

Preparation of High Purity Sodium 5-Nitrotetrazolate (NaNT): An Essential Precursor to the Environmentally Acceptable Primary Explosive, DBX-1

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Abstract. Sodium 5-nitrotetrazolate dihydrate (NaNT) is a useful precursor compound for the synthesis of lead-free primary explosives; however, currently employed syntheses for the compound are tedious, dangerous, and plagued by impurities. Through comprehensive analysis, we elucidate the identity of the most detrimental impurities and further report an improved procedure for preparation of NaNT, which greatly improves the purity, while avoiding the handling of acid cop-

per(II) nitrotetrazolate, a highly sensitive explosive intermediate. In the new procedure, 5-aminotetrazole is diazotized with sodium nitrite, cupric sulfate, and nitric acid. Copper is precipitated as its oxide and the aqueous solution evaporated. After soxhlet extraction with acetone, large crystals of NaNT are obtained. The prepared material is suitable for preparation of lead azide replacement DBX-1 [copper(I) 5-nitrotetrazolate] as evidenced by successful use in M55 stab detonators.

Introduction

The research into new primary explosives for the replacement of lead azide has been very significant in recent years. The major driving force for this work is the high personal and environmental toxicity of lead^[1] and as such, a green primary explosive is sought. Primary explosives are the highly-sensitive explosives used to initiate larger masses of secondary explosives such as TNT (2,4,6-trinitrotoluene). The phenomena unique to a primary explosive is the ability to undergo an extremely rapid deflagration-to-detonation transition (DDT), whereby a reaction front propagated by conduction and convection (deflagration) develops into a shockwave-propagated reaction. Secondary explosives can undergo a DDT as well, however the difference is that a primary will undergo a DDT on a far smaller scale, often on the order of several milligrams, than a secondary, which would simply burn or deflagrate at these small masses.^[2]

Lead azide has been commonly used as a primary explosive since it replaced mercury fulminate in the early 20th century, and has limitations beyond its high toxicity as a result of its lead content. In particular, lead azide is degraded by carbon dioxide and moisture to form toxic hydrazoic acid gas, and the material can also detonate during synthesis if conditions are not rigorously controlled.^[3] While a variety of both existing and new energetic materials have been studied as prospective lead azide replacements including silver azide,^[3b,4] diazodinitrophenol (DDNP),^[5] calcium nitrimino-tetrazolate,^[6] copper chlorotetrazolate,^[2] and copper(II) coordination complexes of the 5-nitrotetrazolate anion,^[7] all of them have limitations preventing their widespread use. Recently reported copper(I) 5-nitrotetrazolate (DBX-1)^[8] differs in that it functions in many cases as a “drop-in” replacement for lead azide, requiring no redesign of manufactured explosive devices beyond the use of DBX-1 as a volumetric replacement for lead azide. As a result of having these similar safety and initiation abilities compared to lead azide, DBX-1 is one of the most promising lead azide replacements to date.

DBX-1 is typically prepared from sodium 5-nitrotetrazolate dihydrate (NaNT), a copper(II) chloride, and a reducing agent (sodium ascorbate).^[8a] as shown in Scheme 1 Unfortunately NaNT is currently not commercially available and must instead be synthesized from 5-aminotetrazole (5-AT) based on the original procedure reported by *von Herz*.^[9] This is done via a modified Sandmeyer reaction in the presence of a copper(II) salt, which produces a very explosive intermediate, the acid salt of copper(II) 5-nitrotetrazolate, $\text{Cu}(\text{NT})_2 \cdot \text{HNT}$ ($\text{NT} = 5\text{-nitrotetrazolate, CN}_5\text{O}_2^-$). This copper salt is filtered off, and if dried is very sensitive towards impact and friction, although while wet the sensitivities are reduced. This wet filtercake is

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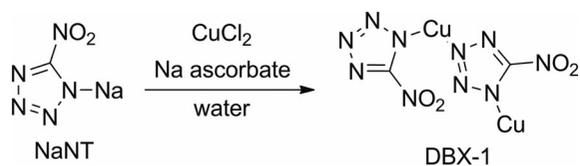
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re-suspended in water and heated with sodium hydroxide yielding copper(II) oxide and an aqueous solution of NaNT, which crystallizes as the dihydrate (although anhydrous NaNT is a very sensitive explosive compound, it is relatively insensitive as the dihydrate). The limiting step in this procedure is the handling of the copper salt, beyond this material being a sensitive explosive, this precipitate filtration step would lead to increased industrial costs and potentially lower yields due to transfer losses. Another major challenge of the traditional NaNT synthesis is the lack of purity of the resulting NaNT. Raw NaNT solutions made from the current procedure do not successfully produce DBX-1 directly, but first require further purification through a tedious, yield-reducing laboratory titration using a Cu^{II} salt to precipitate impurities, which can otherwise interfere with the crystallization of DBX-1.



