) in water according to the method reported by Bottaro et al. [19], and then was evaporated to dryness in vacuum and extracted with acetone to obtain high purity $NaNT(H_2O)_2$. 5-AT ($\geq$98.0 %) was reagent grade and purchased from Tokyo Chemical Industry Co., Ltd. CuCl ($\geq$97.0 %), HNO_3 ($\geq$65.0 %) and $NaNO_2$ ($\geq$97.0 %) were reagent grade and purchased from Sigma-Aldrich. Acetone (CH_3COCH_3, $\geq$99.5 %) and 2-propanol [$(CH_3)_2CHOH$, $\geq$99.8 %] were also purchased from Sigma-Aldrich and used in washing and filtering processes. All solutions were prepared using deionized water.

2.2 Apparatus and Procedures for Synthesis of NaNT $(H_2O)_2$

5-AT, HNO_3 and $NaNO_2$ were used to synthesize NaNT $(H_2O)_2$. Firstly, 2.0 grams of 5-AT and 1.6 ml of HNO_3 were combined in a 50 ml beaker with 9.8 ml of deionized water to prepare solution A, and 3.56 grams of $NaNO_2$ and 20.0 ml of deionized water were mixed in a 250 ml round-bottomed flask to prepare solution B. Both solutions were stirred and heated to 65 °C by a magnetic stirring heater. Solution A was slowly added dropwise to the round-bottomed flask containing solution B using a dropping funnel, while solution B was rapidly stirred and the temperature was maintained at 65 °C. Extensive effervescence occurred on the addition of each drop of solution A, and the addition was temporarily stopped until the effervescence subsided. It took about 48 minutes to add the entire solution A to solution B. During the addition, the color of the mixed solution changed from clear to light yellow, and no solid precipitated from the mixed solution. After the addition was complete, the mixed solution was evaporated to dryness using a rotary vacuum concentrator in a 52 °C water bath. Subsequently, the obtained solid residue was washed by Soxhlet extraction with acetone and dried in a vacuum oven at 50 °C for 4 hours to obtain purified NaNT $(H_2O)_2$.

The synthesized NaNT$(H_2O)_2$ were characterized by means of SEM (Hitachi S-3000H), NMR (Bruker AVIII 500 MHz), FTIR (PerkinElmer Spectrum 100), EA (Elementar Vario EL cube), UV-Vis (ChromTech CT-8600) and STA TG-DSC (Netzsch STA 449 F3 Jupiter®). SEM was used to observe the morphology and size of the synthesized product. ^{15}N-NMR, ^{1}H-NMR and ^{13}C-NMR were used to determine the types and amount of nitrogen, hydrogen and carbon atoms present in the molecule, respectively, and to confirm the structure of the synthesized product. Dimethyl sulfoxide-d6 (DMSO-d6) was used as the solvent in NMR experiments because of its good solubilizing ability for NaNT $(H_2O)_2$. FTIR was conducted to analyze the functional groups of the synthesized product in the 4000–500 cm^{-1} region with a spectral resolution of 4 cm^{-1}. EA was carried out to determine carbon (C), nitrogen (N), hydrogen (H), oxygen (O) and sodium (Na) contents of the synthesized product and to confirm the desired product. UV-Vis was used to measure the absorption spectrum of the synthesized product at 25 °C. A cell with an optical path length of 1 cm was used. Simultaneous TG-DSC measurement was carried out in a nitrogen atmosphere at a heating rate of 2 °C min^{-1} using the sample weight in the range of 0.5–1.0 mg to study the thermal properties of the synthesized product.

2.3 Design of Experimental Conditions for Synthesis of DBX-1

Taguchi method is one of the most widely used design methods, which is making use of an orthogonal array from the experimental design to study more variables in minimal number of experiments [2,3,4,20,21,22,23]. An $L_9(3^4)$ orthogonal array with four control factors and three levels was used to design the experimental conditions in this study. Four control factors were selected, including reaction temperature, reaction time, concentration of NaNT$(H_2O)_2$ and molar ratio of NaNT$(H_2O)_2$ to CuCl, each at three levels, as shown in Table 1. The above four factors were assigned to the $L_9(3^4)$ orthogonal array containing nine experimental conditions as shown in Table 2.

2.4 Apparatus and Procedures for Synthesis of DBX-1

NaNT$(H_2O)_2$ and CuCl were used to synthesize DBX-1. Firstly, 1.0 g of NaNT$(H_2O)_2$ and a certain amount of deionized water (13.3, 10.0, or 8.0 g) were mixed in a 250 ml round-bottomed flask to prepare solution A, and the required amount of CuCl (0.50, 0.46, or 0.38 g) was added to a 50 ml beaker with 5.0 ml of deionized water to prepare solution B. Solution A in the round-bottomed flask was stirred and heated to a certain temperature (90, 95 or 100 °C) by a magnetic stirring heater, and then solution B was slowly added dropwise to solution A using a dropping funnel. After the addition was complete, the mixed solution was still maintained at its original temperature for a certain time (30, 60 or 90 min) to form DBX-1. Finally, the precipitate of DBX-1 was collected by filtration, washed twice with deionized water and once with 2-propanol, and dried in a vacuum oven at 50 °C for 4 hours.

