Environmental Health and Safety
793 Marietta Street, NW
Atlanta, Georgia 30318-0465
PHONE 404-894-4635
FAX 404-894-5042

HIGHLY REACTIVE CHEMICAL SAFETY STANDARD

1. PURPOSE

1.1. The Highly Reactive Chemical Safety Standard at Georgia Tech covers the use of solid and liquid chemicals that are deemed extremely reactive, extremely hazardous, and require additional precautions. This standard outlines the proper processes set forth with expectations for their use as well as safety protocols in the event of an incident. The materials covered in this safety standard include the following categories:

1.1.1. Flammables and combustibles
1.1.2. Explosives
1.1.3. Self-reactive materials (ex. Piranha solution, perchlorates, etc.)
1.1.4. Self-heating substances and mixtures
1.1.5. Highly toxic chemicals (ex. hydrofluoric acid (HF), certain metal powders, etc.)

1.2. This standard outlines the requirements and responsibilities necessary to provide suitable accommodation for the presence of all highly Reactive Chemicals (HRCs) stored and used in GT laboratories. These accommodations include but are not limited to appropriate storage cabinets, applicable gas monitoring systems (permanent and temporary), building fire sprinkler systems, and administrative controls. This standard focuses strictly on solid and liquid reactive chemicals. Highly reactive chemical gases are covered extensively under the Georgia Tech Dangerous Gas Safety Program.

1.3. The HRC Pre-Approval Process was developed by the Georgia Tech Environmental Health and Safety (EHS) department. Pre-approval is determined by the hazard of the chemical being requested. This is reviewed by the department on case-by-case basis depending on the hazard of the chemical and/or process. HRCs that require pre-approval **before purchase** may be but are not limited to pyrophoric chemicals, highly flammable materials, explosives, self-reactive materials/mixtures, self-heating substances/mixtures, organic peroxides, highly toxic substances, and chemicals that react with water to emit a flammable gas. For the purposes of this program, pyrophoric liquids, solids, and gases are defined in section 6. You will find a list of HRCs in Appendices at the end of this Standard. Purchase of HRCs prior to pre-approval is restricted. For more information on purchases requiring pre-notification to Georgia Tech Environmental Health and Safety (EHS) and pre-approval by the Georgia Tech Chemical and Environmental Safety Committee (GT CESC), here is a link to the EH&S Restricted Purchase Items: https://www.ehs.gatech.edu/sites/default/files/dg_restricted_purchases.pdf

2. GOAL

2.1. The primary goal of this program is to assure standardization and uniform application of a safety program pertaining to the use of all HRCs in all Georgia Tech laboratories while remaining flexible enough to accommodate unusual and/or short duration research applications. This standard informs all individuals of the EHS requirements for handling, using, and storing various HRCs.

3. SCOPE

3.1. This standard applies to all persons, including but not limited to faculty, staff, students, and visiting scientists, conducting research in Georgia Tech facilities.

3.2. This standard applies to all qualified use of HRCs including reagents, solids, and liquids. Any fume hood applications involving highly reactive chemicals shall be reviewed by EHS

3.3. This standard is effective immediately in all Georgia Tech facilities.

4. RESPONSIBILITIES

4.1. **Laboratory Users/Owners/Managers are responsible for:**

4.1.1. Ensuring that all Highly Reactive Chemical requirements for utilizing the above outlined chemicals in the laboratory have been met and approved by Georgia Tech EH&S.

4.1.2. Ensuring that the EH&S Restricted Purchases process is followed for any applicable highly reactive chemicals as described in section 1.3.

4.1.3. Ensuring that all staff are properly trained on the safe handling and use of all highly reactive chemicals in the laboratory as well as all emergency procedures. All training must be documented for each employee.

4.1.4. Any incidents involving injuries or damage to property must be reported to Georgia Tech police and Georgia Tech EH&S immediately.

4.1.5. All waste must be disposed of properly.

4.2. **GT EHS is responsible for:**

4.2.1. Reviewing and approval of all highly reactive chemical documentation as needed for individual laboratories. Provide technical and chemical guidance when necessary to assist laboratory in gaining approval as a highly reactive chemical user.

4.2.2. Training on the proper handling and use of highly reactive chemicals upon request.

4.2.3. Approving the purchase of highly reactive chemical through the EH&S highly reactive chemicals Pre-Approval Process.

4.2.4. Conducting periodic comprehensive inspections/audits.

4.2.5. Assisting in any safety or health related incidents.

5. FUNDAMENTAL REQUIREMENTS

5.1. **Highly Reactive Chemicals Approval Process**

5.1.1. Some purchases/acquisitions for the usage of specific reactive chemicals under this program, such as pyrophoric materials, must be reviewed and pre-approved by GT EHS prior to purchase. Proper training and documentation must be completed with the assistance of EHS prior to the use or acquisition of explosives. Contact GT EHS for assistance.

5.1.2. The Chemical and Environmental Safety Committee (CESC) reviews and approves the acquisition of certain HRCs that are new use at Georgia Tech or new to research group.

5.1.3. The request form for chemical purchase/acquisition can be found on the EH&S website.

  5.1.3.1. Restricted Purchases Chemical Form: https://www.ehs.gatech.edu/chemical/documents

5.1.4. All faculty at Georgia Tech interested in utilizing HRCs such as pyrophoric or water reactive chemicals must follow the EHS Pre-Approval Process as well as fill out EHS review documentation. See below for links to all required documents to acquire and use items requiring pre-approval. These items are on a case-by-case basis.

  5.1.4.1. EHS HRC Pre Notification Form
  5.1.4.2. EHS HRC SOP
  5.1.4.3. EHS HRC Training Record

5.1.5. All laboratory groups seeking approval for the use of HRCS must have completed a Lab Safety Plan, have a current chemical inventory (reconciliation of inventory is up to date), and have a complete lab training record (Appendix V or hyperlinks to all forms). All required EH&S laboratory training must also be current. The aforementioned documents will be used to write a complete and detailed SOP outlining exactly how the HRC materials will be used. The Laboratory Safety Plan will include the below listed information:

Table I: HRC EHS Documentation Description

Pre-Notification Form: Purchase of HRC or Process Equipment	Laboratory Standard Operating Procedure	Laboratory Training Record
This document is completed to notify EHS of the intent to order or use a HRC. It contains the following information: • General contact Information • Chemical information & characteristics • Objective or purpose of use	This document is initiated when using a HRC. It contains the following information: • General SOP information • General contact information • Chemical-specific characteristics & information • Hazards • Safety requirements • SOP procedure steps • Emergency procedures • Additional requirements	This document lists all individuals who are trained to handle a specific HRC in the lab and who trained them: • Name of trainee • Name of trainer • Date trained • Proficiency level Novice: Proficient: Trainer: • Process/task trained

5.2. **General Requirements for use of HRCs:**

5.2.1. Safety Data Sheets (SDS): Shall be available to employees for all hazardous materials regulated by NFPA 400. These will be kept via an electronic or hard copy format and must be readily available when necessary.

5.2.2. Equipment, machinery, and/or detection/alarm systems associated with the use, storage, or handling of hazardous materials shall be listed and approved.

5.2.2.1. Manual emergency shutoff valves (Emergency Stop or E-Stop) and remotely located manually activated shutdown controls for emergency shutdown shall be identified. The location shall be clearly visible, and indicated by means of a sign (if applicable).

5.2.2.2. Equipment shall be tested no less than annually, in accordance with manufacturer's requirements, with approved industry standards or with an approved schedule

5.2.3. Requirements for supply piping: Any supply piping for liquids and solids having a health hazard rating of Class 3 or 4 in accordance with NFPA 704 shall be in accordance with the following:

5.2.3.1. Piping and tubing used for the transmission of HRC liquids shall have welded, threaded, or flanged connections throughout except for connections located within a ventilated enclosure. They may also have an alternative method of containment.

5.2.3.2. Piping and tubing used for the transmission of HRC liquids shall be enclosed in fired resistance-rated construction or concealed spaces in areas not classified as protection level areas.

5.2.4. Storage Cabinets shall be constructed of metal and the interior will be treated, coated, constructed of materials that are nonreactive with hazardous material. Shelving shall be treated, coated, or constructed of materials that are compatible with reactive chemicals.

5.2.5. Solid and liquid HRCs stored in closed containers are not required to comply with natural ventilation requirements (mechanical exhaust ventilation). (Section 6.2.1.5 NFPA 400)

6. DEFINITIONS

6.1. **Auto Ignition Temperature (AIT):** Temperature at which a material will ignite on its own and burn in the presence of sufficient oxygen. (ACC)

6.2. **Blasting Agent:** Material or mixture intended for blasting that meets the requirement of the DOT "Hazardous Materials Regulations," as set forth in Title 49, Code of Federal Regulations (C.F.R.), Parts 173.56, 173.57, and 173.58, Explosive 1.5D. (NFPA 495, 20021)

6.3. **Combustible Liquid**: Liquid that has a closed cup flash point ≥ 100°F (37.8°C). (NFPA 30)

6.3.1. **Class II:** Liquids having flash points ≥ 100°F (37.8°C) and below 140°F (60.0°C).

6.3.2. **Class III**: Liquids having flash point ≥ 140°F (60.0°C) and below 200°F (93.4°C).

6.4. **Control Area:** A building or portion of a building that in which flammable and combustible liquids are allowed to be stored, dispensed, and used or handled in quantities that do not exceed the maximum allowable quantity (MAQ) as established by NFPA 30.

