Awareness and Localization of Explosives-Related Threats (ALERT)
A DHS Center of Excellence for Explosive Detection, Mitigation, and Response

Headquartered at
Northeastern University

ALERT Safety Program
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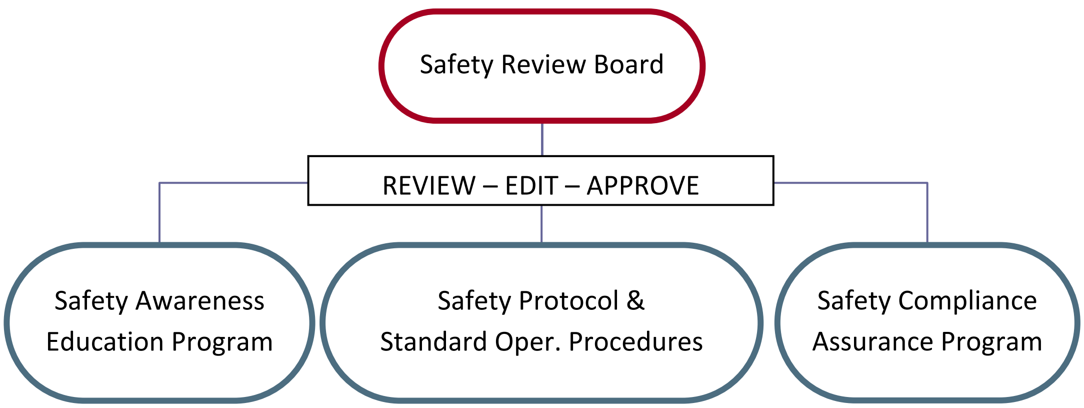
Mission/Vision

The Department of Homeland Security (DHS) Center of Excellence for Explosives Detection, Mitigation, and Response, also known as ALERT (Awareness and Localization of Explosives-Related Threats) conducts transformational research, develops advanced technology, and educates students and practitioners in effective characterization, detection, mitigation and response to the explosives-related threats facing the country and the world. While striving for that goal, safety is of paramount importance. Handling of energetic materials requires constant vigilance. This document outlines the components of the ALERT Safety Program: a Safety Review Board, a Safety Awareness Education Program, Safety Protocols and Standard Operating Procedures, and a Safety Compliance Assurance Program. It is our hope that by taking the time to create and review these safe-operating procedures, practitioners will have a heightened awareness of the hazards and take appropriate care.



Safety Review Board

To aid in creating appropriate overarching safety protocols, a team of outside experts were employed. The Safety Review Board (SRB) is drawn from a variety of backgrounds: academia, industry, Department of Defense and Department of Energy. The Board and this document are not intended to supersede the existing safety protocols at each institution; rather, this document and the SRB are put in place to offer basic guidance. ALERT is responsible for keeping the SRB available for consultation and reach-back in future years of operation. Each institution and each individual is responsible for safety, and each must create and maintain safety protocols and standard operating procedures (SOP) which meet the minimum level established by the "ALERT Safety Protocol and Standard Operating Procedures."

The functions of the Safety Review Board are to provide input and review into:

1. these Safety Protocol and Standard Operating Procedures
2. the Safety Awareness Education Programs
3. the Safety Compliance Assurance Plan (SCAP)
4. other ongoing safety issues
5. all safety incidents (annual SCAP audit results) and approve corrective action plans.

Table 1. Composition of the Safety Review Board (SRB)

Bill Koppes (Chair)	Synthetic Chemist	Navy, Indian Head <ret>	301-744-4256 301-434-6380	william.koppes.ctr@navy.mil bilsukopp@verizon.net
Andrew Clapham	Chemistry Dept Safety Officer	University of Rhode Island	401-874-5084	aclapham@chm.uri.edu
Mike Coburn	Synthetic Chemist	Los Alamos National Lab <ret>	505-473-2037	mdcoburn@cybermesa.com
Jimmie Oxley	Explosive Research	University of Rhode Island	401-874-2103 401-559-1120	joxley@chm.uri.edu
Alex Schuman	Explosive Safety	Navy, Indian Head	301-744-1711 804-224-9590	aschus7793@aol.com alexander.schuman@navy.mil
Ronald Willey	University Safety Officer	Northeastern University	617-373-3962 781-492-4956	r.willey@neu.edu

Safety Awareness Education Program

The most important feature in creating a “safety culture” is education—education in laboratory and field best practices. Most of the ALERT institutions already provide this. However, researchers should be periodically re-indoctrinated about lab safety and hazards. We propose a program on laboratory safety and specifically explosive safety.