Scheme 1. Synthesis of DBX-1.

In this work, we initially performed a thorough study of the challenges to synthesize DBX-1 when using these raw NaNT solutions, including an investigation of the specific impurities, which ultimately prevent formation of DBX-1. A safer and simplified procedure for the preparation of NaNT was thus developed and detailed herein. It is demonstrated that the produced material from the new procedure is of sufficient purity to be used for the preparation of DBX-1. The DBX-1 prepared from this NaNT functions comparably to current state-of-the-art DBX-1 in stab detonators and is of comparable sensitivity.

Results and Discussion

1 Impurity Investigation

Challenges of Using Raw NaNT

This section outlines the details surrounding reaction monitoring of attempted DBX-1 syntheses comparing the “raw NaNT solution” (e.g. that prepared directly by the von Herz method with no additional purification) versus a “purified NaNT solution” using in-situ tools. These tools allowed the investigators to note distinct differences between the reactions. For the purposes of this investigation the purified NaNT solution was prepared via the established method of titrating the raw NaNT with a solution of a Cu^{II} salt as mentioned above. In general, DBX-1 offline reaction monitoring proved quite challenging as the reaction proceeds through unstable intermediates that could not be easily isolated or characterized. The DBX-1 reaction conditions in the study were based on the published DBX-1 procedure^[8a] and used the same stoichiometry, the same lot of DBX-1 seed crystal, and the same lots of reagents except for the source of NaNT.

As expected, the raw NaNT solution did not successfully produce DBX-1. Upon addition of the initial dose (ca. 1/3 total dose) of sodium ascorbate reducing agent to the raw NaNT solution, a gel-like material was formed. A blue/aqua solution turned to an olive/grey suspension and the presence of solids was obvious although the in-situ camera, Mettler Toledo’s Particle Vision Measurement (PVM®), but showed no sign of crystalline material. The particle counter, Mettler Toledo’s Focused Beam Reflectance Measurement (FBRM®) tool, indicated over 90,000 fine particles at this stage and the reaction mixture remained cloudy and also showed no signs of crystalline material. A second dose of sodium ascorbate failed to convert the slurry to crystalline DBX-1 and merely diluted the fine counts as measured by FBRM® to approximately 60,000 counts of less than 100 μm particle size. The solids were identified using a combination of off-line tools including High Performance Liquid Chromatography (HPLC), Karl Fischer Titration, and Atomic Absorption. The result was a mixture of material that included water, 5-nitrotetrazole and copper.

The initial stages of the DBX-1 synthesis using Cu^{II} -purified NaNT in place of raw NaNT produced similar observations as described above. Upon addition of the initial dose of sodium ascorbate, a gel-like material was formed with no evidence of crystalline DBX-1. After an apparent induction period of several minutes, a very different phenomenon was noticed. These events included a visual change in reaction mixture turbidity (it became clear) and an almost instantaneous drop in the counts of fine particles (see Figure 1). As the fines dropped the PVM almost instantaneously identified crystalline DBX-1 (see Figure 2). The event only lasted seconds and produced the beautiful rust colored crystals indicative of DBX-1 product. The second dose of reducing agent was started (denoted by the second start on the x axis) after formation of the DBX-1 crystals was identified.

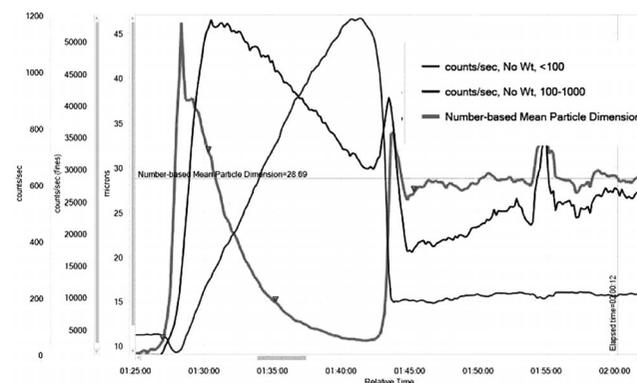


Figure 1. Focused Beam Reflectance Measurement (FBRM®) data after DBX-1 crystallization.

To further elucidate the details of the pure NaNT to DBX-1 reaction progress, various reactions to DBX-1 were monitored using in-situ infrared (IR) and Raman spectroscopy. The tools proved valuable in understanding both the intermediate and product formation. The two tools are quite complementary; Mettler Toledo’s ReactIR® (infrared) detects species in solution, while Raman will detect species in both solution and in solid form.