6.5. **Corrosive:** A chemical that causes either irreversible alterations in or visible destruction of tissue by chemical action at the site of contact. GHS defines skin corrosion as the production of irreversible damage to the skin, namely visible necrosis from the application of the test substance over a 4-hour time period. Acids and bases are common corrosives. (29 C.F.R. § 1910.100 App A)

6.6. **Cylinders:** Vessels used to store gases at above atmospheric pressure.

6.7. **Explosive:** An explosive substance (or mixture) is a solid or liquid that is capable of producing gas at such a temperature, pressure, and speed as to cause damage to the surroundings. This can be completed via a chemical reaction of some form. Pyrotechnic substances are an example of a known explosive substance. (NFPA 495 & 29 C.F.R. § 1910.1200 App B)

6.7.1. **Highly Explosive Material**: Explosive materials characterized by a very high rate of reaction, high-pressure development, and the presence of a detonation wave.

6.7.2. **Low Explosive Material**: Explosive materials characterized by deflagration or a low rate of reaction and the development of low pressure.

6.7.3. Classification of explosives are assigned one of six divisions depending on the type of hazard they present. For our purposes, we will focus on the first three divisions:

6.7.3.1. **Division 1.1:** Substances, mixtures, and articles, which have a mass explosion hazard. A mass explosion is one, which affects almost the entire quantity present virtually instantaneously. Examples are dynamite, nitroglycerin, picric acid, lead azide, fulminate of mercury, black powder, and blasting caps.

6.7.3.2. **Division 1.2:** Substances, mixtures, and articles, which have a projection hazard but not a mass explosion hazard, such as photographic flash powders and fireworks.

6.7.3.3. **Division 1.3:** Substances, mixtures, and articles which have a fire hazard and either a minor blast hazard or a minor projection hazard or both, but not a mass explosion hazard, the combustion of which gives rise to considerable radiant heat or which burn one after another producing minor blast or projection effects.

6.7.4. **Potentially Explosive Chemical (PEC)**: Materials that may oxidize, decompose, polymerize, or become in some way subsequently become explosive when subjected to heat, light, or friction, or mechanical force.

6.8. **Fire Compartment:** Area of building separated from adjacent areas by a fire separation, which is comprised of fire resistant construction. In new construction, barriers are built into walls to slow a fire if it starts (fire rated walls). (NFPA 45)

6.9. **Flash Point:** Minimum temperature at which a liquid gives off a vapor within a test vessel in sufficient concentration to form an ignitable mixture with air near the surface of the liquid. (29CFR1910.106)

6.10. **Flammable:**

6.10.1. Flammable liquids are classified by the NFPA based on their flash points. OSHA defines a flammable liquid as having a flash point of not more than 93°C (199.4°F). (29 C.F.R. § 1910.1200 App B). Further classification defines Class I flammable liquids as having flash points below 100°F (37.8°C) and vapor pressure not exceeding 40 lbs./in^2 at 100°F (37.8°C). Class I is further subdivided by the NFPA 30 standard into the below criteria:

6.10.1.1. **Class IA:** Liquids having flash points below 73°F (22.8°C) and BP below 100°F (37.8°C). Flammable aerosol can s are in this category. NFPA Diamond=4

6.10.1.2. **Class IB:** Liquids having flash points below 73°F (22.8°C) and BP at or above 100°F (37.8°C). NFPA Diamond = 3

6.10.1.3. **Class IC:** Liquids having flash points at or above 73°F (22.8°C) and below 100°F (37.8°C). NFPA Diamond = 3

6.10.2. A flammable solid is a solid, which is readily combustible, or may cause or contribute to fire through friction. (GHS) The classification criteria are as follows (**Category I Burning Rate Test**):

6.10.2.1. Substance or mixture other than metal powder: wetted zone stops fire for at least 4 minutes and burning time < 45 s or burning rate > 2.2 mm/s. Metal powders burn time ≤ 5 minutes.

6.10.2.2. Substance or mixture other than metal powder: wetted zone stops fire for at least 4 minutes and a burning time of < 45 s or burning rate of > 2.2 mm/s. Metal powders burn time > 5 minutes and ≤ 10 minutes

6.11. **Flammability Range**: A key factor used to determine a solvent's flammability. Flash point is also as a factor. The lower explosion limit and the upper explosion limit make up the limits of flammability for a material. (ACC)

6.12. **Gas cabinet:** A continuously ventilated enclosure for gas cylinders, which also provides automatic gas, shut off when leaks are detected or when gas flow exceeds pre-set levels (see section 10).

6.13. **Georgia Tech Dangerous Gas Monitoring System (GT DGMS):** An integrated gas-monitoring system that covers all Georgia Tech buildings where dangerous gases are used. This system monitors laboratories for gas leaks, gas releases, ventilation failures, power failures, and alarms locally to warn users as well as send messages alerting GT Environmental Health and Safety and GT Police.

6.14. **Georgia Tech Environmental Health and Safety (GT EHS):** provides occupational and environmental protection services to comply with applicable regulations and to prevent occupationally induced disease, injury, property loss, and degradation to the environment.

6.15. **Georgia Tech Chemical and Environmental Safety Committee (GT CESC):** provides policy recommendations, oversees the development of procedures by EHS to monitor and enforce lab safety and chemical hygiene plans. Receives periodic risk assessment reports and reviews compliance with policies and procedures.

6.16. **Lower Explosion Limit (LEL):** Lowest concentration of vapor in air at which the vapor/air mixture will burn. (ACC)

6.17. **Maximum Allowable Quantity per Control Area (MAQ):** Threshold quantity of hazardous material in a specific hazardous material in a specific hazard class that once exceeded requires the application of additional administrative procedures, construction features, or engineering controls.

6.18. **Permissible Exposure Limit (PEL):** Limits set by OSHA to protect workers against the adverse effects of exposure to chemical substances. PELs limit the amount or concentration of a substance in the air and are based on an 8-hour time weighted average exposure.

6.19. **Organic Peroxide**: Any organic (carbon containing compound) which can be a liquid or solid containing the bivalent -O-O- structure and, as such, is considered a derivative of hydrogen peroxide (29 C.F.R. § 1910.1200 App B). The main physical hazard of organic peroxides are fire and explosion hazards (*see* chapter 8 of this standard). The instability of the peroxy group is what makes peroxides hazardous. During decomposition, they give off heat at a rate that rises as temperature rises. If a peroxide gives off flammable vapors, these vapors can easily catch on fire. Organic peroxides may also be corrosive or toxic.

6.20. **Oxidizing Liquid:** A liquid, which, while itself is not necessarily combustible, may, generally by yielding oxygen, cause or contribute to the combustion of other material. (29 C.F.R. § 1910.1200 App B)

6.21. **Pyrophoric:**

6.21.1. Pyrophoric gases include gases that will ignite spontaneously on contact with air at temperatures of ≤ 130°F ((29CFR1910.1200). Examples include silane, disilane, diborane, and phosphine. A detailed outline of the requirements specific for flammable gases, including pyrophoric gases, can be found in the document, Georgia Tech Dangerous Gas Safety Program. A copy of the manual can be found at GTDGMS.

6.21.2. Pyrophoric liquids will ignite within 5 minutes when added to an inert carrier and exposed to air. They also can ignite or char filter paper upon contact with air within 5 minutes. Examples include tert-butyl lithium and diethyl zinc. (GHS & 29CFR1910.1200AppB)

6.21.3. Pyrophoric solids ignite within five minutes upon coming in contact with air. Examples of include white or yellow phosphorus. (GHS & 29 C.F.R. § 1910.1200 App B)

6.22. **Self-Accelerating Decomposition Temperature (SADT)**: Lowest temperature for the self-reactive chemical to remain stable before it will undergo self-accelerating decomposition.

6.23. **Self-Heating**: Substance or mixture as a solid or liquid substance, other than a pyrophoric, which by reaction with air and with no other energy supplied is liable to self-heat. This substance differs from pyrophoric in that it will only ignite when in large amounts (kilograms) and after extended periods, e.g. hours or days. (GHS & 29 C.F.R. § 1910.1200 App B)

6.23.1. **Category 1**: Materials that are more reactive and self-heat more readily and in smaller amounts.

6.23.2. **Category 2**: Materials that are less reactive and self-heat in large amounts (kgs).

6.24. **Self-Reactive:** Substances or mixtures that are thermally unstable. They are in liquid or solid form and are liable to undergo a strongly exothermic decomposition even without the participation of oxygen. When heated under confinement, the self-reactive material will possess explosive properties and is liable to detonate, deflagrate rapidly, or show a violent effect. Self-reactive materials are classified in one of seven categories. The first three are applicable to this safety program. (GHS & 29 C.F.R. § 1910.1200 App B)

6.24.1. **TYPE A: A** substance or mixture can detonate or deflagrate rapidly, as packaged.

6.24.2. **TYPE B:** A substance or mixture possessing explosive properties which, as packaged, neither detonates nor deflagrates rapidly, but is liable to undergo a thermal explosion in that package.

6.24.3. **TYPE C:** substance or mixture possessing explosive properties when, as packaged cannot detonate or deflagrate rapidly nor undergo a thermal explosion.

6.25. **TLV (Threshold Limit Value):** Exposure limit established by the American Conference of Governmental Industrial Hygienists (ACGIH). The TLV for a chemical substance is defined as a concentration in air, typically for inhalation or skin exposure. There are three types of TLVs:

6.25.1. **TWA:** Time Weighted Average, e.g., 8hrs/day, 40 hrs./week.

6.25.2. **STEL:** Spot exposure for a duration of 15 minutes, cannot be repeated more than 4 times per day.

6.25.3. **C:** Ceiling limit is the absolute exposure limit that should not be exceeded at any time.