The synthesized DBX-1 were characterized by means of SEM (Hitachi S-3000H), FTIR (PerkinElmer Spectrum 100), UV-Vis (ChromTech CT-8600) and STA TG-DSC (Netzsch STA 449 F3 Jupiter®). SEM was used to observe the morphology and size of the synthesized product. FTIR was conducted to analyze the functional groups of the synthesized product in the 4000–500 cm^{-1} region with a spectral resolution of 4 cm^{-1}. Simultaneous TG-DSC measurements were carried out in a nitrogen atmosphere at heating rates of 1, 2, 5 and 10 °C min^{-1} using the sample weight in the range of 0.5–1.0 mg to study the thermal properties of the synthesized product.

Table 1. The control factors and levels of the Taguchi experiments.

Control factor	Level		
	1	2	3
A. Reaction temperature (°C)	90	95	100
B. Reaction time (min)	30	60	90
C. Concentration of NaNT$(H_2O)_2$ (wt.%)	0.075	0.1	0.125
D. Molar ratio of NaNT$(H_2O)_2$ to CuCl	1.5	1.25	1.15

Table 2. The $L_9(3^4)$ orthogonal array of the Taguchi experiments.

Exp. No.	Reaction temperature (°C)	Reaction time (min)	Concentration of $NaNT(H_2O)_2$ (wt.%)	Molar ratio of $NaNT(H_2O)_2$ to CuCl
A1	90	30	0.075	1.5
A2	90	60	0.1	1.25
A3	90	90	0.125	1.15
A4	95	30	0.1	1.15
A5	95	60	0.125	1.5
A6	95	90	0.075	1.25
A7	100	30	0.125	1.25
A8	100	60	0.075	1.15
A9	100	90	0.1	1.5

2.5 Sensitivity Tests

The impact sensitivity of the synthesized DBX-1 powder was determined by the BAM fallhammer (Reichel & Partner GmbH). The Bruceton method [24] was used to evaluate the impact sensitivity, which was based on a statistical analysis by determining the drop height (H_{50}) at which there was 50% probability of obtaining an ignition. Each sample was tested utilizing a 0.375 kg dropweight for 30 times to obtain a H_{50}. The impact energy (E_{50}) was calculated using the formula $E_{50}(\text{Joule}) = mgH_{50}$, where m is dropweight mass [kg], g is acceleration due to gravity [$m\,s^{-2}$], and H_{50} is drop height [m].

The friction sensitivity of the synthesized DBX-1 powder was determined by the BAM friction tester (Reichel & Partner GmbH). The 1 of 6 method was used to evaluate the friction sensitivity, which was defined as the smallest load at which an audible or visible decomposition reaction is obtained from at least one out of six trials. The measurement range of friction load was from 0.5 to 360 N.

The electrostatic spark sensitivity of the synthesized DBX-1 powder was determined by the small-scale electrostatic spark sensitivity tester (OZM Research X SPARK 10). The measurement of the electrostatic spark sensitivity was based on the principle of capacitive discharge driven through the granular bed of the test sample. If the sample had flash, spark, burn, odor or noise other than instrument noise, it should be tested at the next lower level until 20 consecutive failures were reported. The discharge energy was calculated using the formula $E(\text{Joule}) = {}^1/_2 CV^2$, where C is capacitance [μF], and V is voltage [kV]. The measured discharge energy ranged from 25 μJ to 25 J.

3 Results and Discussion

3.1 Characterization of Synthesized $NaNT(H_2O)_2$

3.1.1 SEM Image

The morphology and size of the synthesized product crystals were observed by SEM. Figure 1 shows the SEM image of synthesized $NaNT(H_2O)_2$ powders. As can be seen from Figure 1, the synthesized $NaNT(H_2O)_2$ powder has an irregular plate-like morphology and a large size. It is clear that the plates are closely packed with one another.

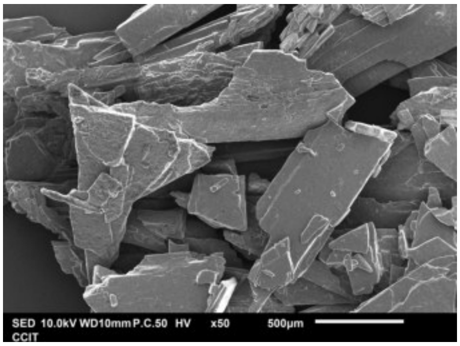


Figure 1. SEM image of synthesized $NaNT(H_2O)_2$ powders.

3.1.2 NMR Spectrum

The structure of the synthesized product was confirmed by NMR spectroscopy. Figures 2–4 show the ^{15}N-NMR, ^{1}H-NMR, and ^{13}C-NMR spectra of the synthesized $NaNT(H_2O)_2$ in DMSO-d6. ^{15}N-NMR spectrum shows that two signals at 316.6 (N2, N5) and 397.2 (N3, N4) ppm correspond to the nitrogen atoms in the tetrazole ring, and one signal at 357.5 (N1) ppm corresponds to the nitrogen atom in the nitro group. ^{1}H-NMR spectrum exhibited two main signals at 4.0 and 2.5 ppm, which correspond to the hydrogen atoms in water of crystallization and DMSO-d6 solvent, respectively. Another small signal at 8.2 ppm may be attributed to a small amount of 5-nitro-1H-tetrazole (HNT), which is a by-product of the reaction. The acidic hydrogen on the HNT is easily replaced by a metal cation, giving salts of the tetrazolate anion with better energetic properties and higher thermal stability [25]. In the ^{13}C-NMR spectrum, the two main signals at 168.7 and 39.2 ppm correspond to the carbon atoms in the tetrazole ring (C6) and DMSO-d6 solvent, respectively. Another small signal at 149.4 ppm may also be