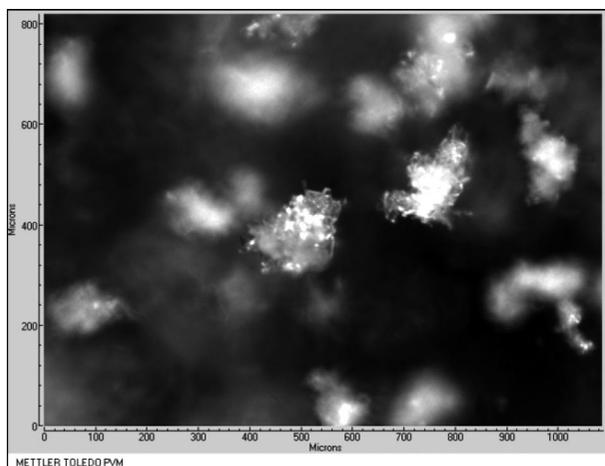


Figure 2. Particle Vision Measurement (PVM®) identifying crystalline DBX-1.

While monitoring the DBX-1 reactions made from purified NaN_T using ReactIR®, several peaks of interest clearly increased during the induction period (no DBX-1 crystals formed during the induction period). These same peaks, most likely key intermediate(s), decreased in intensity as DBX-1 formed. The reaction monitoring began with just copper(II) chloride in solution followed by the addition of NaN_T at $T = 90\text{ }^{\circ}\text{C}$. At this point copper(II) nitrotetrazolate was formed but remained in solution (if the temperature fell below $T = 60\text{ }^{\circ}\text{C}$ a blue precipitate of the copper(II) nitrotetrazolate – a known compound^[7] – formed). After the temperature stabilized at $T = 90\text{ }^{\circ}\text{C}$, the first dose of sodium ascorbate was added to the solution. At this point, the ReactIR® detected new peaks at 1552, 1444, 1423, and 1321 cm^{-1} which typically grew in during the induction period. The ReactIR® software utilizes a program called ConcIRT, which uses a mathematical algorithm known as curve-resolution. Curve-resolution algorithms have the capability to group wavenumber values that change absorbance intensity in the same manner. For each group, ConcIRT calculated the associated component spectrum and relative concentration profile. As each new reaction spectrum was acquired, ConcIRT re-analyzed all the reaction spectra and updated the individual component spectra and profiles. Thus, the calculation results evolved as the reaction proceeded and additional components such as intermediates were detected. ConcIRT identified a component associated with these peaks, the spectrum is shown in Figure 3.

As described earlier, the ensuing induction period results in an increase in fine particles as monitored by FBRM®. The ReactIR® also detects an increase in concentration of a species in solution during this induction period (see blue line in Figure 4). The dotted purple line is the Raman intensity of the intermediate over time, whereas the dotted green line is the product DBX-1. The red line is the total dose of sodium ascorbate reducing agent.

A final experiment was completed with a very slow dose of the reducing agent in an attempt to monitor the formation of intermediate and product using the in-situ Raman probe. A

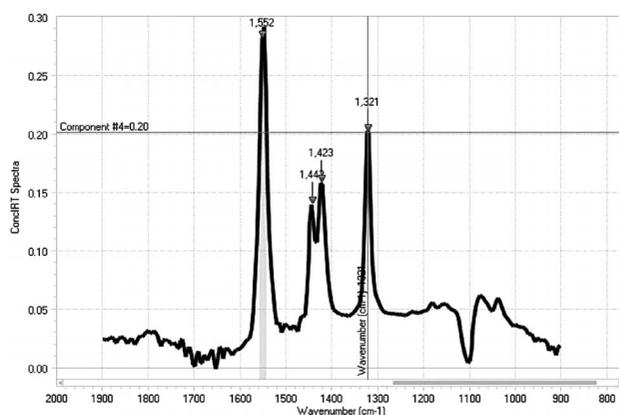


Figure 3. Intermediate peaks appearing during induction period – identified by ConcIRT as Component #4.

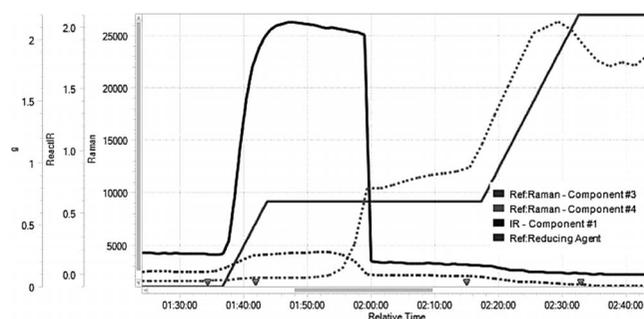


Figure 4. ReactIR® trends of intermediate formation and disappearance.