Drawing on the resources of our own ALERT researchers and those of the Department of Defense (DoD) and National Laboratories, a Safety Awareness Education Program will be created to supplement the safety education in participating institutions. At course completion, students should be able to determine whether an operation is safe or not. If not, he should know what approach he should take to make the operation safe. Topics will include

- basic laboratory best practices
- DoD contractor safety manuals and storage regulations
- required testing and the meaning of test results
- handling requirements specific to each explosive
- historic explosive accidents for a “lessons learned”

The SRB will have input into the safety education program. It is intended that the “Explosive Safety Protocols and Procedures” course be offered every six months, and that each individual who participates in the ALERT program attends within six months of joining the program and at least every other year thereafter. The course will be offered online and in person, with instructors visiting each institution so that researchers will have the opportunity to meet the instructors face to face. Principal Investigators at each institution will have an opportunity to supplement the instruction as appropriate for their institution.

Safety Compliance Assurance Plan

How can we ensure safety? Education is the first step, but education must be coupled with the knowledge that unsafe practices will not be tolerated. As with written protocols, compliance must start with the practitioners. Co-workers must be vigilant when it concerns the safety of their colleagues.

The Safety Compliance Assurance Plan will require the SRB to review each of the components of the Safety Program:

- The ALERT Safety Protocol and Standard Operating Procedures
- The ALERT Safety Awareness Educational Program
- The on-site safety practices of each NU-led ALERT partner institution using energetic materials.

Operation

Annually the SRB will review and edit the overarching Safety Protocols and Standard Operating Procedures. Recommendations will be made to the ALERT administration at Northeastern when appropriate.

Annually, the SRB will visit each NU-led ALERT partner institution using energetic materials to audit each institution's safety program as practiced, which includes safety protocols and standard operating procedures, additional safety awareness education efforts, and on-site safety practices. The SRB will decide how best to audit these safety programs. For example, the SRB may make use of reviews performed by an institution's Safety and Risk Management department. If the safety program is found to be deficient, recommendations and a plan for remediation will be provided by the SRB, and a schedule for compliance will be created and followed. Northeastern will monitor compliance. Failure to comply in a timely fashion will result in a stop work order.

Safety Protocol and Standard Operating Procedures

To create a common culture of safety, this section has been created and reviewed by the participants/researchers as well as the Safety Review Board (SRB). ALERT researchers are responsible for creating, implementing and maintaining these overarching Safety Protocol and Standard Operating Procedure (SOP) references. From time to time it may be necessary to augment or alter this document; such changes or additions will require a fresh review. Each institution and researcher is responsible for creating and maintaining safety protocols and SOPs appropriate for his research area. The overarching Safety Protocol and Standard Operating Procedure serves as a guideline, a minimum standard. The next level of action is written protocols for operations written by the researcher, reviewed and modified by colleagues and supervisors, and signed by the safety committee and the researcher. Signing the protocol is the researcher's agreement to operate in a safe manner. It is up to each institution to demonstrate they have created a culture of safety.

Introduction & Safety Philosophy

In working with chemicals, certain "best practices" are overarching. These are outlined in a number of texts, most notably the National Research Council's *Prudent Practices in the Laboratory: Handling and Disposal of Chemicals* (1995, ISBN-10: 0-309-05229-7). The book provides general guidance on good housekeeping, personnel protective equipment, pre-planning and documentation of operations, storage and disposal. Common sense demands that MSDS (material safety data sheets) be available and reviewed for all materials handled and that personnel in the laboratory wear appropriate protective gear, e.g. safety glasses, face shields, or full-face masks. Established laboratory safety protocols should be followed or adapted as necessary with review. However, safety ultimately rests on the individual's attitude and knowledge. As new protocols become necessary, they should be added. Every researcher must be part of this process; it is essential for their safety and for the safety of everyone around them. This document is not intended to replace or supersede protocols already in place; all the normal safety precautions applicable to chemicals apply. The additional hazard is uncontrolled release of energy. In handling a known energetic material, e.g. TNT, sufficient literature exists that the researcher should know the specific hazards faced. For unknown species or mixtures, some general guidelines can be followed until more specific information is obtained. A useful source for general hazard warnings is *Bretherick's Handbook of Reactive Chemical Hazards*, 7^{th} ed, P Urben; 2006.