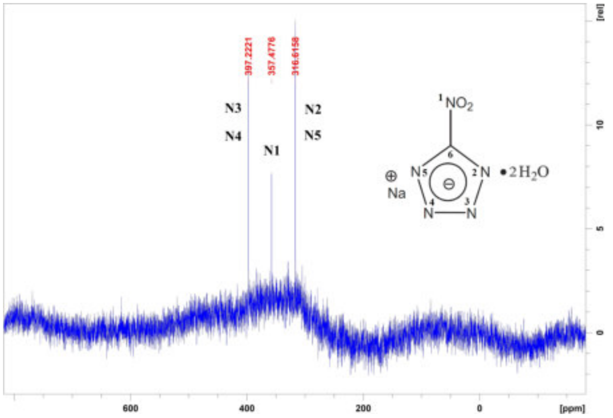


Figure 2. ^{15}N-NMR spectrum of synthesized $NaNT(H_2O)_2$ in DMSO-d6.

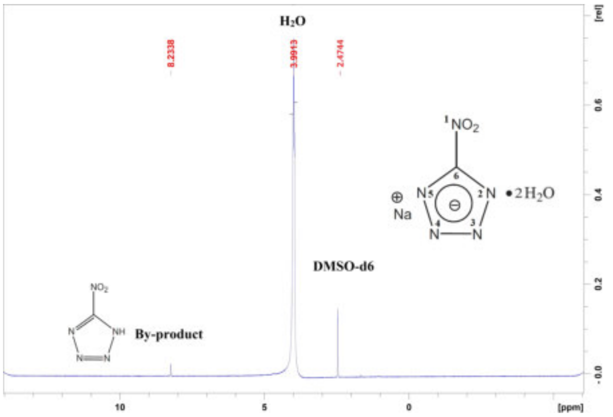


Figure 3. ^{1}H-NMR spectrum of synthesized $NaNT(H_2O)_2$ in DMSO-d6.

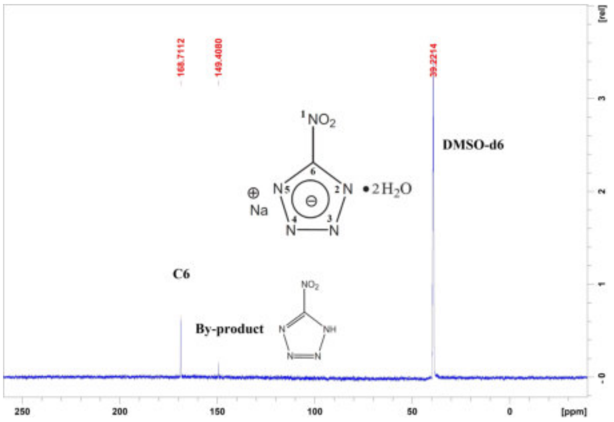


Figure 4. ^{13}C-NMR spectrum of synthesized $NaNT(H_2O)_2$ in DMSO-d6.

attributed to a small amount of by-product HNT. The above NMR analysis can be used to confirm that the synthesized product is $NaNT(H_2O)_2$.

3.1.3 FTIR Spectrum

The functional group of the synthesized product was analyzed by FTIR. Figure 5 shows the FTIR spectrum of synthesized $NaNT(H_2O)_2$. The aromatic C=N and C=C stretching are observed at 1447, 1421, 1399, 1272, 1192, 1172, 1066, 1041, 842, 669 and 543 cm^{-1}, indicating the presence of a tetrazole ring structure. In addition, Tr-NO_2 symmetric and asymmetric stretching are found at 1323 and 1546 cm^{-1}, respectively, and O–H stretching of water of crystallization is found at around 3443 cm^{-1}. These analysis results are similar with the report of Klapötke et al. [26]. Therefore, the FTIR spectrum can further verify that the synthesized product is $NaNT(H_2O)_2$.

3.1.4 EA Analysis

The elemental composition of the synthesized product was analyzed by EA. The analysis result shows that the synthesized $NaNT(H_2O)_2$ contained 7.1 wt.% carbon (C), 41.2 wt.% nitrogen (N), 2.3 wt.% hydrogen (H), 36.6 wt.% oxygen (O) and 12.8 wt.% sodium (Na), which are very close to the theoretical values of $NaNT(H_2O)_2$ composition (6.9 wt.% C, 40.5 wt.% N, 2.3 wt.% H, 37.0 wt.% O and 13.3 wt.% Na). Among them, the oxygen and sodium contents are slightly lower in the synthesized product, possibly due to the presence of a small amount of HNT by-product.

3.1.5 UV-Vis Spectrum

The absorption spectrum of the synthesized product was measured by UV-Vis. The synthesized $NaNT(H_2O)_2$ was dissolved in deionized water to prepare test solutions with concentrations of 2.49E-4, 1.66E-4 and 1.24E-4 mol/L. Figure 6 shows the UV-Vis spectra of the synthesized NaNT $(H_2O)_2$ at different concentrations. It is found that the char-

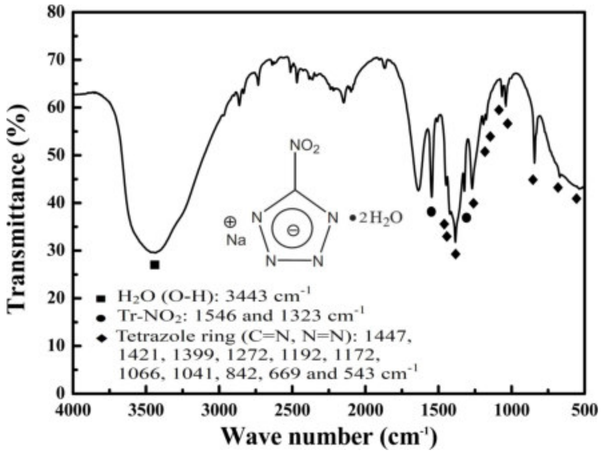


Figure 5. FTIR spectrum of synthesized $NaNT(H_2O)_2$.