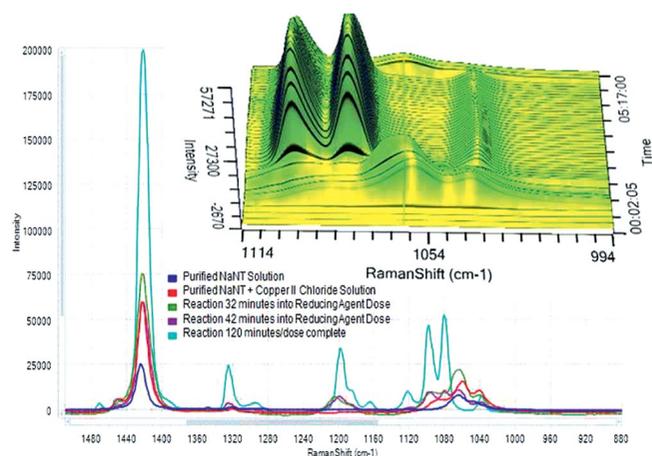


Figure 5. Raman spectra as a function of time compared with waterfall plot.

slow dose of reducing agent was added to the reactor over 120 min. Figure 5 shows the spectra of a DBX-1 reaction at specific times starting with a reference spectra of NaN_T solution (dark blue), NaN_T solution and copper(II) chloride solution combined (red), reaction mixture ca. 32 min after dosing reducing agent (green), reaction mixture ca. 42 min after dosing reducing agent (purple), and finally at the conclusion of the reducing agent dose (light blue). Figure 5 also shows a clear

transition through the intermediate(s) directly to the formation and growth of DBX-1. The complementary aspect of the IR (monitoring in solution) and Raman (monitoring both in solution and precipitates) was our ability to track species both in solution and out. Using our analytical standards we could also determine that the material in solution was not DBX-1, but a nitrotetrazole intermediate.

Impurities Identified in Raw NaNT

Given the disparity in success between “raw” and “purified” NaNT solutions described in the previous section, it was hypothesized that an impurity in the raw NaNT solution was contributing towards varying DBX-1 reaction results including the inability to produce DBX-1 at all. NaNT synthesis has never been optimized for scale-up nor have adequate analytical methods been developed to analyze NaNT. The investigating teams from Nalas Engineering and Pacific Scientific utilized various analytical methods to identify impurities in the NaNT solutions that impeded the reaction to DBX-1.

As described earlier, in order to successfully be used for DBX-1 synthesis, NaNT must currently be purified by a tedious, yield-consuming selective precipitation of impurities via reaction with a Cu^{II} salt, followed by filtration of the copper/impurity containing solids. The resulting purified NaNT, suitable for preparation of DBX-1, remains after treatment. Given that the raw NaNT solution must contain a significant amount of DBX-1-inhibiting impurities, while the Cu^{II}-purified solution does not, a comparative analysis of the impurity profiles of the two solutions was undertaken to determine, which impurities were most crucial to preventing the proper crystallization of DBX-1. LC and HPLC methods were utilized as the best means to identify the specific impurities. Samples of 1,5'-bistetrazole and 5,5'-bistetrazole were analyzed using HPLC and LC-MS; these materials were used as standards to identify impurities in raw NaNT solutions. Initial LC-MS analysis of the raw NaNT solutions showed that 5-AT (the starting material), 1H-tetrazole, and 5,5'-bistetrazole appear as impurities in NaNT solution; the amounts of these impurities were quantified in samples of raw and purified NaNT (Table 1). Simple analysis, however, is not sufficient to conclude, which of the detected impurities, if any, played a role in inhibiting DBX-1 crystallization.

To better elucidate the most critical impurities, a sample of the precipitated solid copper(II) complex formed by treating raw NaNT solution with copper(II) chloride was prepared for LC-MS analysis. As the unwanted impurities most likely precipitated following the addition of Cu^{II}, this solid was an ap-

pealing place to start. The analysis showed that there are three major compounds in the sample in addition to 5-nitrotetrazole. The first peak in the copper(II) solid has a *m/z* of 137.0 and is 5,5'-bistetrazole. The second peak has a *m/z* of 84.1 and has been identified as 5-AT. The third peak was identified as 1H-tetrazole with an *m/z* of 69.0. The presence of 5-nitrotetrazole indicates that the current Cu^{II} purification method also precipitates the desired product, and therefore reduces the yield of the process.

Five-point calibrations were made for 5-AT, 1H-tetrazole, and 5-nitrotetrazolate to quantify the amounts of these materials in the raw and Cu^{II}-purified batch NaNT as well as in both samples of 5,5'-bistetrazole. The calibrations for the 5-nitrotetrazolate were done using a solution supplied by Pacific Scientific made using purified NaNT dihydrate. The concentrations used in the calibrations were based on mg·mL⁻¹ of the 5-nitrotetrazolate in the solution, excluding the mass of the associated sodium ion and two waters of crystallization so that the amount of 5-nitrotetrazolate in the calibration and in any samples could be compared directly, regardless of whether the sample contains sodium (DBX-1 or any possible intermediate). The results of the calibrations show good linearity and quantitation to below 0.02 mg·mL⁻¹. The results in terms of weight percentage are listed in Table 1.

The 5,5'-bistetrazole is present in the raw NaNT solution at 0.01 % by weight, and completely removed to below detectable levels in the NaNT purified by the copper(II) titration/purification.