In general, the concern in the laboratory is synthesis and handling of bulk energetic materials. The issues are sensitivity and stability. **Sensitivity** is the ease with which a material can be caused to react by relatively mild insult (something a human might inadvertently impart—impact, friction, electrostatic discharge) as opposed to the input of a shock wave (i.e. from a detonator). Sensitivity is generally determined experimentally at a small-scale. It is essential to get this information as soon as possible. Furthermore, although a scaled-up formulation is more hazardous, it is usually not more sensitive. (A possible exception is a change to more sensitive impurities with increase in batch size.) **Stability** refers to the capacity of an *energetic* material to maintain its chemical composition for long periods at ambient temperature (such as during storage). A material that lacks stability may undergo catastrophic reaction on its own with no apparent additional input of energy. The temperature at which an energetic material maintains stability is a function of its chemistry, its quantity, and its degree of contamination. Generally, contaminated materials degrade more readily than pure ones; their degradation may be quiescent or violent. Large quantities of material undergo self-heating more readily than small quantities because their decomposition generates heat that raises the temperature that accelerates decomposition. Therefore, during scale-up of a synthetic process, stability tests are run at various stages.

In handling energetic material the rule is to minimize

- quantity of material
- time of exposure
- number of people exposed

and to maximize distance or introduce an adequate barrier commensurate with the amount of material.

Safety is an attitude: you are responsible for safety.

You make the decision whether to:
Follow the manuals
Follow the SOPs
Stop work when unsafe conditions are present

You make the decision to deviate from the above procedures because:
It worked before
It's quicker
It's easier
It's cheaper

General SOP for Energetic Operations

The key to safety is knowledge, including the knowledge that the individual is entirely responsible for his safety. In addition, proper supervision is always required when working with energetic materials. Herein are general safety protocols, but a specific SOP must be written and approved for each new operation or new energetic material. Review by someone other than the author is important. The key is planning ahead, even to the point of determining final disposal when the material is no longer required.

Know the Literature

In any laboratory, there are a number of operations that by their nature are hazardous. While this protocol may address chemical hazards, it should be acknowledged that there are well-known hazards in handling electrical equipment and compressed gases. For commercial instrumentation, knowing the literature may be a matter of reading the user manual or undergoing formal training. For other operations it may be necessary to write a Standard Operating Procedure (SOP). A search of the literature must be conducted before a new energetic material is synthesized. The aim is to determine how to safely make the material and what properties are known – sensitivity, thermal stability, reactivity, and toxicity. For synthesis of a proposed new compound where there is no literature, a brief review of materials with analogous functionality or structure is acceptable. After reviewing the literature the researcher must write a proposed operating protocol. This protocol should be reviewed by co-workers and by the laboratory supervisor.

Contents of a Standard Operating Procedure (SOP)

1. Introduction:
    a. Scope – what operations (range or work), facility, equipment are covered
    b. Responsible person or department
    c. If procedure serves to waive some standard, call this out.
2. Safety:
    a. General safety that minimize exposure to hazardous operations or toxins
    b. Personnel & explosives limit for each operation
    c. Specific emergency controls
    d. Specific safety protocol (e.g. color coding)
    e. Protective clothing & equipment
3. Operation:
    a. Location
    b. Sequence
    c. Statement if no simultaneous tasks are allowed
4. References

General Operating Guidelines

A number of operations (such as initial weighing, melting, filtration, recrystallization, differential scanning calorimetry (DSC) sample preparation, GC/LC standard preparation, processes which deal with bulk energetic substances) require a higher level of care than energetic materials that have been dissolved in solvent (such as in stock solution preparation). It should be recognized that while addition of solvent reduces sensitivity of the explosive, it also decreases the explosive's shelf-life. Before adding a solvent to an explosive, the researcher must check for compatibility/reactivity.