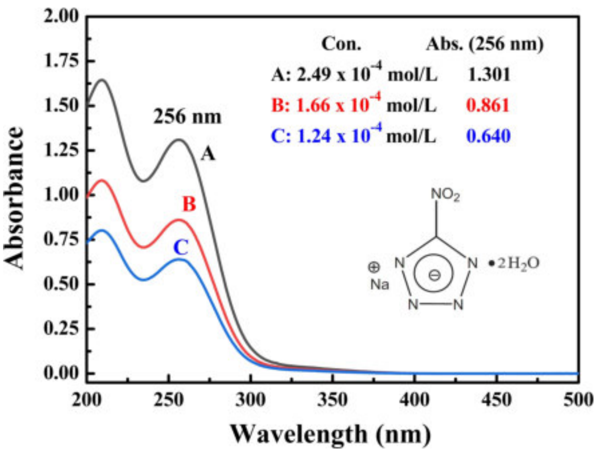


Figure 6. UV-Vis spectra of synthesized $NaNT(H_2O)_2$.

acteristic absorption peak of 5-nitrotetrazolate (NT, $CN_5O_2^-$) appears at around 256 nm, and the peak intensity increases with increasing $NaNT(H_2O)_2$ concentration. The relationship between peak intensity and $NaNT(H_2O)_2$ concentration can be obtained by linear regression analysis as follows:

$$Y = 5281.3X - 0.0152$$

The parameters Y and X in the formula represent the peak intensity and the $NaNT(H_2O)_2$ concentration (mol/L), respectively. The molar absorptivity of $NaNT(H_2O)_2$ is 5281.3 $mol\,L^{-1}\,cm^{-1}$. Fronabarger et al. [12] have also reported a similar experimental result.

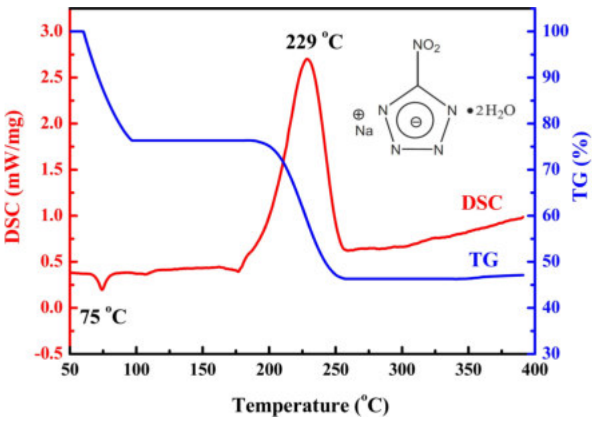


Figure 7. TG-DSC curves of synthesized $NaNT(H_2O)_2$.

3.1.6 TG-DSC Thermogram

The thermal properties of the synthesized product were studied by simultaneous TG-DSC analysis. Figure 7 shows the TG-DSC curves of synthesized $NaNT(H_2O)_2$. It is found that the DSC curve exhibits a small endothermic peak at around 75 °C, while the TG curve indicates a weight loss of about 20% at this temperature. Therefore, this peak can be attributed to dehydration of the water of crystallization. The same analysis has also been reported by Marimuthu et al. [27]. In addition, the DSC curve also shows an exothermic peak at around 229 °C, which can be reasonably attributed to the decomposition of NaNT, because the TG curve shows continuous weight loss.

3.2 Analysis and Verification of Taguchi Experiments for Synthesis of DBX-1

A series of synthesis experiments for DBX-1 formation with different operating parameters, such as the reaction temperature (90, 95 and 100 °C), the reaction time (30, 60 and 90 min), the concentration of $NaNT(H_2O)_2$ (0.075, 0.1 and 0.125 wt.%) and the molar ratio of $NaNT(H_2O)_2$ to CuCl (1.5, 1.25 and 1.15) were carried out, and then the effects of the operating parameters on the yield of DBX-1 were examined. The experimental results are given in Table 3 which were converted into a signal-to-noise (S/N) ratio using the Taguchi method. The S/N ratio was used as the measure of the effect of noise factors on the target characteristics [2,3,4,22,23]. The yield of DBX-1 was chosen as the quality characteristic in this study. The analysis of yield used larger-the-better type, a larger value represented by a higher yield, as well as a better quality characteristic. Table 4 presents the range and contribution rank of each factor for the yield of DBX-1. In the table, the target values for different levels of each factor are the arithmetic average of the target values corresponding to each level. The range is the difference between maximum and minimum of the target values on each factor and the rank represents the order of effect of each factor on the quality characteristic [2,3,4,22,23]. The trend of parameter influence for the three factors is shown in Figure 8. In the figure, levels A3, B1, C1 and D3

Table 3. Experimental results of Taguchi's orthogonal array for yield of DBX-1.