6.26. **Toxicity:** Acute toxicity refers to any adverse effects occurring following oral or dermal administration of a single dose of a substance, or possibly multiple doses, within a 24-hour time window. An inhalation exposure is a 4-hour timed exposure. The GHS defines acute toxicity estimates (ATE) as LD_{50} (oral & dermal) or LC_{50} (inhalation) values. There are five ATE categories within the various routes of exposure, with five being the least toxic and one being the most.

6.26.1. Oral and Dermal Exposure Routes: The classification of these exposure routes are expressed in LD_{50}, and measured in mg/Kg of bodyweight. (GHS). In toxicology**,** LD_{50}, is the median lethal dose (or the lethal dose, 50%). It is defined as the amount of a toxic agent, given sufficient amount to kill 50 percent of the animal test specimen population within a specified amount of time. Oral or dermal exposure is a single dose administration. The lower the LD_{50} value in each ATE category, the higher the toxicity.

6.26.1.1. Oral Hazard Category (mg/Kg): ATE categories 1-5 are expressed in mg/Kg and are 5, 50, 300, 2000, and 5000 respectively.

6.26.1.2. Dermal Hazard Category (mg/Kg): ATE categories 1-5 are expressed in mg/Kg and are 50, 200, 1000, 2000, and 5000 respectively.

6.26.2. Inhalation Exposure Routes: Manifesting respectively in the form of gases, vapors, dusts, and mists. The classification of these exposure routes are expressed LC50 and measured in (ppm/V) for gases and (mg/L) for vapors, dusts, and mists. (GHS)

6.26.2.1. In toxicology, LC_{50} is the median lethal concentration, 50%, of a toxin. It is the dose required to kill 50 percent of the animal test specimen population within a specified amount of time. (GHS) In the case of gases, vapors, dusts, and mists, the exposure time is 4 hours.

6.26.2.2. Dust: A solid particle of a substance or mixture that has been suspended in a gas. Gas is usually suspended air and averaging 1 to 100µm.

6.26.2.3. Mist: Liquid droplets of a substance or mixture suspended in a gas. Gas is usually suspended in air and averaging 1 to 100µm in droplet size.

6.26.2.4. Vapor: A gaseous form of a substance or mixture that has been released from its liquid or solid state.

6.26.3. Mixtures LD_{50}/LC_{50}**:** An approach that is used for the determination of the classification of mixtures is a tiered system. It is based strictly upon the amount of information that is available about the mixture and its various components. (GHS)

6.26.3.1. Classification Criteria for Mixtures of Exposure Routes**:** When there is evidence of relevant toxicity via multiply routes of exposure, those routes must be classified.

6.26.3.1.1. A relevant ingredient exists in a concentration of >1% (by w/w) for solids, liquids, dust, mists, vapors, and v/v for gases.

6.26.3.2. Classification Criteria for Mixtures where acute toxicity data is available for the complex mixture**:**

6.26.3.2.1. Mixtures that have been tested for acute toxicity (the acute toxicity is known) will use the same classification criteria as described in this section.

6.26.3.2.2. Classification Criteria for Mixtures where acute toxicity data is not available for the complex mixture (bridging principles)**.**

6.27. **Upper Explosion Limit (UEL):** Highest concentration of vapor in air at which the vapor/air mixture will burn. (ACC)

6.28. **Water Gel:** Explosive or blasting agent that contains a substantial portion of water. (NFPA 495, 2001)

7. Flammable and Combustible Storage and Usage Requirements

7.1. **Flammable/Combustible Substances and Mixtures:** Flammables and combustible chemicals include such materials as pyrophoric, organics solvents, oils, greases, tars, oil base paints. Flammable gases are covered in the Georgia Tech Dangerous Gas Safety Program.

7.2. There are several factors that aid in determining the flammability of a solvent. Flash point and auto Ignition temperature will help to determine the level of hazard when handling flammable materials. (ACC)

7.2.1. Flash Point: The flash point is an indication of how susceptible the material would be to ignition. Full combustion of a flammable solvent occurs at a higher temperature than the flash point is called the fire point. The lower the flash point, the more volatile the substance is, the more potential for flammability to exist. Flash point is also a function of pressure. As pressure is decreased in a vessel, the flash point of the contents is lowered.

7.2.1.1. AIT of a flammable liquid or solvent is useful in determining the level of hazard, especially if the application or process is an elevated temperature processor experiment. It is an estimation of the maximum temperature that a mixture of a flammable solvent in air can reach before self-ignition.

7.3. AIT of a flammable liquid or solvent is useful in determining the level of hazard, especially if application or process is an elevated temperature processor experiment. It is an estimation the maximum temperature that a mixture of a flammable solvent in air can reach before self-ignition.

7.3.1. The Lower Explosion Limit (LEL) is the lowest end of this flammable range and is also the lowest concentration of vapor in air at which the mixture will burn.

7.3.2. The Upper Explosion Limit (UEL) is the highest concentration of vapor in air at which the mixture will burn.

7.4. Sources of Ignition: There are many activities that can act as sources of ignition and exceed the minimum ignition energy of a flammable solvent.

7.4.1. Flames and Smoldering ignition sources include~~:~~ open flames, gas burners, welding torches, and catalysts.

7.4.2. Hot Surfaces~~:~~ may cause ignition of flammable solvent or mixtures if the surface is at a temperature above the auto ignition temperature.

7.4.3. Friction & Impact ignition occurs if the task being performed causes sparks or generates high heat.

7.4.4. Electrical Discharges includes static electricity. Static electricity is produced by agitation of a flammable solvent by means of motion. By grounding the container, the charge is dissipated on the container only. Once static charges have accumulated in a liquid, they will dissipate over time (relaxation time) depending upon the conductivity of the solvent.

7.5. Flammable and Combustible Liquids/Solids Permissible Storage and Use:

7.5.1. The maximum allowable quantity (MAQ) of a flammable liquid per control area in an educational occupancy is storage in excess of 10 gallons (38L of Class I and Class II liquids combined). The maximum allowable quantity (MAQ) of a flammable solid per control area in an educational occupancy is storage in excess of 5 lbs. (NFPA 400)

7.5.2. **Storage Requirements:** Store in a cool, dry environment free from extreme temperature or humidity. Keep away from heat, flames, and other sources of ignition.

7.5.3. When storing 10 gallons or more of flammable liquid, a flammables storage cabinet is required to be used. It is recommended for quantities of 1 gallon or more. The cabinet must be of appropriate construction: steel, self-closing doors, and a 3-point latch arrangement.

7.5.4. A flammable-safe/explosion-proof refrigerator must be used to store flammable materials. Use of domestic refrigerators to store flammable liquids is not permitted. The components are sources of ignition, which may cause a fire or explosion when the flammable vapors from the chemicals are present.

7.5.5. Use only non-sparking tools made of materials such as brass, bronze, copper/nickel alloys, etc. to eliminate friction-induced sparks made by metal-to-metal contact.

7.5.6. Flammable and combustible liquids must be stored in metal or polyethylene safety containers that have been approved for such storage if using anything other than glass reagent bottles:

7.5.6.1. UL listed container equipped with a self-closing cap, automatic vent, and flame arrester.

7.5.6.2. Current carrying insert embedded into the can for proper grounding, and a funnel (non-plastic).

7.5.6.3. Class IA and Class IB flammable liquids can be stored in glass containers 1 gallons (4L) capacity) if the required purity would be affected by storage in a metal container or if the liquid can cause excessive corrosion of the metal container. Many glass container suppliers offer shatter-resistant coatings to protect from accidental breakage and are recommended.

7.6. Highly Reactive Pyrophoric/Water-Reactive Liquids and Solids Permissible Storage and Use:

7.6.1. The maximum allowable quantity (MAQ) of pyrophoric or water-reactive liquid and solid per control area in an educational occupancy is one liquid gallon and one pound. (NFPA 400)

7.6.2. **Storage Requirements:** Pyrophoric and water-reactive chemicals, liquid or solid, must be stored under an inert atmosphere or a liquid such as kerosene or mineral oil. Avoid areas with heat/flames, oxidizers, and water sources.

7.6.3. Prior to purchase and use of pyrophoric materials and water-reactive chemicals, follow the approval process outlined in section 6.1.

7.6.4. New users of pyrophoric or water-reactive reagents must work under the close supervision of the PI or designated competent person. All experiments and procedures shall be considered a two-person task and shall be performed under the buddy system.

7.6.5. **Requirements for Engineering Controls:**

7.6.5.1. Pyrophoric or water-reactive liquid shall be handled and used in a certified glove box or fume hood.

7.6.5.2. Pyrophoric or water-reactive solids shall only be handled in an appropriate glove box.

7.6.5.3. Oven dry all glassware prior to use.

7.7. **Pyrophoric Liquid Transfer**: By using proper needle and syringe techniques, pyrophoric liquids can be handled safely in the laboratory. NFPA requirements for pyrophoric liquid transfer include the use of approved containers and for the process to occur via a closed piping system or approved engineered transfer system. Contact your laboratory PI or Georgia Tech EH&S for training in proper laboratory techniques. Below are examples of appropriate, closed system methods that can be used for pyrophoric liquid transfer.

7.7.1. **Sure/Seal® Septum-Inlet Transfer:** The Aldrich Sure/Seal® packaging system (Fig 1) provides a convenient method for storing and dispensing small volumes of air sensitive reagents. The adapter protects the contents of the containers from air and moisture

7.7.2. **Transferring Pyrophoric Reagents with a Syringe (fig. 2):** A needle from an inert gas (review SDS for compatibility) source with a bubbler outlet is inserted into the bottle. The goal is to ensure that the pressure is equalized in reagent bottle using an inert gas source. The reagent syringe is flush dried with an inert gas and the needle is then inserted to the bottle. The plunger is gently pulled to draw liquid into the syringe. Glass syringes with a Teflon-tipped plunger work best for this method. Best practice is to not to fill the syringe more than 60%. Force any excess reagent or bubbles back into the reagent bottle when the desired volume is reached and quickly transfer the syringe to the reaction vessel by puncturing a rubber septum.