Table 2 highlights the weight percents of the two detected impurities, 5-AT and 1H-tetrazole relative to the total amount of impurities. The main impurity in the NaNT solution is 5-AT, the starting material for NaNT. Poor overall conversion is most likely the cause of the 5-AT impurity being present in high levels in NaNT; the conversion is currently being investigated by Nalas Engineering.

II Improved Synthesis of Purified NaNT

Synthesis

Given the role that low thresholds of 5-AT and 1H tetrazole impurities clearly play in the successful synthesis of DBX-1 from NaNT, we endeavoured to develop a procedure for synthesizing pure NaNT as efficiently as possible, while avoiding the tedious, time consuming, and reduced yield Cu^{II} titration and filtration, which is currently required. As an added refinement, we also desired to eliminate the handling of the intermediate acid salt of copper(II) 5-nitrotetrazolate, Cu(NT)₂·HNT;

Table 1. Weight percent of impurities in raw NaNT, Cu^{II}-purified NaNT, and in the copper complexed solid which precipitates from the raw NaNT upon Cu^{II} treatment.

Component	Raw NaNT solution /wt-%	Purified NaNT solution /wt-%	Copper impurity complex /wt-%
5-AT	0.68	0.33	7.90
1H-Tetrazole	0.47	0.18	10.62
5,5'-Bistetrazole	0.01	ND ^{a)}	0.48
5-Nitrotetrazolate	15.60	11.24	53.27

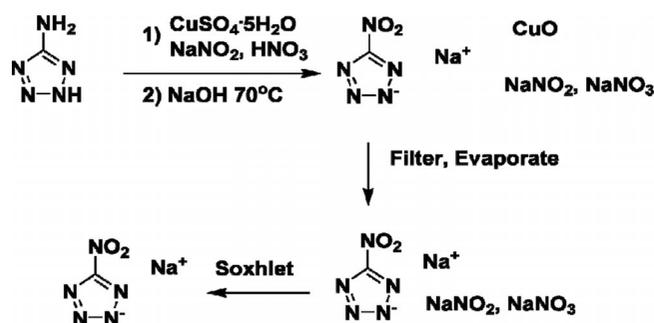
a) ND = not detected.

Table 2. Amounts of 5-AT and 1H-tetrazole as weight percent relative to total amount of impurities.

Impurity component	Raw NaNT /wt-%	Purified NaNT /wt-%	Impurity removed /wt-%
5-AT	4.06 %	2.80 %	1.26 %
1H-Tetrazole	2.80 %	1.55 %	1.25 %
Total	6.86 %	4.35 %	2.51 %

this compound is not only slow and difficult to isolate, but if dried too thoroughly is a highly sensitive and dangerous explosive.

In short, our improved NaNT synthesis procedure begins from an aqueous solution of 5-aminotetrazole, nitric acid, and a trace of copper(II) sulfate pentahydrate is added dropwise to a pre-chilled (5–10 °C) solution of sodium nitrite and copper(II) sulfate. During addition the temperature of the solution is allowed to rise to 15–18 °C. Once this temperature range is reached, the addition is continued at a slightly slower rate and the flask immersed in a water bath. The temperature of the reaction is maintained by the raising or lowering of the flask within the water bath, and by the addition of small chunks of ice to the water bath. By following this procedure exactly, we have never observed a single microdetonation as has been known for this reaction.^[7–9] We were, however, able to force microdetonations by the rapid addition of aminotetrazole solution to the reaction under strong cooling. It appears that the key factor preventing microdetonations is a very slow addition rate. After addition is completed, the solution is allowed to stir for 30 min and dilute nitric acid is added, followed by the warming of the solution to room temperature and stirring for another hour. An aqueous solution of sodium hydroxide is added until pH 8 is reached and the solution is heated to 70 °C, where it is maintained for 2 h. The precipitated copper oxide is filtered off through kieselguhr (diatomaceous earth) and the aqueous filtrate evaporated under vacuum at a temperature no higher than 35 °C. The solid residue is soxhlet extracted with acetone and the acetone slowly evaporated yielding crystals of sodium nitrotetrazolate dihydrate in over 80 % yield. Crystals are isolated by filtration through a Buchner funnel without paper, or a pasta strainer, as small amounts of a non-crystalline solid occasionally precipitates as the nitrotetrazolate crystallizes. The NaNT crystals are often greater than half a centimetre in dimension and the non crystalline solid can easily be removed by this type of filtration. The NaNT can be recrystallized from acetone. Scheme 2 illustrates this process.

**Scheme 2.** Improved synthesis of NaNT.

Infrared and Raman spectroscopic results were identical to those in the literature, as were ¹H proton and ¹³C carbon NMR spectra.