Synthesis of a new material or synthesis of a material by a researcher who has not previously made that material in the laboratory is restricted to 500 mg. This does not mean making this much material is advisable; that needs to be reviewed on an individual basis. Synthesis of a new material requires generation of a new protocol or modification of an existing protocol. If the material has never been synthesized before, then the researcher must look to analogous compounds and assume the worst case. Initial isolation of a solid of unknown hazard should be preceded by first taking a small sample for drying and then testing by lab scale methods. Once small amounts of material have been made, differential scanning calorimetry (DSC), impact, and flame tests must be performed to determine what constitutes safe handling. It should be emphasized that sensitivity testing is relative. Results should be compared to the performance, under identical conditions, of a material well known to the researcher or the laboratory. No synthesis shall be performed without a written, approved, and signed SOP. Synthesis by a new researcher of a material for which a laboratory protocol exists requires review and signature of the new researcher, supervisor and safety committee (if applicable).

I. Location

A hood or glove box is preferred when working with chemicals. A hood or glove box is considered necessary when the chemical or energetic material is volatile and has health implications, e.g. nitroglycerine. Explosives synthesis must be performed in a working hood with a pull-down sash and a blast shield (a polycarbonate shield of at least 0.25" thickness) in place. The shield should be secured so that a blast does not launch it. During explosive synthesis in the hood there should be no excess or superfluous glassware or chemicals. The hood should be labeled with the energetic process, the name of the chemist and emergency contact information. There should be a clear path to the closest safety shower, eyewash station, and exit. Exit/Entrance doors to the laboratory should be unlocked or open such that an escape or help is accessible should an emergency occur. If there is a choice of which hood to use for explosive synthesis, the choice should be governed by what other operations are being performed nearby. For example, burn rate testing should not be conducted adjacent to explosive synthesis. Care should be taken that personnel passing through are properly protected.

II. Personal Protective Equipment (PPE)

a. Protective eyewear should be worn at all times
b. A full length lab coat (100% cotton to avoid static)
c. Nitrile gloves are appropriate for most chemical applications
d. Close-toed shoes
e. Long-pants are generally a good idea, but not required. It should be noted that even one layer of clothing protects the skin from burns, chemicals and glass shards.

Note: Those working with primary explosives may want to consider extra protection against electrostatic discharge.

III. Contiguous Operations

The researcher should not work alone. At least one person should be nearby and aware that the researcher is conducting work. For synthesis operations the supervisor or laboratory manager should be present in the building and made aware that a synthesis process is in progress. The supervisor or laboratory manager should sign and date the student's notebook which describes the full experiment.

a. Operations with solid energetic materials should, as much as possible, be performed away from where others are working.
b. Never handle the solid energetic material when alone in the laboratory.
c. Take care not to have flammables or flames in the range of explosive operations.

IV. Storage

a. Separate storage must be maintained for solid explosives, liquid explosives, and detonators. Considering the volatility and low thermal stability of some of the homemade energetic materials, storage in an explosion-proof freezer is advisable.
    i. Energetic solids are to be stored in a safe with limited access.
    ii. Energetics of unknown stability should be stored in a separate safe.
    iii. Detonators are to be stored in a separate safe.
    iv. Storage of energetic solutions depends on the material to be stored.
    v. Solid explosives should be stored in containers without screw caps.
b. Storage of excess energetic materials should be avoided, and the researcher should consider storage of these materials in multiple small containers rather than in one lot.

V. Handling

a. Handle the smallest amount of energetic possible.
b. Operations, in which an energetic material may be subjected to sufficient friction to cause accidental ignition, should always be undertaken with caution:
    i. use wooden splints instead of metal spatulas
    ii. never filter energetics through fritted glass; use paper filters
    iii. roto vap operations should employ a Teflon sleeve
    iv. use of mortar and pestle for grinding may be hazardous depending on the material. It should not be used with black powder or primaries. For black powder a ball mill may be acceptable, but use of a ball mill must be reviewed
    v. operations using a detonator/EBW must be reviewed