7.7.3. **Transferring Pyrophoric Reagents with a Double-Tipped Needle (fig. 3):** This technique should be used when transferring >20mL of reagent. The same process is followed for transferring pyrophoric reagents with a syringe in reagents to set up for the reagent bottle (Fig 2). The double tipped needle method can transfer pyrophoric liquids to a larger volume container such as a graduated cylinder. This calibrated addition of reagent is performed in a closed system with the transfer vessel being under constant purge of inert gas. Control rate of the transfer of the pyrophoric liquid can be done if a Luer® lock syringe valve is installed between the two long needles as shown in the diagram in figure 2.

Fig. 1 Sure/Seal® Septum Inlet Transfer Adapter

7.8. **Personal Protection Equipment Requirements for Flammables/Combustibles including Pyrophoric & Water-Reactive Chemicals**: The level and type of PPE required is dependent upon the task being performed in the laboratory as well as the hazard level and quantity of chemical being used. Consult the Laboratory Safety Manual for PPE specific requirements for your laboratory as well as the SDS for the materials you are using. Any questions or concerns in reference to PPE requirements, should be directed to EH&S for a risk assessment. The following PPE recommendations are only recommendations based upon non-specific situations:

7.8.1. Safety glasses that meet the ANSI Z.87.1 1989 standard must be worn when working with chemicals in the laboratory. Depending upon the level of splash hazard, chemical goggles as well as an added face shield may be appropriate. A face shield is recommended any time there is a high risk of explosion potential for a large splash hazard, or a highly exothermic reaction is underway.

7.8.2. Chemical gloves should consist of at a minimum nitrile but double gloving with nitrile underneath neoprene gloves can add an extra layer of protection. Consult EHS if other gloves are needed or there are questions regarding the use of best glove selection.

7.8.3. A lab coat or apron comprised of materials that are not easily ignited (not made from nylon or polyester). Nomex® (flame resistant fiber) lab coats or full body suits are specially made for working with flammable materials.

7.9. **Requirements for Waste Management:**

7.9.1. Never open a container-containing residue to the atmosphere.

7.9.1.1. Prior to disposal, all pyrophoric materials should be destroyed (quenched) by hydrolysis and/or neutralization with adequate cooling.

7.9.2. Ensure waste is stored in compatible waste container.

7.9.3. Use secondary containment for hazardous waste. Ensure all waste containers are closed when not in use.

7.9.4. Use the GT database to initiate and create a waste label.

7.9.4.1. Collect all waste as per the appropriate designated waste stream. Contact EH&S Hazardous Materials Unit with any questions or concerns.

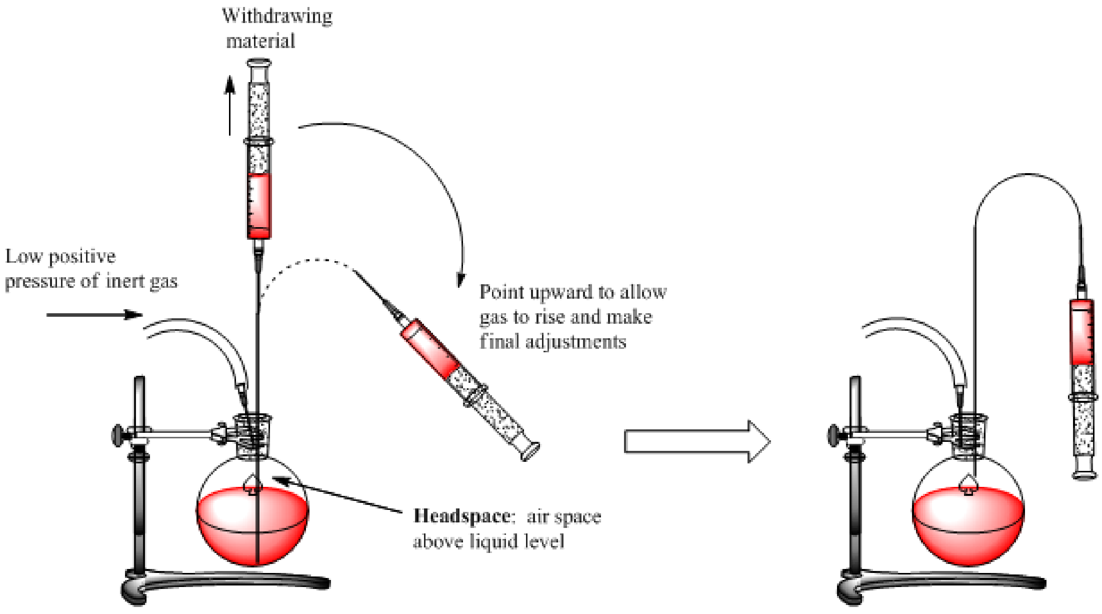

Fig. 2 Proper Methods of Transferring Pyrophoric Reagents: Syringe Technique

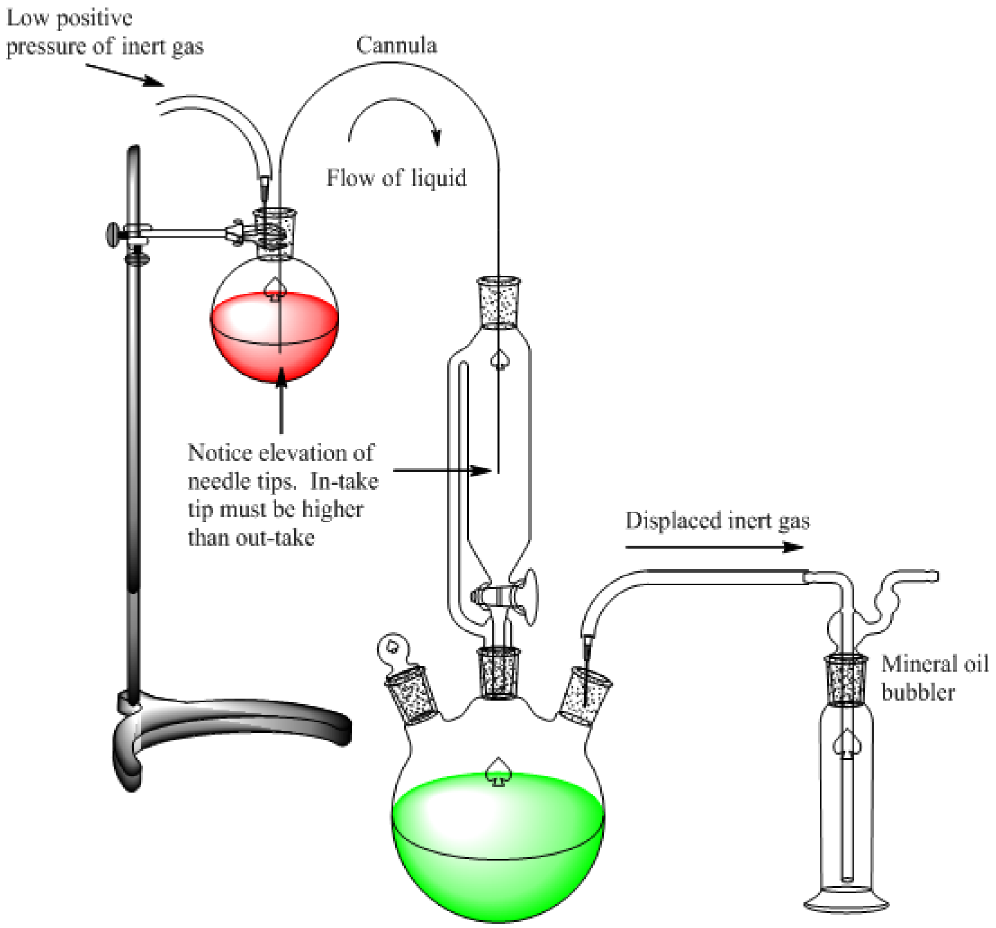

Fig. 3 Proper Methods of Transferring Pyrophoric Reagents: Cannula/Double-tipped Needle Transfer Technique

8. EXPLOSIVES STORAGE AND USAGE REQUIREMENT

8.1. **Potentially Explosive Chemicals (PECs)** are materials that may oxidize, decompose, polymerize, become contaminated, or unstable in some way that may cause them to become explosive when subjected to heat, light, friction, or mechanical shock. A variety of PECs can be found in an academic laboratory setting. Examples are peroxidizable compounds, perchloric acid, piranha, aqua regia, and picric acid. A peroxidizable compound is capable of reacting with atmospheric oxygen to form potentially explosive peroxides. They can be organic or inorganic. Best laboratory practices for storage and handling are discussed below per specific types of PECs.

8.1.1. Oxidizers/Peroxides: Many oxygenated organic compounds become increasingly hazardous in the laboratory upon prolonged storage. This is because explosive peroxides are formed from organic chemicals through exposure over time to air or light. Organic peroxides are very sensitive to impact, friction, heat, and light. They react dangerously with other substances and can undergo explosive decomposition. Peroxides form in freshly distilled, non-distilled, and non-stabilized ethers within less than two weeks. Most explosions occur during the process of distilling or purifying a mixture (containing perchlorate or peroxide-forming chemicals). OSHA defines an oxidizing liquid as a liquid, which, while itself is not necessarily combustible, may~~,~~ generally, by yielding oxygen, cause or contribute to the combustion of other material. (29 C.F.R. § 1910.1200 App B) An organic peroxide is a liquid or solid organic compound containing the bivalent -O-O- structure and as such is considering a derivative of hydrogen peroxide.