Use of New NaNT for the Preparation of DBX-1

We have synthesized two small scale batches (PA-DBX #1 and #2) of 2–3 g each and one intermediate scale batch (PA-DBX #3) of 8–10 g of DBX-1 from our NaNT. The procedure used to synthesize DBX-1 was based on literature methods.^[5,6] For each batch, sensitivity tests, thermal stability by differential scanning calorimetry (DSC), and performance tests were performed and compared to the standard DBX-1 that was obtained from PSEMC (Pacific Scientific Energetic Materials Company, inventors of DBX-1).

There seems to be a noticeable difference in the Ball Drop Impact results and this could be attributed to the inherent error associated with this relatively crude test; for instance, the manner and precise location, at which the steel ball impacts the explosive particles can vary and lead to inconsistent results. Friction and electrostatic sensitivity was consistent across all of our batches of DBX-1 as well as PSEMC DBX-1 (Table 3) In terms of determining the effectiveness of a primary explosive, sensitivity tests results are generally only predictive in how to safely handle the material; in order to determine if the explosive is practical or not, performance tests need to be done to see how well the material behaves in actual items, such as detonators.

Table 3. Sensitivity Data of PSEMC and ARDEC DBX-1.

Name	Ball Drop Impact (in.)	BAM Friction / N	ESD /J
PSEMC DBX-1	NG @ 30	GO @ 0.1	NG @ 0.0016
PA-DBX #1	NG @ 8	GO @ 0.1	NG @ 0.0025
PA-DBX #2	NG @ 30	GO @ 0.1	NG @ 0.0020
PA-DBX #3	NG @ 4	GO @ 0.1	NG @ 0.0025

Performance tests consisted of loading DBX-1 as a transfer charge in U.S. Army M55 stab detonators. Standard M55 detonators consist of three separate explosive layers, pressed sequentially into a metal detonator cup as shown in Figure 6. The first layer is 15 mg of the stab initiation mix (NOL-130); it is a combination of lead azide, lead styphnate, barium nitrate, antimony sulfide, and tetrazene [1-(5-tetrazolyl)-3-guanyltetrazene hydrate], pressed at 70,000 psi. The second layer is 51 mg of transfer charge, lead azide, pressed at 10,000 psi. Lastly, the third layer is 19 mg of output charge, RDX, pressed at 15,000 psi.

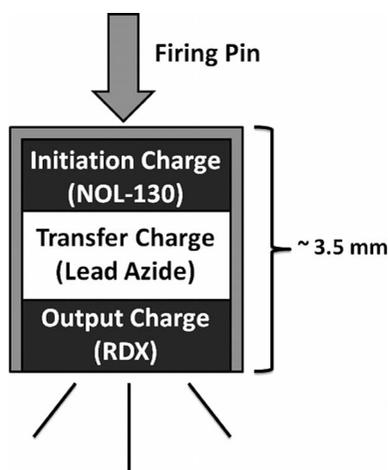


Figure 6. Diagram of M55 Stab Detonator.

To measure DBX-1 performance, lead azide was replaced with DBX-1 in the loaded M55's. Only 40 mg of DBX-1 was used compared to 51 mg of lead azide due to the inherent density differences between the two materials. M55 detonators were loaded using Arbor hand presses (Figure 7a) and tested for performance (Figure 7b,c). The M55 detonator was placed in a plastic fixture, as shown in Figure 7b and a 0.25 oz ball was dropped onto the firing pin from a height of 3 inches. For a standard M55 detonator, the exploding item creates a dent of greater than 0.01" on a steel plate. Dent depths were measured using a laser profilometer (Figure 7d).

All M55 control detonators prepared with standard PSEMC DBX-1 created dents of the requisite depth. Both batches PA-DBX #2 and PA-DBX #3 were prepared using a seed crystal from this PSEMC batch of DBX-1 and PA-DBX #1 was created using a seed crystal from a previously acquired batch of PSEMC DBX-1.

For the initial PA-DBX #1 sample, only 4 of 10 detonators met the specifications of dent depth greater than 0.01". Other detonators would initiate but would not go high order (e.g. the RDX output charge did not appear to detonate). This could be attributed to a density problem or a run up distance issue.

Given the unreliability of the stab-initiated tests, a second round of testing was performed using a hot nichrome wire to initiate the detonators in place of the NOL-130 stab mix and firing pin. This test was successful and all nine detonators functioned, showing that DBX-1 is more susceptible to this method of initiation. Figure 8 shows the electrical ignition setup.

