Research
Research Laboratory & Safety Services

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Highly Reactive Chemicals Hazard Class
Standard Operating Procedure

1. Purpose

This standard operating procedure (SOP) is intended to provide guidance on how to safely work with highly reactive chemicals in a University of Arizona (UA) laboratory. Laboratory personnel should review this SOP, as well as the appropriate Safety Data Sheet(s) (SDSs), before using highly reactive chemicals. If you have questions concerning the requirements within this SOP, contact the Approval Holder (AH)/Approval Safety Coordinator (ASC), or the Research Laboratory & Safety Services (RLSS).

2. Scope

This hazard class SOP only addresses safety issues specific to the high reactivity hazard of a chemical; several hazard class SOPs may be applicable for a specific chemical. Organic peroxides are considered to be both explosives and highly reactive chemicals; refer to both hazard class SOPs for work with these chemicals.

3. Hazard Description

Highly reactive chemicals are those that, under certain circumstances, are unstable and may cause a physical hazard. The following hazards are included within this hazard class:

- Self-reactive: Chemicals outside of the explosive, oxidizing, and organic peroxide classifications that undergo a highly exothermic (heat-releasing) decomposition in the presence of heat
    - Ex: Arsine, Diborane, Hydroxylamine, etc.
- Pyrophoric: Chemicals that ignite, even in small quantities, when exposed to air
    - Ex: Silane gas, Dichloroborane, White phosphorous, etc.
- Self-heating: May catch fire: Chemicals, other than pyrophorics, that self-heat when exposed to air, even in the absence of an energy supply such as a hot plate
    - Ex: Magnesium, Sodium sulfide, etc.
- Organic peroxides: Chemicals that may be liable to explosive decomposition, burn rapidly, be sensitive to impact/friction, or react dangerously with other substances
    - Ex: Hydrogen peroxide, Diethyl ether, Tetrahydrofuran, etc.
- Water-reactive: Chemicals that either react violently or release a toxic (or flammable) gas upon contact with water
    - Ex: Calcium oxide, Phosphorous pentachloride, Sodium, Potassium, etc.

Peroxides are some of the most common and most shock-sensitive chemicals found in laboratories. Organic peroxides supply both the oxygen and the fuel source required to start a fire; all they need is a spark. Some chemicals are naturally occurring organic peroxides (e.g. hydrogen peroxide). However, others can form peroxides with air, moisture, impurities, or even time during regular storage (e.g. isopropyl ether, diethyl ether). Once peroxides have been formed, an explosion can occur when distilling,

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concentrating or evaporating these chemicals. Explosions can even be caused by twisting off a cap of a reagent bottle if peroxides formed between the threads of the cap.

4. General Control of Hazards

The Highly Reactive Chemicals hazard class includes a wide variety of hazards. Though basic control measures may be implemented for the class as a whole, the SDS of highly reactive chemicals should be consulted for specific information on hazard controls and safety measures.

The following general control measures should be implemented whenever using or handling highly reactive chemicals:

- Whenever possible, use a less hazardous alternative chemical to complete the experiment.
- Minimize the quantity and/or concentration of highly reactive chemicals used or synthesized to the smallest amount immediately needed for an experiment.
- Plan experiments involving highly reactive chemicals carefully, including consulting the SDS(s). Do not handle highly reactive chemicals until all safety precautions have been read and understood.
- Ensure an appropriate fire extinguisher is nearby before using highly reactive chemicals.
- All containers of highly reactive chemicals should be dated as soon as they are received, and never opened after their expiration date.
- Combine highly reactive chemicals to other chemicals slowly, watching for increased heat or release of gases.
- Consider the additional hazards of scaled-up reactions that may not be obvious on a smaller scale.
- Consult your AH/ASC if you are working with a new chemical, or if you are unsure of the safety precautions required for the highly reactive chemical.
- Provide a mechanism for adequate temperature control and heat dissipation when handling these chemicals.

5. Engineering Controls

Since many highly reactive chemicals liberate a flammable and/or toxic gas when exposed to water vapor or air, they must be used in a chemical fume hood to prevent exposure to these gases.

If a chemical is air-sensitive, it should be used in a glove box under an inert atmosphere. If a glove box is not available, consult your AH/ASC on how to control the hazards involved with air-sensitive highly reactive chemicals.

Utilize safety barricades or shields if there is a possibility of an explosion or violent chemical reaction. Place these barricades so that all laboratory workers in the area are protected from the explosion hazard.