Exp. No.	A1	A2	A3	A4	A5	A6	A7	A8	A9
Amount after purification (g)	0.51	0.55	0.40	0.69	0.50	0.61	0.64	0.72	0.59
Yield after purification (%)	49.1	53.4	38.7	67.0	48.4	59.5	62.2	70.0	57.3

Table 4. Range and contribution rank of each factor for yield of DBX-1 (unit: %).

Level	Control factors			
	A Reaction temperature	B Reaction time	C Concentration of $NaNT(H_2O)_2$ (wt.%)	D Molar ratio of $NaNT(H_2O)_2$ to CuCl
1	47.07	**59.43**	**59.53**	51.60
2	58.30	57.27	59.23	58.37
3	**63.17**	51.83	49.77	**58.57**
Range	**16.10**	**7.60**	**9.77**	**7.0**
Rank	**1**	**3**	**2**	**4**

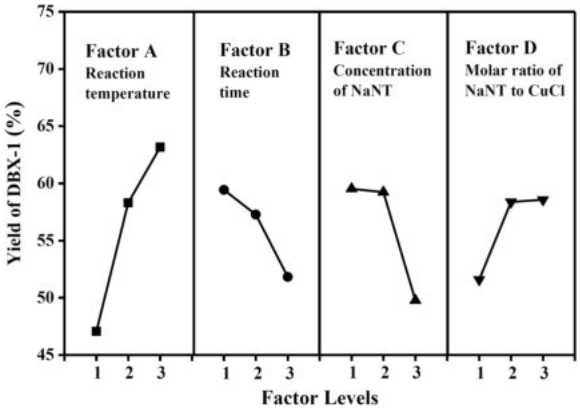


Figure 8. The trend of parameter influence for four factors on yield of DBX-1.

have the largest value of yield for the factors reaction temperature, reaction time, Concentration of $NaNT(H_2O)_2$ and molar ratio of $NaNT(H_2O)_2$ to CuCl, respectively. Based on above study, the maximum value of yield may be found under the conditions that the reaction temperature is 100 °C, the reaction time is 30 min, the concentration of NaNT $(H_2O)_2$ is 0.075 wt.% and the molar ratio of $NaNT(H_2O)_2$ to CuCl is 1.15. It is also observed that the order of the effect of each factor on this quality characteristic is reaction temperature $>$ concentration of $NaNT(H_2O)_2 >$ reaction time $>$ molar ratio of $NaNT(H_2O)_2$ to CuCl. The reaction temperature (factor A) has the greatest influence. Additional confirmatory experiments were performed to verify the effectiveness of the optimal parameters identified with the Taguchi method. The optimal design factor was the A3B1C1D3 parameter combination for the yield of DBX-1. Table 5 gives the results of the confirmatory experiment. This experiment was repeated three times and the average value was calculated. The experimental results indicate that the A3B1C1D3 parameter combination produces a larger yield of DBX-1 than the other combinations. The Taguchi method was successful in predicting this optimal parameter combination in order to obtain the maximum yield. In this way, the maximum yield of DBX-1 can reach 72.2 %.

Table 5. Results of confirmation experiments.

Optimal parameter combination	Exp. No.	Amount after purification (g)	Yield after purification (%)
A3B1C1D3	1	0.74	71.6
	2	0.77	74.5
	3	0.73	70.6
	Average value	**0.75**	**72.2**

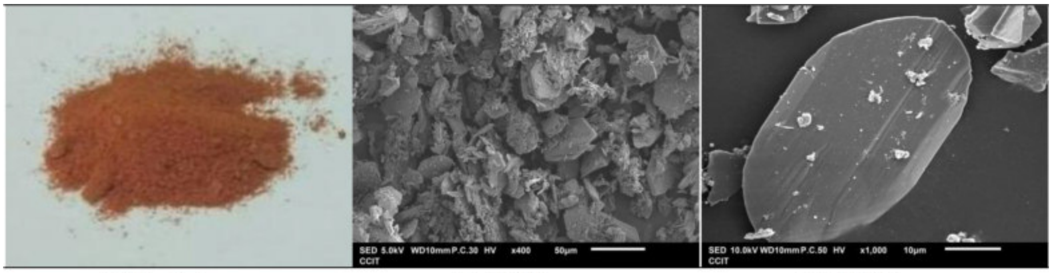
3.3 Characterization of Synthesized DBX-1

3.3.1 SEM Image

Figure 9 shows the photo and SEM images of synthesized DBX-1 powder under the operating condition of optimal parameter combination (A3B1 C1D3). As can be seen from Figures 9(a) and (b), the synthesized DBX-1 powder is rust red in color and shows the state of flaky aggregation, respectively. In addition, from Figure 9(c), it can be observed that the synthesized DBX-1 powder shows a hexagonal flaky structure.

3.3.2 FTIR Spectrum

The FTIR spectrum of synthesized DBX-1 is shown in Figure 10. The aromatic C=N and C=C stretching are observed at 1488, 1471, 1452, 1423, 1122, 1097, 833, 669 and 653 cm^{-1}, indicating the presence of a tetrazole ring structure. Tr-NO_2 symmetric and asymmetric stretching are observed at 1326 and 1548 cm^{-1}, respectively. In addition, the weak O–H stretching of water is found in the range of 3550–3000 cm^{-1}, which indicates that a small amount of moisture remains on the surface of DBX-1. These analysis results are similar to previous literature [12,13,14]. Therefore, the FTIR spectrum can verify that the synthesized product is DBX-1.