8.1.1.1. **Criteria for Oxidizing Liquids (**29 C.F.R. § 1910.1200 App B**):**

8.1.1.1.1. **Category I:** A chemical in which the 1:1 mixture by mass of chemical/cellulose tested spontaneously ignites, or the mean pressure rise time of the 1:1 mixture (by mass of the chemical/cellulose) is less than that of 1:1 mixture by mass of 50% perchloric acid and cellulose.

8.1.1.1.2. **Category II**: A chemical in which the 1:1 mixture (by mass of chemical/cellulose) tested exhibits a mean pressure rise less than or equal to the mean pressure rise time of the 1:1 mixture, by mass of the 40% aqueous sodium chlorate solution & cellulose. Also, the criteria for Category I has not been met.

8.1.1.1.3. **Category III: A** chemical in which the 1:1 mixture (by mass of chemical/cellulose) tested exhibits a mean pressure rise less than or equal to the mean pressure rise time of the 1:1 mixture, by mass of the 65% aqueous nitric acid & cellulose. In addition, the criteria for Category I & II have not been met.

8.1.1.2. **Criteria for Oxidizing Solids (29CFR1910.1200AppB):**

8.1.1.2.1. **Category I:** A chemical in which the 4:1 or 1:1 sample to cellulose ratio (by mass) tested exhibits a burning time less than the mean burning time of a 3:2 mixture (by mass of potassium bromate and cellulose).

8.1.1.2.2. **Category II**: A chemical in which the 4:1 or 1:1 sample to cellulose ratio (by mass) tested exhibits a burning time equal to or less than the mean burning time of a 2:3 mixture (by mass of potassium bromate and cellulose). Also, the criteria for Category I has not been met.

8.1.1.2.3. **Category III: A** chemical in which the 4:1 or 1:1 sample to cellulose ratio (by mass) tested, exhibits a mean burning time equal to or less than the mean burning time of 3:7 mixture (by mass of potassium bromate and cellulose) and the criteria for Category I & II have not been met.

8.1.1.3. **Criteria for Organic Peroxides (29CFR1910.1200AppB):** Any organic peroxide shall be considered for classification in this class unless it contains:

8.1.1.3.1. Not more than 1% available O2 from organic peroxides when containing not more than 1% hydrogen peroxide; or

8.1.1.3.2. Not more than 0.5% available O2 from the organic peroxides when containing more than 1% but not more than 7% hydrogen peroxide.

8.1.1.4. **Organic Peroxide Classification:**

8.1.1.4.1. **TYPE A:** As packaged, it can detonate or deflagrate rapidly.

8.1.1.4.2. **TYPE B**: Possessing explosive properties, which as packaged, it neither detonates nor deflagrates rapidly but is liable to undergo thermal explosion in that package.

8.1.1.4.3. **TYPE C**: Possessing explosive properties, which as packaged, it cannot detonate nor deflagrate rapidly and is not liable to undergo thermal explosion in that package.

8.1.1.5. **Storage Requirements for Peroxide Forming Chemicals:**

8.1.1.5.1. Develop a proper inventory management system for peroxide forming chemicals in the lab which includes the following:

8.1.1.5.1.1. Record opening date and date chemical should be discarded on the label.

8.1.1.5.1.2. Periodically check containers for any bulging due to overpressure. Do not touch or disturb a peroxide former that has visible crystals. The crystals are explosive, shock, friction and heat sensitive. Call EH&S for help in removing.

8.1.1.6. **Testing and Disposal Requirements for Peroxidizable Chemical. Use peroxide test strips to perform testing of containers:**

8.1.1.6.1. Any container that is opened shall be tested every 3 months. Dispose of any chemicals with greater than or equal to 100-ppm peroxides.

8.1.1.6.2. Unopened containers should be tested at or before the expiration date or after 12 months for concentration of peroxides.

8.1.1.6.3. Never test containers of an unknown age or origin. Old bottles may contain concentrated peroxides that present a serious hazard when opening the bottle. Contact Georgia Tech EH&S for assistance with managing these containers.

8.1.1.6.4. Peroxide test strips are commonly used as the test method for quantifying peroxide concentration. They can have a short shelf life after the container is opened, so store under dry, inert atmosphere. This will aid in prolonging their shelf life. See the manufacturer’s instructions regarding the use of your specific test strips.

Example: Sigma Aldrich Link to Peroxide Test Strips.

Fig. 4 Peroxide Test Strips

8.1.1.7. **Organic Peroxides and Peroxide Forming Solvents**: The main hazards associated with organic peroxides are fire and explosion hazards. They may also be toxic or corrosive depending upon the material, route of exposure, and dose or amount of exposure that could harm the body. The peroxy group, or double oxygen, is what makes a peroxide both useful and hazardous. An unstable functional group decomposes easily giving off heat that increases as the temperature increases. As the peroxide decomposes, it may give off flammable vapors, which can easily catch on fire.

Storage and Usage Requirements for Organic Peroxide:

8.1.1.7.1. Organic peroxides and peroxide forming materials will be stored under an inert gas (nitrogen) and kept away from heat and light. Do not submit materials to friction, grinding, or other forms of impact.

8.1.1.7.2. Keep peroxides cool but do not refrigerate. Liquid organic peroxides should never be allowed to freeze.

8.1.1.7.3. Use ceramic or plastic spatulas. Do not use metal.

8.1.1.7.4. Check peroxide forming materials for the presence of peroxides every 3 months using peroxide indicator test strips.

8.1.1.7.5. Peroxide forming solvents will be checked for the presence of peroxides prior to heating. Dispose of any chemicals with greater than or equal to 100-ppm peroxides.

8.1.1.7.6. Do not repackage organic peroxides in glass containers with screw caps or glass stoppers.

8.1.1.7.7. The Chemical Inventory Management System (CMIS) will send automatic notifications for peroxide forming chemicals one year after purchase.

Fig. 5 Platinum being dissolved in Aqua Regia

8.1.1.8. Aqua Regia: Aqua regia (Latin for “royal water” or “king’s water”) is a solution of concentrated hydrochloric and nitric acids in a mix ratio of 3:1. The solution can be used to dissolve metals from substrates, etching, or cleaning glassware of organic or metal particles. The nitro-hydrochloric acid is extremely corrosive and may result in an explosion or skin burns if not handled appropriately. It is usually a fuming yellow or red solution.

8.1.1.8.1. Always use laboratory glass containers such as Pyrex®~~,~~ as aqua regia solutions can corrode metal containers as well as melt plastic.

8.1.1.8.2. Mix the aqua regia components immediately prior to use and always add the nitric acid to the hydrochloric acid very slowly in a fume hood. Be cautious of the solution becoming very energetic and potentially explosive.

8.1.1.8.3. The container can become very hot and should be handled with care. Closed containers of aqua regia shall not be stored~~,~~ as oxidation occurs over time releasing various explosive gases.

8.1.1.8.4. Do not mix aqua regia solutions with organic compounds as this may cause an explosion

8.1.1.9. Perchloric Acid and Perchlorate Salts**:** perchloric acid ($HClO_4$) is a powerful oxidizing, strong acid. Perchloric acid may react violently with organic matter and reducing agents. Other hazards include unpredictable explosive reactions, explosions initiated by physical contact (impact), dermal hazards to skins and eyes, and toxicity properties. Solutions of other strong acids including perchlorate salts have the entire above listed hazard characteristics.

Storage and Usage Requirements for Perchloric Acid/Salts:

8.1.1.9.1. Digestions and other procedures performed with perchloric acid at elevated temperatures and/or above 72.5%, concentration must be performed in **specifically designed/designated perchloric acid (wash down) fume hood**. The hoods are equipped with water sources that spray the ducts and baffles of the hood to remove any perchlorate residues that may have formed there.

8.1.1.9.2. Do not heat perchlorate solution to dryness

8.1.1.9.3. EH&S must be contacted before beginning any work with hot processes involving perchloric acid (i.e. acid digestion).

8.1.1.9.4. Heating perchloric acid outside of a designated perchloric acid fume hood is strictly forbidden.

8.1.1.9.5. Do not store perchloric acid on a wooden shelf. Perchloric acid bottles will always be stored using secondary containment.

8.1.1.9.6. Perchloric acid and perchlorates must NOT be stored with organic materials or heated with sulfuric acid.

8.1.1.10. Piranha: Piranha is a solution that is used to remove organic residues from substrates. Two different solutions are used in the laboratory, the most common being the acid piranha: a 3:1 mixture of sulfuric acid (H_2SO_4) with hydrogen peroxide (H_2O_2). The second is the basic form of piranha, which is a 3:1 mixture of ammonium hydroxide (NH4OH) with hydrogen peroxide (H_2O_2). When heated, both solutions are equally dangerous. The acidic piranha solution is self-initiated while the basic form of the solutions requires heating to 60°C to start any reaction. Piranha solution is extremely energetic and potentially explosive. When heating, it can become very hot (> 100°C). Handle the solution with care using thermally protective gloves.

Storage and Usage Requirements for Piranha:

8.1.1.10.1. Mixing piranha with organic compounds generates enormous quantities of heat and gas, which may cause an explosion.