VI. Lab Scale Safety Testing

These tests are early warnings to the researcher that the material he is handling is energetic (flame test) and is or is not sensitive to impact (hammer) and/or friction. The test results only have meaning when compared against those of a material with which the researcher is familiar, e.g. PETN (pentaerythritol tetranitrate).

a. **Flame Test:** The test involves burning small amount (less than a match head, ~ 20 mg) of energetic material held on a metal spatula over a low flame. All flammables burn but the quickness of the event suggests the degree of hazard (Figure 1). *Caution: never reuse the metal spatula from one burn test to the next. The possibility exists that you thoughtlessly stick a hot metal spatula into the bulk explosive!*

b. **Hammer Test:** Using a two-pound hammer and place no more than 40 mg (a match-head amount) of the energetic material on the anvil apparatus in the laboratory. If impact results in a “pop” this material can be considered “impact sensitive”

c. **Friction Test:** A small amount (20 mg, match head size) of energetic is scraped on the bottom of a mortar with a wood splint to test the sensitivity to friction.

RDX Sugar TATP

Figure 1. Flame Test (courtesy Oxley/Smith lab URI)

Scale-up Considerations: Decision Logic

The decision to scale up a reaction involves many considerations. The first consideration, why is more material needed. The need for the material should be weighed against the additional hazard that always accompanies scale-up. In most, but not all instances, it is safer to make many small batches, which are stored separately until used. Obviously, the more energetic material that is present in one location, the more violent and catastrophic the reaction, should accidental initiation occur.

As discussed, both sensitivity and stability are considerations in judging the best handling procedure for energetic materials. The ability to decide what compounds are safe to work with is based on the test protocol, although general guidance has been given in this document. To a degree, the decision is based on known hazards of known explosives or analogous compounds.

Stability can, and often is, quantified and modeled by determining the activation energy (Ea) and frequency factor (A) of decomposition. With Ea and A known, the researcher can predict at what temperature or at what scale catastrophic thermal runaway can occur. Sensitivity must be empirically determined. Factors that control sensitivity are primarily a result of particle size and/or contamination. For this reason there is variation, lab to lab, in results. Although guidance can be drawn from the reports of others, it is important to determine sensitivity using your laboratory apparatus and comparing your results to a compound whose properties you understand. PETN is suggested.

The theoretical yield of a new synthesis should not be more than 500 mg. Scale-up of a previously performed synthesis requires supervisor approval. A DSC, impact and flame tests must have been performed. Scale up above 5 grams must be reviewed by the supervisor and the laboratory safety committee. A special SOP must be written. Overnight or extended reactions must be reviewed.

Degree of Hazard

Not all energetic materials are equally hazardous. It is important to differentiate among them based on their hazard. This, of course, means an unknown material should be considered in the most hazardous category and handled appropriately until evidence of its sensitivity and stability have been collected and reviewed.

In general, military explosives have been classified as primary or secondary based on their ease of initiation. **Primary explosives** can be initiated by dropping, impacting, friction or electrostatic discharge. Known primary explosives include the following

- mercury fulminate, lead picrate, lead styphnate,
- lead azide $Pb(N_3)_2$, diazodinitrophenol (DDNP or diazo)
- m-nitrophenyldiazonium perchlorate, copper acetylide, fulminating gold,
- Hg 5-nitrotetrazole,
- tetramine-cis-bis(5-nitro-2H-tetrazolateo-N_2)Co(III)perchlorate
- tetracene, TATP, HMTD, nitrogen sulfide (N_4S_4), nitrosoguanidine,
- potassium chlorate/red phosphorus (P_4);, K dinitrobenzofuroxan (KDNBF),

This list should suggest to the researcher features indicative of a potential primary explosive; for example, heavy metal salts may be primary explosives. Impact, friction and ESD testing should be done to confirm or allay this suspicion.

With the exception of TATP, synthesis of primary explosives shall not be scaled beyond 2 grams without a specific safety committee review. For the experienced researcher 5-gram batches of TATP are permissible with supervisor's approval. Synthesis of larger batches requires review and a new SOP.