(a) Photo image (b) SEM image (c) SEM image

Figure 9. The photo and SEM images of synthesized DBX-1 powder under the operating condition of optimal parameter combination.

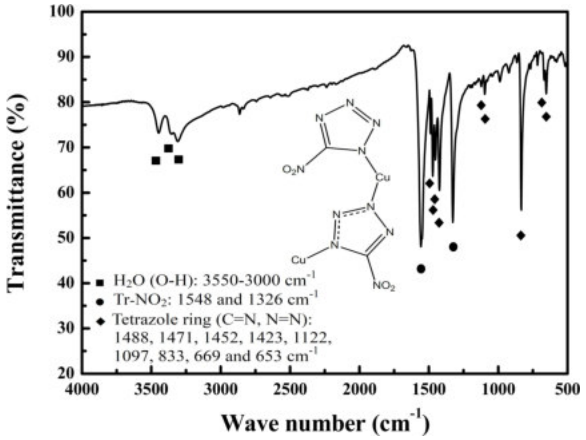


Figure 10. FTIR spectrum of synthesized DBX-1.

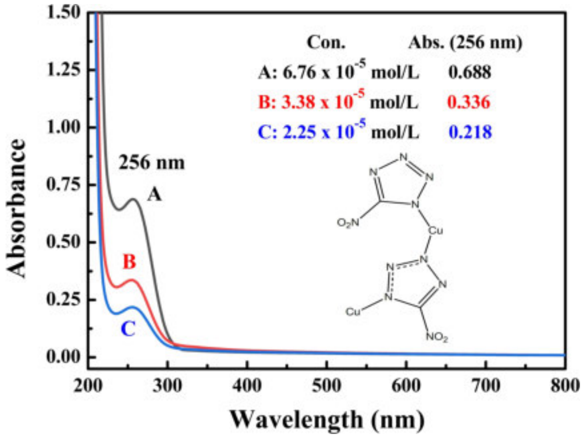


Figure 11. UV-Vis spectrum of synthesized DBX-1.

3.3.3 UV-Vis Spectrum

1.2 mg (3.38E-6 mole) of synthesized DBX-1 was dissolved in 2 ml of 1 N sodium hydroxide and filtered to remove rust-colored copper(I) oxide (Cu_2O), and then deionized water was added to the filtrate to prepare test solutions with concentrations of 6.76E-5, 3.38E-5 and 2.25E-5 mol/L. Figure 11 shows the UV-Vis spectra of the synthesized DBX-1 at different concentrations. The characteristic absorption peak of NT appears at around 256 nm, and the peak intensity increases with increasing DBX-1 concentration. The equation of relationship between peak intensity and NaNT $(H_2O)_2$ concentration is described in Section 3.1.5. Because 1 mole of DBX-1 can produce 2 moles of NT. Based on the above equation, the theoretical relationship between peak intensity and DBX-1 concentration can be built as follows:

$$Y = 10562.6X - 0.0152$$

The parameters Y and X in the formula represent the peak intensity and the DBX-1 concentration (mol/L), respectively. The molar absorptivity of DBX-1 is 10562.6 $mol\,L^{-1}\,cm^{-1}$. The measured and theoretical absorbance values at 256 nm for solutions with different concentrations of DBX-1 are listed in Table 6. The purity of the synthesized DBX-1 can be determined by comparing the measured absorbance of NT to the theoretical absorbance of NT. The results indicate that the purity of the synthesized DBX-1 is about 98 %.

Table 6. UV-Vis measurement results of DBX-1.

Exp. No	Concentration of DBX-1 (mole/L)	The absorbance of NT at 256 nm		Purity of DBX-1 (%)	
		Measured	Theoretical		
1	6.76E-5	0.688	0.699	98.4	98
2	3.38E-5	0.336	0.342	98.2	
3	2.25E-5	0.218	0.222	98.2	

3.3.4 TG-DSC Thermogram

Figure 12 shows the TG-DSC curve of the synthesized DBX-1. It is found that the DSC curve exhibits a strong exothermic peak at around 321 °C, which can reasonably be attributed to the decomposition of DBX-1, because the TG curve shows continuous weight loss. Fronabarger et al. [16] and Pu et al. [14] have also reported similar experimental results. In addition, Figure 13 presents the DSC curves of the synthesized DBX-1 at heating rates of 1, 2, 5 and 10 °C

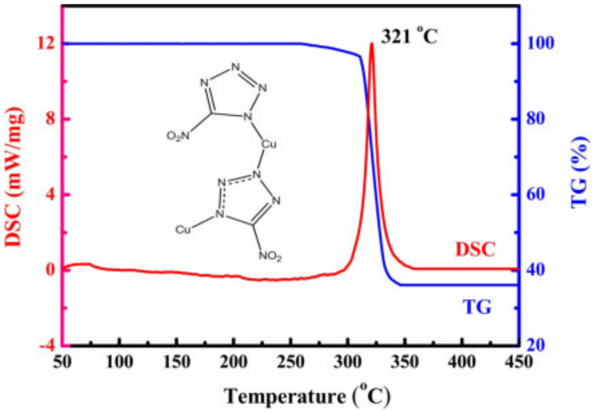


Figure 12. TG-DSC curves of synthesized DBX-1.