8.1.1.10.2. When handling piranha, always use Pyrex containers. Piranha solutions can melt plastic containers.

8.1.1.10.3. Always add the peroxide to the acid **very slowly**. Peroxide concentrations greater than 50% can create an explosion due to the immediate exothermic reaction. While heating the piranha solution it is also very likely to become very hot. Attempting to pick up a beaker could result in an injury or spill.

8.1.1.10.4. Leave the piranha solution in an open container to cool. Storing in a closed container could result in an explosion. Do not store piranha waste in a closed container until it is completely cooled.

8.1.1.10.5. Do not mix hot piranha solutions with any organic compounds (acetone, photoresist, isopropyl alcohol, etc.). This may cause an explosion.

8.1.1.10.6. Adding acids or bases to piranha or spraying with water will accelerate the reaction.

8.1.1.10.7. Anything removed from piranha solution should be rinsed with copious amounts of deionized water.

8.1.1.10.8. Piranha solutions can only be made the day that they are to be used. **They may not be made in advance or stored.** Containers used to make the piranha should be 3X larger than the volume of piranha that you intend to make.

8.1.1.10.9. Piranha solutions may only be made in the fume hood or exhaust ventilated chemical bench.

8.1.1.10.10. Containers holding piranha must be made from laboratory glassware only, such as Pyrex and be clearly labeled with RTK compliant warning information.

8.1.1.11. A known explosive substance (or mixture) is a solid or liquid, which is in itself able to, by way of chemical reaction, to produce gas at such a temperature, pressure, and speed as to cause damage to the surroundings. Pyrotechnic substances are in this category even though they do not emit any gases. One such example is RDX, an explosive nitroamine more powerful than TNT. RDX is highly utilized in military applications as the base for many common military explosives.

Security and Safety of Explosive Materials (NFPA 495, 2001)

8.1.1.11.1. No person shall be in possession of explosive materials or conduct an operation or activity requiring the use of explosive materials or perform or supervise the loading and firing of explosive materials without first obtaining the proper permit.

8.1.1.11.2. Individuals who conduct an operation or activity that uses explosive materials shall obtain a permit to use explosive materials and shall be responsible for the results and consequences.

8.1.1.11.3. Such person shall ensure that loading and firing are performed or supervised by a person possessing a permit to blast.

8.1.1.11.4. Exception for laboratories engaged in testing explosive materials, other than conducting test blast explosions, shall require only a permit to use.

8.1.1.11.5. Accidents that cause injury to persons or property damage due to explosive material shall be reported immediately to the Georgia Tech Police Department.

Storage and Usage Requirements of Poly-nitro Compounds: Acquisition of explosive poly nitro compounds is restricted under Georgia Tech Rules and may involve permitting —under the above described Federal Regulations and/or Fire Safety Regulations, including laboratory quantities.

8.1.1.11.6. Only immediate use quantities may be purchased.

8.1.1.11.7. The stock of poly-nitro will be stored separately from other lab chemicals.

8.1.1.11.8. Poly-nitro compounds will be inspected quarterly for degradation or dehydration. These compounds become more sensitive with age. A designated person or persons shall be clearly identified as responsible for conducting and documenting this quarterly inspection.

8.1.1.11.9. Poly-nitro materials will be disposed of through EH&S when the project for which they were purchased ends or 1 year after purchase.

8.1.1.11.10. Poly-nitro containers must be handled by the container bottom, not the lid or cap.

8.2. Picric Acid: Picric acid of 2, 4, 6-trinitrophenol is a solid organic compound. It must be kept wet with water because the dry solid is explosive. This material is used in ammunitions and explosives, in laboratories for staining microscopic specimens, and in the pharmaceutical industry. Picric acid is incompatible with metals including Copper, lead, zinc, aluminum, ammonia, concrete, plaster, salts, and oxidizers. Picrate salts are more explosive than picric acid. Avoid heat, flame, ignition sources, shock, dryness, and the above listed incompatible materials.

Storage and Usage Requirement for Picric Acid:

8.2.1. Picric Acid is a dangerous explosion hazard when the material becomes dry. If you discover that the material has become dry, contact EHS immediately, do not handle or touch.

8.2.2. Do not store picric acid in metal containers. Use containers made of polyethylene, polypropylene, Teflon®, or glass.

8.2.3. Wet wipe screw closure to ensure that solids do not form on the threads.

8.2.4. Small spills can be cleaned up with wet paper towels and stored in plastic or glass bottles prior to contacting EHS. Call EHS for assistance with larger spill. Contact EHS to report all spills.

8.3. **Personal Protection Equipment Requirements for PECs and Known Explosive Compounds:** The level and type of PPE required is dependent upon the task being performed in the laboratory as well as the hazardous level and quantity of chemical being used. The following PPE recommendations are recommendations based upon non-specific situations. Please note PPE requirements for working with the above listed PECs vary from lab to lab. Consult the laboratory policy on PPE specific requirements for your laboratory as well as the SDS for the materials you are using.

8.3.1. When working with PECs and known explosives, solutions, you must don an acid PPE (acid apron).

8.3.2. Other requirements include safety glasses that meet ANSIZ.87.1 1989 standard must be worn.

8.3.3. Depending upon the level of splash hazard, chemical goggles as well as an added face shield may be appropriate. A face shield is required any time there is a high risk of explosion, a large splash hazard, or a highly exothermic reaction.

8.3.4. Chemical gloves should consist of, at the least, nitrile but double gloving with nitrile underneath neoprene gloves can add an extra layer of protection.

8.3.5. A basic full-length laboratory coat or apron.

8.3.6. Any questions or concerns in reference to PPE requirements, contact EH&S for a risk assessment at **lab-chemicalsafety@gatech.edu**

8.4. **Requirements for Waste Management of PECs**

8.4.1. Collect all waste as per the appropriate designated waste stream. Contact EH&S with any questions or concerns.

8.4.2. Piranha waste must be stored in a glass container, never plastic. Only close Piranha and aqua regia waste containers when solution is completely cooled.

8.4.3. Ensure waste is stored in compatible waste container. Use secondary containment for hazardous waste. Ensure all waste containers are closed when not in use.

8.4.4. Use the GT CMIS database to initiate and create a waste label.

8.4.5. Contact GT EHS Hazardous Materials Unit for proper disposal of the waste.

9. Self-Reactive Chemicals Storage and Use Requirements

9.1. **Self-Reactive Substances and Mixtures:** As defined under GHS, explosives, organic peroxides, and oxidizers are excluded as self-reactive substances or mixtures. A self-reactive is a thermally unstable liquid or solid liable to undergo a strongly exothermic decomposition even without participation of oxygen (air). (GHS) Please note that peroxides and oxidizers are covered specifically in chapter 8.

9.1.1. **Type A:** Can detonate or deflagrate rapidly when packaged.

9.1.2. **Type B:** Explosive properties and which, as packaged, neither detonates nor deflagrates rapidly, but is liable to undergo a thermal explosion.

9.1.3. **Type C:** Explosive properties when the substance cannot detonate or deflagrate rapidly or undergo a thermal explosion.

9.2. **Self-Reactive Substances and Mixtures Permissible Storage and Use:**

9.2.1. Hazards: There are broad range of Self-Reactive chemicals, which yield a broad range of hazards. Examples are as follows:

9.2.1.1. Temperature requirements are an issue for some chemicals, (i.e. azo compounds). They may have a Self-Accelerating Decomposition Temperature (SADT), the lowest temperature for the self-reactive chemical to remain stable before it will undergo self-accelerating decomposition, potentially resulting in a fire or detonation.

9.2.1.2. During the decomposition process, self-reactive chemicals may degas. This can cause a bulging container unless a specially vented cap is used. If a vent cap is used, keep vented containers upright.

Several factors can increase the hazardous chemical nature when conducting reactions. These include the following:

9.2.1.2.1. Surface area
9.2.1.2.2. Ability to remove heat from reaction
9.2.1.2.3. Rate of reagent addition
9.2.1.2.4. Changes in reactant concentration
9.2.1.2.5. Catalysts.

9.3. **Storage and Usage Requirements of Self-Reactive Chemicals:** Some self-reactive chemicals are dangerously reactive. They can decompose if exposed to:

9.3.1. Sunlight
9.3.2. Slight heat
9.3.3. Friction
9.3.4. Mechanical shock
9.3.5. Contamination
9.3.6. Incompatible materials.

Please consult the Handling and Storage section of the SDS for the self-reactive material in use for specific requirements. Refer to applicable manufacturer's special instructions or recommendations. If you have any questions or concerns, contact Georgia Tech EH&S at lab-chemicalsafety@gatech.edu.

9.4. **Personal Protection Equipment Requirements for Self-Reactive Substances:** The level and type of PPE required is dependent upon the task being performed in the laboratory as well as the hazard level and quantity of chemical being used. The following PPE recommendations are recommendations based upon non-specific situations. Please note PPE requirements for working with self-reactive chemicals vary from lab to lab. Consult the laboratory policy on PPE specific requirements for your laboratory as well as the SDS for the materials you are using.

9.4.1. Safety glasses that meet ANSI Z87.1 2010 standard must be worn.

9.4.2. Depending upon the level of splash hazard chemical goggles as well as an added face shield may be appropriate.

9.4.3. A face shield is required any time there is a high risk of explosion, a large splash hazard, or a highly exothermic reaction.

9.4.4. Chemical gloves should consist of at the least nitrile but double gloving with nitrile underneath neoprene gloves can add an extra layer of protection.

9.4.5. A basic full-length laboratory coat or apron.

Any questions or concerns in reference to PPE requirements, contact EH&S for a risk assessment.