Secondary explosives require a shock wave to initiate them to detonate under typical use conditions. In conditions outside those of normal use for which secondary explosives have been developed, they may become more or less sensitive, so the handler must be aware of published data on the sensitivity of a particular explosive for the entire environment being considered. They should always be handled with respect. The properties of secondary military high explosives (PETN, TNT, RDX, HMX, C4, Comp B, HNS, TATB) have been well-characterized, but unless the researcher reviews the literature he does not benefit from the lessons of others. For the researcher synthesizing a new chemical, he might recognize explosive potential by high oxygen or high nitrogen content. For the researcher attempting to synthesize a new explosive, he should, for purposes of safety, assume he has succeeded. It is not intended that secondary explosives be scaled beyond 5 grams and then only if a written approved protocol has been executed.

Some explosive mixtures are so insensitive or so low energy that they have sometimes been termed **tertiary explosives**. This category is generally populated by ammonium nitrate (AN) formulations, e.g. ANFO (AN/fuel oil), some AN emulsions. Materials such as these can usually be handled on a ***laboratory scale*** without concern of explosive hazards (though of course there is the chemical hazard). However, particle-size and the addition of fuel make a difference in the performance, stability, and sensitivity of an energetic formulation. For example, AN with aluminum or any metal is more powerful and more sensitive than AN with hydrocarbons. AN with sugar and sulfur have poor thermal stability. Finding these exceptions and making appropriate safety provisions are the reasons DSC, flame, and impact tests are performed as soon as 500 mg of a formulation is made.

Synthesis of tertiary explosives may be safer than that of secondary. However, it is best to remember particle size and purity are major factors in sensitivity and stability. For example, pure urea nitrate is usually insensitive and relatively stable, but this is not true if it becomes acidic. The source of acid may be incomplete rinsing, failure to recrystallize the material or decomposition due to long term or high temperature storage.

Example SOP: Synthesis of Homemade Explosive Urea Nitrate (UN)

I. Introduction

A. Scope: Synthesis of urea nitrate from urea and concentrated nitric acid

B. Responsible Party: Preparations of UN must be approved by the Supervisor.

II. Safety

A. General Safety: The reaction is carried out in a fume hood to minimize exposure to fumes from concentrated nitric acid. Safety glasses and gloves are necessary for this procedure.

B. Personnel Limit and Explosive Limit: Any graduate student must obtain written permission from the Supervisor before beginning synthesis. Undergraduates may perform synthesis under the instruction of a graduate student who has received permission from the Supervisor. UN may be made in batches of 5g theoretical yield. With specific permission it may also be made in 25g batches.

C. Specific Emergency Controls: None

D. Specific Safety Protocol: As UN is formed, its solubility is limited and stirring will cease or become difficult. It is important to wash away any unreacted acid to avoid decomposition in storage. If acid-free, UN is stable and relatively insensitive.

E. Protective Clothing and Equipment: Safety glasses and nitrile gloves.

F. Spill Procedures: Spills of urea are swept into a suitable solid waste container. Spills of concentrated nitric acid are washed with copious amounts of water, wiped dry, washed with 10% sodium bicarbonate solution dried. Spills of Urea Nitrate are swept into a suitable container and neutralized immediately as discussed in references.

III. Operations

A. Location: in hood

B. Sequence: Water is added to a round bottomed flask immersed in room temperature water, followed by the gradual addition of the nitric acid, with stirring. The urea is ground and gradually added to the stirring solution. No significant temperature rise should occur; if it does cease addition of urea and cool the water bath. The mixture is stirred for 1 hour, filtered and rinsed with cold methanol. The product is air dried and placed in a labeled "pop top" type container.

C. Sample Lab Notebook Entry:

Reagent	**Source**	**MW (g/mol)**	**Theo. Wt (g)**	**Actual Wt**	**mols**	**mol ratio**
Urea	Organic Shelves	60.06	2.44		0.041	1:1
HNO_3 (65% wt)	Acid Cabinet	63.01	3.94		0.041	1:1
Water	Distilled Tap	18.02	5.08		0.282	7:1
Product						
UN		123.07	5.00		0.041	1:1

IV. References

Oxley, J.C., Smith, J.L., Naik, S. "Determination of Urea Nitrate and Guanidine Nitrate Vapor Pressures by Isothermal Thermogravimetry," Propellants, Explosives, Pyrotechnics, Feb 08

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Suzuki et al., US Patent 5659080