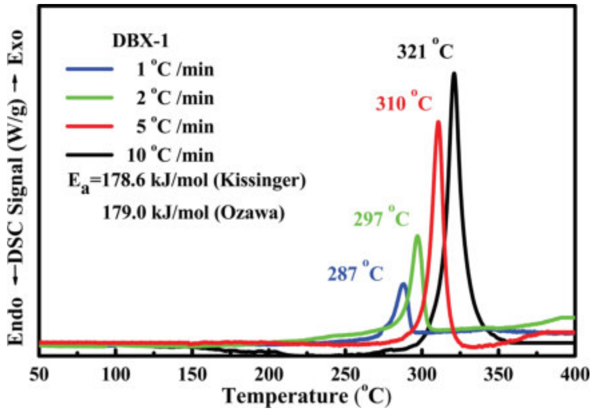


Figure 13. DSC curves of synthesized DBX-1 at different heating rates and its decomposition activation energy (calculated).

min^{-1}. The decomposition activation energies of DBX-1 calculated by Kissinger and Ozawa methods [28] are 178.6 and 179.0 kJ/mol, respectively.

3.4 Sensitivity Analysis of Synthesized DBX-1

The impact, friction and electrostatic spark sensitivities of the synthesized DBX-1 were determined by BAM fallhammer, BAM friction tester and electrostatic spark sensitivity tester, respectively. Each experiment was run three times and the average value was calculated. Sensitivity test results of DBX-1 compared to lead azide (LA) are shown in Table 7. The impact sensitivity (E_{50}), friction sensitivity and electrostatic spark sensitivity are 51 mJ, 0.4 N and 7.3 mJ, respectively. It is found that the sensitivity of DBX-1 to impact, friction and spark is almost the same as those for LA.

4 Conclusion

This study successfully used Taguchi's experimental design method to obtain the optimal parameter combination to achieve the maximum yield of DBX-1. The optimal synthesis parameters were as follows: the reaction temperature was 100 °C, the reaction time was 30 min, the concentration of $NaNT(H_2O)_2$ was 0.075 wt.% and the molar ratio of $NaNT(H_2O)_2$ to CuCl was 1.15, and then the maximum yield after purification could reach 72.2 %. In addition, the synthesized DBX-1 had been confirmed by SEM, FTIR, UV-Vis and TG-DSC analyses. The thermal analysis indicated that the decomposition activation energies of DBX-1 calculated by Kissinger and Ozawa methods were 178.6 and 179.0 kJ/mol, respectively. The sensitivity test indicated that the impact sensitivity, friction sensitivity and electrostatic spark sensitivity of DBX-1 were 51 mJ, 0.4 N and 7.3 mJ, respectively, which were almost the same as those for LA.

Acknowledgements

This research was financially supported by the System Manufacturing Center, National Chung Shan Institute of Science and Technology, R.O.C. under grant number of YR08109P095PE-CS.

Data Availability Statement

No data available.

Table 7. Sensitivity test results of DBX-1 compared to lead azide (LA).

Explosive	Exp. No	Impact sensitivity H_{50} (mm)	E_{50} (mJ)	Friction sensitivity (N)	Electrostatic spark sensitivity (mJ)
DBX-1	1	13	48	0.4	7.5
	2	14	51	0.3	7.5
	3	15	55	0.4	7.0
	Average value	**14**	**51**	**0.4**	**7.3**
LA [1]			89	0.1	4.7

References

[1] M. A. Ilyushin, I. V. Tselinsky, I. V. Shugalei, Environmentally friendly energetic materials for initiation devices, *Cent. Eur. J. Energ. Mater.* **2012**, *9*, 293.

[2] J. S. Li, C. C. Chang, K. T. Lu, Optimization of the synthesis parameters and analysis of the impact sensitivity for tetrazene explosive, *Cent. Eur. J. Energ. Mater.* **2020**, *17*, 5.

[3] J. S. Li, F. J. Chen, H. W. Yang, K. T. Lu, Optimization of the process parameters for the synthesis of high purity 4,6-dinitrobenzofuroxan (4,6-DNBF), *Propellants Explos. Pyrotech.* **2020**, *45*, 1102, https://doi.org/10.1002/prep.201900413.

[4] J. S. Li, F. J. Chen, H. W. Yang, K. T. Lu, Study on synthesis and characterization of primary explosive KDNBF with different morphologies, *Propellants Explos. Pyrotech.* **2020**, *45*, 1313, https://doi.org/10.1002/prep.202000052.

[5] N. Fischer, T. M. Klapötke, J. Stierstorfer, Calcium 5-nitriminotetrazolate- A green replacement for lead azide in priming charges, *J. Energ. Mater.* **2011**, *29*, 61.

[6] D. Fischer, T. M. Klapötke, D. G. Piercey, J. Stierstorfer, Copper salts of halo tetrazoles: Laser-ignitable primary explosives, *J. Energ. Mater.* **2012**, *30*, 40.

[7] M. H. V. Huynh, M. A. Hiskey, T. J. Meyer, M. Wetzler, Green primaries: environmentally friendly energetic complexes, *Proc. Natl. Acad. Sci. U. S. A.* **2006**, *103*, 5409.

[8] T. M. Klapötke, D. G. Piercey, N. Mehta, K. D. Oyler, M. Jorgensen, S. Lenahan, J. S. Salan, J. W. Fronabarger, M. D. Williams, Preparation of high purity sodium 5-nitrotetrazolate (NaNT): An essential precursor to the environmentally acceptable primary explosive, DBX-1, *Z. Anorg. Allg. Chem.* **2013**, *639*, 681.