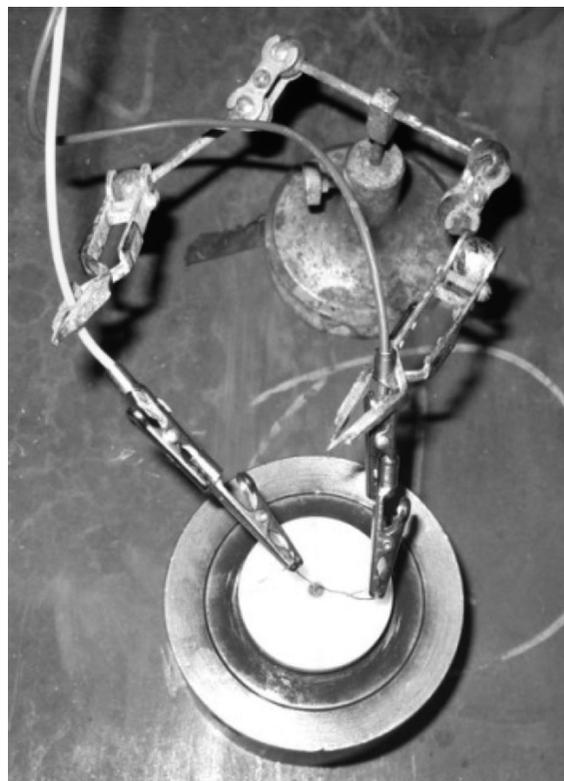


Figure 8. Setup of electrically initiating M55 detonators.

Subsequent batches of DBX-1 showed greatly improved performance. All detonators prepared with PA-DBX #2 met the dent depth requirement except for one. Since batch PA-DBX #2 produced successful results, a larger batch of 10 g

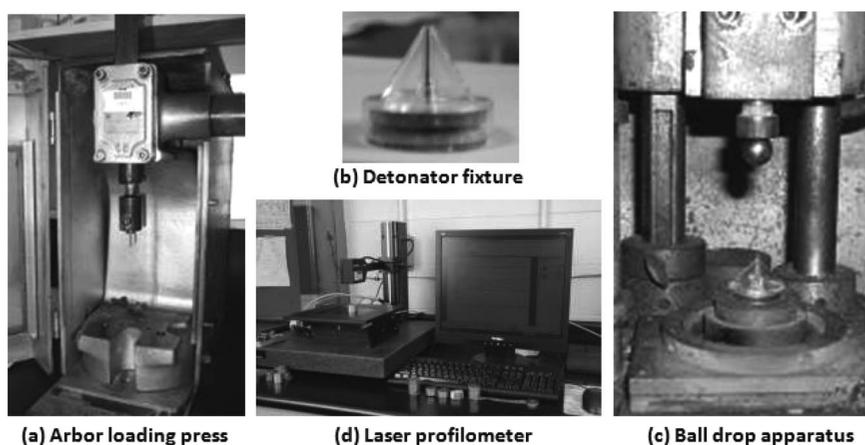


Figure 7. Detonator loading and testing equipment.

(PA-DBX #3) was made. PA-DBX #3 performed perfectly, as 10/10 detonators functioned successfully (Table 4).

Table 4. Energetic properties for all prepared energetic compounds.

Batch	Initiation method	# Tests	# >0.01''
PSEMC DBX-1	Stab	10	10
PA-DBX #1	Stab	10	4
PA-DBX #1	Electric	9	9
PA-DBX #2	Stab	10	9
PA-DBX #3	Stab	10	10

The source of the variation between the initial batch and the later two could be a result of several factors, including non-optimal particle size and/or the presence of impurities. Given that different sources of seed crystal were used, this could also be an indication of the reaction's dependence on adequate seeding. The unusual behavior of PA-DBX #1 prompted us to study it by DSC (Differential Scanning Calorimetry). Two samples each of PA-DBX #1 and control PSEMC DBX-1 were studied by DSC ($5\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$). PA-DBX #1 samples had DSC onsets at 305.9 and 307.0 $^{\circ}\text{C}$, whereas PSEMC DBX-1 had onsets at 304.0 and 305.0 $^{\circ}\text{C}$. The peak temperature in the DSC was 312.4 and 313.0, and 309.5 and 311.5 $^{\circ}\text{C}$ for PA-DBX #1 and PSEMC DBX-1, respectively. Given the reasonably close similarity in the DSC measurements between the two samples, this data suggests that significant amounts of impurities are not present, therefore leaving crystal size/morphology as parameters, which are most likely to contribute to the performance discrepancies. Although overall the performance of the synthesized DBX-1 was quite favorable in detonators, future studies of this procedure will include more refined optimization to increase the reliability of the success rate.

Conclusions

The investigating teams from Nalas Engineering and Pacific Scientific utilized various analytical methods to identify impurities in the NaNT solutions that impede the reaction to DBX-1. The main impurity in the NaNT solution is 5-AT, the starting material for NaNT. Poor overall conversion is most likely the cause of the 5-AT impurity being present in high levels in NaNT. The cause of the poor conversion is currently being studied.