9.5. **Requirements for Engineering Controls:**

9.5.1. Any self-reactive material should be handled and used in a certified glove box or fume hood.

9.5.2. Consult the SDS for any specific engineering control requirements.

9.6. **Requirements for Waste Management:**

9.6.1. Collect all waste as per the appropriate designated waste stream. Contact EH&S Hazardous Materials Unit with any questions or concerns and to coordinate pick-up/disposal.

9.6.2. Ensure waste is stored in compatible waste container.

9.6.3. Use secondary containment for hazardous waste. Ensure all waste containers are closed when not in use.

9.6.4. Use the GT CMIS database to initiate and create a waste label.

10. Self-Heating Chemicals Storage and Use Requirements

10.1. **Self-Heating Substances and Mixtures:** Any liquid or solid, other than a pyrophoric, which by reaction with air and without energy supply, is liable to self-heat. What differentiates a self-heating substance from a pyrophoric is that a self-heating material, by definition, will only ignite when in larger amounts and after a long period of time.

10.1.1. Hazards: As defined in GHS, there are two categories:

10.1.1.1. **Category I:** These self-heating materials are more reactive, self-heat more readily and may catch fire. A positive result is obtained in a test using a 25 mm sample cube at 140°C.

10.1.1.2. **Category II**: These materials self-heat in larger quantities and may catch fire.

10.1.1.2.1. A positive result is obtained in a test using g a 100mm sample cube at 140° C and a negative result is obtained in a test using a 25 mm cube sample at 140°C and **t**he substance or mixture is to be packed in packages with a volume of more than 3m^3 or;

10.1.1.2.2. A positive result is obtained in a test using g a 100 mm sample cube at 140° C and a negative result is obtained in a test using a 25 mm cube sample at 140°C, a positive result is obtained in a test using a 100 mm cube sample at 120°C and the substance or mixture is to be packed in packages with a volume of more than 450 L; or

10.1.1.2.3. A positive result is obtained in a test using a 10mm sample cube at 140°C and a negative result is obtained in a test using a 25 mm cube sample at 140°C and a positive result is obtained in a test using a 100 mm cube sample at 100°C.

10.1.2. Materials that will undergo self-heating do so very slowly whereby the amount of heat produced during this process exceeds the rate of heat loss. The temperature will rise, which may lead to ignition and combustion.

10.1.2.1. The degree of the fire hazard associated with self-heating substances is based on four interrelated forces:

10.1.2.1.1. The volume of the material**.**

10.1.2.1.2. The rate of the reaction.

10.1.2.1.3. The temperature of the surroundings.

10.1.2.1.4. The availability of oxygen or moisture.

10.2. **Self-Heating Substances and Mixtures Permissible Storage and Use**

10.2.1. **Storage and Requirements:** Please consult the Handling and Storage as well as the Hazard Identification section of the SDS for the self-heating material in use regarding specific requirements and a thorough understanding of the properties of the material being used. Refer to applicable manufacturer's special instructions or recommendations.

10.2.1.1. Self-heating substances should be kept away from heat, light, moisture, flammable, or combustible materials.

10.2.1.2. Work in an inert environment when risk of self-heating to the point of ignition is high.

10.2.1.3. To minimize the hazard, work should be conducted using the smallest scale possible and the amount on hand should be at a minimum.

10.2.2. **Personal Protection Equipment Requirements for Self-Heating:** Level and type of PPE required is dependent upon the task being performed in the laboratory as well as the hazardous level and quantity of chemical being used. The following PPE recommendations are recommendations based upon non-specific situations. Please note PPE requirements for working with Self-Heating chemicals vary from lab to lab. Consult the laboratory policy on PPE specific requirements for your laboratory as well as the SDS for the materials you are using.

10.2.2.1. Safety glasses that meet the ANSI Z87.1 2010 standard must be worn.

10.2.2.2. Depending upon the level of splash hazard, chemical goggles as well as an added face shield may be appropriate.

10.2.2.3. A face shield is required any time there is a high risk of explosion, a large splash hazard, or a highly exothermic reaction.

10.2.2.4. Chemical gloves should consist of at the least nitrile. However, double gloving with nitrile underneath neoprene gloves adds an extra layer of protection.

10.2.2.5. A basic full-length laboratory coat or apron is required.

10.3. **Requirements for Engineering Controls:**

10.3.1. Collect all waste as per the appropriate designated waste stream. Contact EH&S Hazardous Materials Unit with any questions or concerns and to coordinate pick-up/disposal.

10.3.2. Use secondary containment for hazardous waste. Ensure all waste containers are closed when not in use.

10.3.3. Use the GT CMIS database to initiate and create a waste label.

11. Toxic Chemicals Storage and Use Requirements

11.1. **Toxic gases used in sprinkler and non-sprinkler equipped laboratories:**

A detailed outline of the requirements specific for Toxic gases can be found in the document, Georgia Tech Dangerous Gas Safety Program. Dangerous Gases | Environmental Health & Safety

11.2. **Toxic Solids and Liquids:** The GHS definition of acute toxicity refers to adverse effects occurring following oral or dermal administration of a single or multiple dose of a substance given within 24 hours or an inhalation exposure within 4 hours.

11.2.1. Acute toxicity values are expressed at approximate LD_{50} (oral, dermal) or LC_{50} (inhalation) values as acute toxicity estimates (ATE).

11.2.1.1. Oral Exposure Route: ATE categories 1-5 are expressed in mg/Kg and are 5, 50, 300, 2000, and 5000 respectively.

11.2.1.2. Dermal Exposure route: ATE categories 1-5 are expressed in mg/Kg and are 50, 200, 1000, 2000, and 5000 respectively

11.2.2. NFPA 400 Classifies Toxic versus Highly Toxic Material for oral and dermal exposure routes. Toxic Material: A material that produces a lethal dose or lethal concentration within the following parameters:

11.2.2.1. Chemical or substance that has a median lethal dose (LD_{50}) of more than 5mg/Kg but no more than 500 mg/Kg of body weight when administered orally to albino rats weighing between 200gand 300geach.

11.2.2.2. Chemical or substance that has a median lethal dose (LD_{50}) of more than 200 mg/Kg but no more than 100 mg/Kg of body weight when administered by continuous contact for 24 hours, or less if death occurs within 24 hours, with bare skin of albino rabbit weighing between 2-3 kg.

11.2.3. **Highly Toxic Material**: A material that produces a lethal dose or lethal concentration within the following parameters:

- 11.2.3.1. A chemical or substance that has a median lethal dose (LD_{50}) of 50 mg/Kg or less of body weight when administered orally to albino rats weighing between 200g and 300g each.
- 11.2.3.2. A chemical or substance that has a median lethal dose (LD_{50}) of more than 200 mg/Kg or less of body weight when administered by continuous contact for 24hours, or less if death occurs within 24 hours, with bare skin of albino rabbit weighing between 2-3 kg or albino rats weighing 200-300 gm each.

11.2.4. **High Hazard Level 4 Contents** include materials that are acute health hazards limited to the following hazard categories:

11.3. **Hydrofluoric Acid**: A solution that is comprised of hydrogen fluoride and water. Hydrofluoric acid is also a contact poison. After coming in contact with the skin, this corrosive material will cause deep tissue burns and eventual liquidation of tissues. By disrupting the electrolyte balance in the body, hydrofluoric acid causes systemic toxicity resulting in cardiac arrest. The pain delay is 1-24 hours after exposure.

11.3.1. **Treatment for dermal exposure to Hydrofluoric Acid:** Calcium gluconate is the only dermal treatment available if you are exposed to HF. Application of 2.5 to 33% calcium gluconate gel. Use for dermal treatment only. It is not a burn ointment. It will aid to react with the HF in the area where it was absorbed. Follow the GT emergency response procedure which is as follows:

- 11.3.1.1. Rinse affected area for 5 minutes.
- 11.3.1.2. Apply the dermal treatment of Calgonate©, calcium gluconate to the exposed area.
- 11.3.1.3. Print 4 copies of the SDS and call the Georgia Tech Police.
- 11.3.1.4. Do not let anyone other than medical personnel remove the calcium gluconate from the affected area.

Fig. 6 Calgonate®: Calcium Gluconate Ointment

11.3.2. **Storage and Usage Requirements of HF:**

- 11.3.2.1. Do not store HF in glass containers.
- 11.3.2.2. Store in containers made of polyethylene, fluorocarbon plastic, lead, or platinum. Place in secondary containment.

11.3.2.3. Store in cool, dry area away from glass, metals, water, other acids, oxidizers, alkalis, combustibles, organics, and ceramics.

11.4. **Toxic Chemicals Permissible Storage and Use:**

11.4.1. The maximum allowable quantity (MAQ) of a toxic liquid and solid per control area in an educational occupancy are 125 liquid gallons and 125 solid pound (NFPA 400).

11.4.2. The maximum allowable quantity (MAQ) of a highly toxic liquid and solid per control area in an educational occupancy are three liquid gallons and three solid pound (NFPA 400).

11.4.3. Secondary containment shall be provided for toxic or highly toxic solids or liquids (NFPA 400).

11.4.4. All open containers of toxic or highly toxic materials shall be placed under appropriate ventilation in accordance with NFPA 400.

11.4.5. Store toxic or highly toxic chemicals away from combustible materials. Consult the SDS for special handling or storage requirements.

11.5. **Personal Protective Equipment Requirements for Toxic Compounds:** The level and type of PPE required is dependent upon the task being performed in the laboratory as well as the hazardous level and quantity of chemical being used. The following PPE recommendations are recommendations based upon non-specific situations. Please note PPE requirements for working with the above listed toxic chemicals vary from lab to lab. Consult the laboratory policy on PPE specific requirements for your laboratory as well as the SDS for the materials you are using. When working with toxic chemicals the PPE required is determined by the level of exposure.