6. Personal Protective Equipment

At a minimum, all laboratory workers must wear safety glasses, long pants, closed-toed shoes, a laboratory coat and examination gloves when working with hazardous chemicals in a laboratory.

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Laboratory personnel working with any highly reactive chemicals should wear splash goggles, instead of safety glasses, as well as a 100% cotton or flame-resistant laboratory coat. Heavy gloves and safety barricades should also be considered, depending on the amount and stability of the chemicals being used.

7. Handling and Storage Requirements

Store any highly reactive chemicals away from flammable or combustible materials where they cannot fall or be knocked over easily. Do not store these chemicals in temporary containers (e.g. vials, jars, beakers, etc.); keep them in their original containers. Label all highly reactive chemicals with the date received and the date the container was opened. Because of their high degree of reactivity, only the amount of these chemicals needed for immediate use should be brought into the laboratory. The chemicals' SDSs may be used to obtain specific storage requirements and precautions.

7.1 Self-reactive, Pyrophoric, and Self-heating chemicals:

Store self-reactive, pyrophoric and self-heating chemicals at low temperatures away from direct sunlight, heat, sparks, open flames and hot surfaces. Because pyrophoric chemicals can ignite spontaneously when in contact with air, they must be handled under an inert atmosphere and in a way that prevents exposure to air. Extra care must always be taken when using these chemicals, and laboratory workers should consult their AH/ASC before using them in a laboratory.

Pyrophoric chemicals should be stored under an inert atmosphere or solvent to prevent exposure to air. Storage locations may include inert gas-filled desiccators or glove boxes. If a pyrophoric chemical must be stored below room temperature, the refrigerator/freezer must be an explosion-proof or modified domestic piece of equipment. Only those laboratory workers who have been trained on how to handle highly reactive chemicals should have access to storage areas containing pyrophorics.

7.2 Organic peroxides:

Store organic peroxides at low temperatures, but not at temperatures below the temperature at which they freeze. The sensitivity of most peroxides can be decreased by diluting them with an inert solvent (e.g. hexane). Do not allow contact of peroxides with metal lab ware, tools or equipment.

Peroxide-forming chemicals should be kept away from heat and sunlight and their containers should be tightly sealed after each use. Refrigeration does not prevent peroxide formation. Containers of peroxide-forming chemicals should be labeled with the date received and the date opened. Because of the high potential for fires and explosions, these chemicals must be disposed of one year after the opening of the container, or by the expiration date (whichever is sooner). Laboratory personnel can test for the presence of peroxides to extend the shelf-life by one year.

7.3 Water-reactive chemicals:

Store water-reactive chemicals in closed container in a dry place away from water, sources of water (e.g. sinks and safety showers) and water-containing chemicals (e.g. aqueous buffers, diluted acids). Containers of water-reactive chemicals should be tightly sealed and water-tight.

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8. Waste Disposal

Waste highly reactive chemicals should be collected in compatible containers and segregated from incompatible chemicals. Do not dispose of pure organic peroxides; rather, dilute the peroxides before disposal with water. Dispose of peroxide-forming chemicals one year after the open date or at the expiration date, whichever is sooner. Contact Risk Management Services for further information on the disposal of highly reactive chemicals.

9. Spill and Incident Procedures

Do not attempt to clean up a spill of self-reactive, self-heating, pyrophoric or water-reactive chemicals yourself. Evacuate the area and follow the procedures in the University Chemical Hygiene Plan section on major chemical spills. Inform the RLSS of all major chemical spills.

In the case of an explosion or fire in the laboratory, leave the area immediately, pull the fire alarm, and call 911 from a campus phone (or call 911 from a non-campus phone and mention the incident is on a UA campus).

If a laboratory worker is injured or exposed to highly reactive chemicals, immediately notify the AH/ASC. If a laboratory worker requires immediate medical attention, call 911. Remove contaminated clothing and immediately flush the contaminated areas with water for at least 15 minutes. For eye exposures, immediately remove contact lenses, if present, and flush the eyes with water for at least 15 minutes. Consult the chemical's SDS for more specific information on appropriate first aid. Inform the RLSS and Risk Management Services of the incident as soon as practicable.

10. Designated Area

Designated areas are not required for this hazard class. However, chemicals may belong to multiple hazard classes, and a highly reactive chemical may require a designated area if it belongs to a hazard class that includes particularly hazardous chemicals.