In-situ particle analysis and spectroscopic tools were utilized to monitor and compare reactions using raw NaNT and purified NaNT towards the conversion to DBX-1. Raw NaNT did not successfully convert to DBX-1. The DBX-1 reaction using pure NaNT was monitored by using a variety of in-situ tools that are capable of tracking the main intermediate to DBX-1. The tools proved valuable in understanding both the intermediate and product forming. The data produced by Nalas demonstrates that the intermediate, some form of nitrotetrazole, increases in concentration over a period of time prior to converting to DBX-1 which immediately precipitates from the aqueous liquors. This data supported our hypothesis that the crystallization to DBX-1 is rapid and may be dependent on other factors including degree of mixing. Unfortunately, the

triggering event has yet to be identified although under investigation.

Our new method of isolating sodium nitrotetrazolate dihydrate produces material in high yield, without the intermediate handling of sensitive explosive compounds. This produced NaNT is of sufficient purity for the preparation of DBX-1 of the quality that is required to replace lead azide. However, it does appear that the DBX-1 used as a seed crystal in the synthesis of DBX-1 influences the behavior of the end product.

Experimental Section

All reagents and solvents were used as received (Sigma-Aldrich) if not stated otherwise. NOL-130 stab initiation mix and preformed, 19 mg graphite-blended 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) pellets were purchased from Day & Zimmerman (DZI). Samples prepared for LC-MS analysis were dissolved in ammonium hydroxide and run utilizing a Phenomenex Gemini C6-Phenyl column (4.6 mm \times 150 mm) and a mobile phase of 20 mM ammonium acetate in water pH 7.02 at $0.75\text{ mL}\cdot\text{min}^{-1}$. The HPLC analysis is done using the same chromatographic conditions as the LC-MS, except a 20 mM phosphate solution pH-adjusted to 7.02 with triethylamine (TEA) was used as the mobile phase. Conversion of NaNT solution to DBX-1 was monitored with both in-situ particle counter (Mettler Toledo's Focused Beam Reflectance Measurement or FBRM®) and camera (Mettler Toledo's Particle Vision Microscopy or PVM®), which enabled real-time monitoring of trends associated with fine material (less than 100 microns) and coarse material (100 micron and above) as well as the morphology of the intermediate and product DBX-1. Conversion of NaNT solution was monitored with in-situ infrared (Mettler Toledo's ReactIR®) and Raman spectroscopy. Scanning electron microscopy (SEM) images and energy dispersive spectroscopy (EDS) spectra were collected with an EVEX mini-SEM SX3000. Differential scanning calorimetry (DSC) data were obtained with a heating rate of $5\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ by Henry Grau, ARDEC. Sensitivity tests consisted of Ball Drop Impact, BAM Friction and Electrostatic Discharge (ESD). For each test trial 30 mg of explosives were used. The Ball Drop Impact test for primary explosives is described in MIL-STD-1751A, Method 1016, (20 August 1982); the test subjects a primary explosive to an impact of a free-falling steel ball weighing 28.35 g (1 oz). The small BAM Friction test method is described in STANAG 4487 "Explosives, Friction Sensitivity Tests". The BAM Small Friction test determines the friction sensitivity of the sample. The Electrostatic Sensitivity Test methodology is given in AOP-7 "Manual of Data Requirements and Tests for the Qualification of Explosive Materials for Military Use".

CAUTION! Sodium nitrotetrazolate dihydrate is an energetic material with sensitivity to various stimuli. Particular care should be taken to not excessively dry the material, as anhydrous NaNT is considerably more sensitive than the dihydrate. While we encountered no issues in the handling of this material, proper protective measures (face shield, ear protection, body armor, Kevlar gloves, and earthed equipment) should be used at all times.

Sodium Nitrotetrazolate Dihydrate (NaNT): Anhydrous aminotetrazole (8.48 g, 0.10 mol) and copper sulfate pentahydrate (0.2 g, 0.8 mmol) were added to a solution of nitric acid (9 mL, 65%) in distilled water (60 mL). This was added to a pre-cooled solution of sodium nitrite (20.8 g, 0.30 mol) and cupric sulfate pentahydrate (11 g, 0.044 mol) in distilled water (100 mL). The solution was maintained at 15 to 18 $^{\circ}\text{C}$ during the addition by means of a cool water bath. After addition, the solution was stirred for 30 min at the same temperature

and was followed by the addition of nitric acid (14 mL, 65%) diluted to 20 mL. The solution was allowed to warm to room temperature and was stirred at this temperature for 1 h. Under vigorous stirring, 50% aqueous sodium hydroxide was added until the pH of the solution reached pH 8, and the temperature was increased to 70 °C and was maintained at this temperature for 2 h. The pH was checked and adjusted to pH 8 again if necessary, and filtered through celite. The filtrate was evaporated to dryness (using a 30 °C water bath) and extracted overnight with acetone using a soxhlet. The acetone was allowed to slowly evaporate and was filtered through a Buchner funnel without filter paper or a pasta strainer yielding 13.76 g (0.080 mol) of large colorless-to-light-yellow crystals of sodium nitrotriazolate dihydrate. The analysis obtained was identical to that previously reported in the literature.^[9]

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