11.5.1. Minimum PPE requirements include safety glasses that meet ANSIZ87.1 2010, lab coat, and nitrile gloves.

11.5.2. Depending upon the level of splash hazard, chemical goggles as well as face shield may be appropriate.

11.5.3. A face shield is required any time there is a high risk of explosion, a large splash hazard, or a highly exothermic reaction.

11.5.4. Chemical gloves should consist of at the least nitrile however double gloving with nitrile underneath neoprene gloves can add an extra layer of protection.

11.5.5. A basic full-length laboratory coat or apron.

Any questions or concerns in reference to PPE requirements, contact EH&S for a risk assessment at lab-chemsafety@gatech.edu

11.6. **Requirements for Waste Management of Toxic Substances**

11.6.1. Collect all waste as per the appropriate designated waste stream. Contact EH&S with any questions or concerns.

11.6.2. Ensure waste is stored in compatible waste container. Use secondary containment for hazardous waste. Ensure all waste containers are closed when not in use.

11.6.3. Use the GT Tech CMIS database to initiate and create a waste label.

11.6.4. Contact GT EHS Hazardous Materials Unit for proper disposal of the waste.

12. REFERENCES

12.1. American Chemistry Council, Working with Modern Hydrocarbons and Oxygenated Solvents: A Guide to Flammability, 2011.

12.2. California Fire Chief's Association. Uniform Fire Code, Article 80, January 1987.Georgia International Fire Code Amendments (2007).

12.3. International Fire Code, 2006.

12.4. National Fire Protection Association. Standard 30, 2012, Flammable and Combustive Liquids.

12.5. National Fire Protection Association. Standard 45, 2011, Fire Protection in Laboratories.

12.6. National Fire Protection Association. Standard 400, 2013, Hazardous Materials Code.

12.7. National Fire Protection Association. Standard 495, 2001, Explosive Materials Code.

12.8. National Fire Protection Association. Standard 704, 2012, Standard System for the Identification of the Hazards of Materials for Emergency Response.

12.9. National Research Council, Prudent Practices in the Laboratory, 199

12.10. North Carolina State University, Gas Monitoring Program, 2008.

12.11. Santa Clara County, California Municipal Code. Chapter XIV, Toxic Gas Storage.

12.12. United States Occupational Safety and Health Administration. 29 CFR.1910.1200.

12.13. White, Logan. Hazardous Gas Monitoring. Norwich: Noyes Publications, 2000.

12.14. United Nations, Globally Harmonized System of Classification & Labelling Chemicals, 2009.

13. APPENDICES:

13.1. Common Liquid/Solid Flammable/Combustible/Pyrophoric Materials:

The following is a list of some of the pyrophoric liquid/solid materials that are captured under the Reactive Chemical Safety Program and/or GT Restricted Purchase Rules. This is not a comprehensive list. Researchers are responsible for determining whether the materials they use qualify under the description of a pyrophoric by referring to material' Safety Data Sheet before acquiring the material. If you need assistance in determining if the material you would like to purchase is a pyrophoric, please contact EHS Lab and Chemical Safety:

Material	Formula	CAS	NFPA Toxicity Rating	NFPA Flammability Rating	NFPA Reactivity Rating	NFPA Special Notes
Tetrahydrofuran	C_6H_8O	109-99-9	2	3	2	
Isopropyl Ether	$C_6H_{14}O$	108-20-3	2	3	1	
Vinyl Ether	C_4H_6O	109-93-3	2	4	0	
Acetaldehyde	C_2H_4O	75-07-0	2	4	2	
Cyclohexene	C_6H_{10}	110-83-8	1	3	0	
1,3-Butadiene	C_4H_6	106-99-0	2	4	2	
2-Pentanol	$C_5H_{12}O$	6032-29-7	2	3	0	
4-Methyl-2-pentanol	$C_6H_{14}O$	108-11-2	2	2	0	
Dioxane	$C_4H_8O_2$	123-91-1	2	3	1	
Cyclopentene	C_5H_8	142-29-0	1	3	0	
Ethyl Ether	$(CH_3CH_2)_2O$	60-29-7	1	4	1	

13.2. Appendix II: Common Potentially Explosive Chemicals: Including, Peroxide-Forming Compounds

The following is a list of some of the explosive materials that are captured under the Reactive Chemical Safety Program and/or GT Restricted Purchase Rules. This is not a comprehensive list. Researchers are responsible for determining whether the materials they use qualify under the description of an explosive by referring to material's Safety Data Sheet before acquiring the material. If you need assistance in determining if the material you would like to purchase is considered an explosive, please contact EHS Lab and Chemical Safety:

Material	Formula	CAS	NFPA Toxicity Rating	NFPA Flammability Rating	NFPA Reactivity Rating	NFPA Special Notes
Tetrahydrofuran	C_6H_8O	109-99-9	2	3	2	
Isopropyl Ether	$C_6H_{14}O$	108-20-3	2	3	1	
Vinyl Ether	C_4H_6O	109-93-3	2	4	0	
Acetaldehyde	C_2H_4O	75-07-0	2	4	2	
Cyclohexene	C_6H_{10}	110-83-8	1	3	0	
1,3-Butadiene	C_4H_6	106-99-0	2	4	2	
2-Pentanol	$C_5H_{12}O$	6032-29-7	2	3	0	
4-Methyl-2-pentanol	$C_6H_{14}O$	108-11-2	2	2	0	
Dioxane	$C_4H_8O_2$	123-91-1	2	3	1	
Cyclopentene	C_5H_8	142-29-0	1	3	0	
Ethyl Ether	$(CH_3CH_2)_2O$	60-29-7	1	4	1	

13.3. **Appendix III: Common Self Reactive Chemicals:**

The following is a list of some of the materials considered self-reactive that are captured under the Reactive Chemical Safety Program and/or GT Restricted Purchase Rules. This is not a comprehensive list.~~:~~ Researchers are responsible for determining whether the materials they use qualify under the description of a self-reactive chemical by referring to material's Safety Data Sheet before acquiring the material. If you need assistance in determining if the material you would like to purchase is considered self-reactive, please contact EHS Lab and Chemical Safety:

Material	Formula	CAS	NFPA Toxicity Rating	NFPA Flammability Rating	NFPA Reactivity Rating	NFPA Special Notes
3-Azidosulfonylbenzoic acid	$C_7H_5N_3O_4S$	15980-11-7				
Cyclopentadiene	C_5H_6	542-92-7	1	2	2	
Hydrazine-trinitromethane						
Acetylene	C_2H_2	74-86-2	1	4	3	
Acrylic Acid	$C_3H_4O_2$	79-10-7	3	2	2	
Acrylonitrile	C_3H_3N	107-13-1	4	3	2	
Diketene	$C_4H_4O_2$	674-82-8	2	2	2	
Hydrocyanic Acid	CHN	74-90-8	4	4	1	
Methyl Acrylate	$C_4H_6O_2$	96-33-3	2	3	2	
Vinyl Acetate	$C_4H_6O_2$	108-05-4	2	3	2	
Ethyl Acrylate	$C_5H_8O_2$	140-88-5	2	3	2	

13.4. Appendix IV: Common Self Heating Chemicals:

The following is a list of some of the materials considered self-reactive that are captured under the Reactive Chemical Safety Program and/or GT Restricted Purchase Rules. This is not a comprehensive list.: Researchers are responsible for determining whether the materials they use qualify under the description of a self-heating chemical by referring to material's Safety Data Sheet before acquiring the material. If you need assistance in determining if the material you would like to purchase is considered self-heating, please contact EHS Lab and Chemical Safety:

Material	Formula	CAS	NFPA Toxicity Rating	NFPA Flammability Rating	NFPA Reactivity Rating	NFPA Special Notes
Potassium Sulphide	K_2S_x	37199-66-9	3	1	0	
Sodium Borohydride	$NaBH_4$	16940-66-2	3	0	2	W
Titanium Disulphide	TiS_2	12039-13-3	2	0	1	
N,*N*-Dimethyl-4-nitrosoaniline	$ONC_6H_4N(CH_3)_2$	138-89-6	2	0	2	
Sodium Hydrosulphide	$NaSH \cdot xH_2O$	207683-19-0	3	2	0	

13.5. **Appendix V: Common Toxic Chemicals:**

The following is a list of some of the materials considered toxic that are captured under the Reactive Chemical Safety Program and/or GT Restricted Purchase Rules. This is not a comprehensive list. Researchers are responsible for determining whether the materials they use qualify under the description of a toxic chemical by referring to material's Safety Data Sheet before acquiring the material. If you need assistance in determining if the material you would like to purchase is considered toxic, please contact EHS Lab and Chemical Safety:

Material	Formula	CAS	NFPA Toxicity Rating	NFPA Flammability Rating	NFPA Reactivity Rating	NFPA Special Notes
Hydrofluoric Acid	HF	7664-39-3	4	0	0	ACID
Acrolein	C_3H_4O	107-02-8	3	3	2	
Sulfur Dioxide	SO_2	7446-09-5	3	0	0	
Thionyl Chloride	$SOCl_2$	7719-09-7	4	0	2	
Peracetic Acid	$C_2H_4O_3$	79-21-0	3	2	2	OX
Methyl Vinyl Ketone	C_4H_6O	79-84-4	4	3	2	
Boron Trifluoride	BF_3	7637-07-2	3	0	1	
Bromine	Br	7726-95-6	4	0	0	OX
Cyanogen	C_2N_2	460-19-5	4	4	2	
Ethylene Oxide	C_2H_4O	75-21-8	3	4	3	
Formaldehyde	CH_2O	50-00-0	3	4	0	