[9] J. J. Sabatini, K. D. Oyler, Recent advances in the synthesis of high explosive materials, *Crystals* **2016**, *6*, 5.

[10] D. D. Ford, S. Lenahan, M. Jörgensen, P. Dubé, M. Delude, P. E. Concannon, S. R. Anderson, K. D. Oyler, G. Cheng, N. Mehta, J. Salan, Development of a lean process to the lead-free primary explosive DBX-1, *Org. Process Res. Dev.* **2015**, *19*, 673.

[11] R. Meyer, J. Köhler, A. Homburg, *Explosives*, 7th ed., Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, **2015**, p. 65.

[12] J. W. Fronabarger, M. D. Williams, W. B. Sanborn, *Lead-free primary explosive composition and method of preparation*, International application published under the patent cooperation treaty (PCT) No.: WO 2008/048351 A2, **2008**.

[13] J. W. Fronabarger, M. D. Williams, W. B. Sanborn, *Lead-free primary explosive composition and method of preparation*, United States Patent No.: US 7,833,330 B2, **2010**.

[14] Y. L. Pu, D. L. Sheng, Y. H. Zhu, L. K. Chen, B. Yang, Y. L. Wang, M. H. Xu, Synthesis and Characterization of copper(I) nitrotetrazolate, *Initiators & Pyrotechnics* **2009**, *5,* 43–45.

[15] Y. L. Pu, D. L. Sheng, Y. H. Zhu, L. K. Chen, B. Yang, Y. L. Wang, M. H. Xu, Synthesis process and property of new primary explosive copper(I) nitrotetrazolate, *Chinese Journal of Energetic Materials* **2010**, *18*, 654.

[16] J. W. Fronabarger, M. D. Williams, W. B. Sanborn, J. G. Bragg, D. A. Parrish, M. Bichay, DBX-1 - A lead free replacement for lead azide, *Propellants Explos. Pyrotech.* **2011**, *36*, 541.

[17] E. von Herz, *C-nitrotetrazole compounds*, United States Patent No.: 2,066,954, **1937**.

[18] W. H. Gilligan, M. J. Kamlet, *Method of preparing the acid copper salt of 5-nitrotetrazole*, United States Patent No.: 4,093,623, **1978**, The United States of America as represented by the Secretary of the Navy, Washington, D.C. .

[19] J. C. Bottaro, M. A. Petrie, J. G. Bragg, J. W. Fronabarger, M. D. Williams, Facile method for preparation of 5-nitrotetrazolates using a batch system, United States Patent No.: 9,598,380 B2, **2017**, SRI International, Menlo Park, CA (US); Pacific Scientific Energetic Materials Company, LLC, Chandler, AZ (US).

[20] S. Taguchi, *Taguchi Methods and QFD: Hows and Whys for Management*, American Supplier Institute, Michigan, **1987**, p. 1.

[21] W. G. Cochran, G. M. Cox, *Experimental Design*, 2nd ed., John Wiley & Sons, New York, **1992**, p. 114.

[22] J. S. Li, C. M. Chung, T. M. Yang, C. C. Hwang, K. T. Lu, T. F. Yeh, Combustion rate and light emission of $Mg/NaNO_3/Na_2C_2O_4/$ binder-flares, *Propellants Explos. Pyrotech.* **2018**, *43*, 512.

[23] T. M. Yang, C. S. Su, J. S. Li, K. T. Lu, T. F. Yeh, Recrystallization and micronization of p-toluenesulfonamide using the rapid expansion of supercritical solution (RESS) process, *Crystals* **2019**, *9*, 449.

[24] J. W. Dixon, A. M. Mood, A method for obtaining and analyzing sensitivity data, *J. Am. Stat. Assoc.* **1948**, *43*, 109.

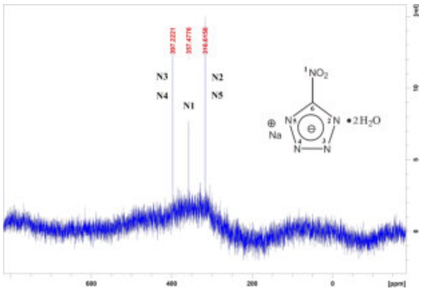
[25] S. R. Ahmad, M. Cartwright, *Laser Ignition of Energetic Materials*, John Wiley & Sons, West Sussex, **2015**, p. 200.

[26] T. M. Klapötke, C. M. Sabaté, J. M. Welch, Alkali metal 5-nitrotetrazolate salts: prospective replacements for service lead(II) azide in explosive initiators, *Dalton Trans.* **2008**, *45*, 6372.

[27] A. Marimuthu, M. B. Talawar, An improved safe method for the synthesis of ammonium 5-nitrotetrazolate (ANT), a key intermediate for the synthesis of green energetic materials (GEMs), *Cent. Eur. J. Energ. Mater.* **2017**, *14*, 861.

[28] J. S. Li, J. J. Chen, C. C. Hwang, K. T. Lu, T. F. Yeh, Study on thermal characteristics of TNT based melt-cast explosives, *Propellants Explos. Pyrotech.* **2019**, *44*, 1270.

Manuscript received: July 6, 2020
Revised manuscript received: August 13, 2020
Version of record online: ■■■, ■■■■



W.-H. Li, K.-C. Tseng, T.-M. Yang, J.-S. Li, K.-T. Lu*

1 – 11

Optimization of Synthesis Parameters and Characterization of Green Primary Explosive Copper(I) 5-nitrotetrazolate (DBX-1)