ENVIRONMENTAL HEALTH AND SAFETY
University of Nebraska-Lincoln

Safe Operating Procedure

(Revised 12/22)

CHEMICAL HAZARD ASSESSMENT & RISK MINIMIZATION

Background

In 2015, the American Chemical Society (ACS) published the guide: Identifying and Evaluating Hazards in Research Laboratories, which is available on the ACS website alongside related tools, examples, and templates. These guidelines were developed in response to a number of accidents involving chemicals, one fatal, which recently occurred at several colleges and universities. The intent being to provide comprehensive guidance on managing the hazards unique to laboratory chemical research in academic settings. As part of the guide, the ACS outlines a risk assessment process to identify, evaluate, and mitigate hazards prior to all chemical manipulations. Nationwide this has been recognized as a prudent practice in college and university laboratory operations.

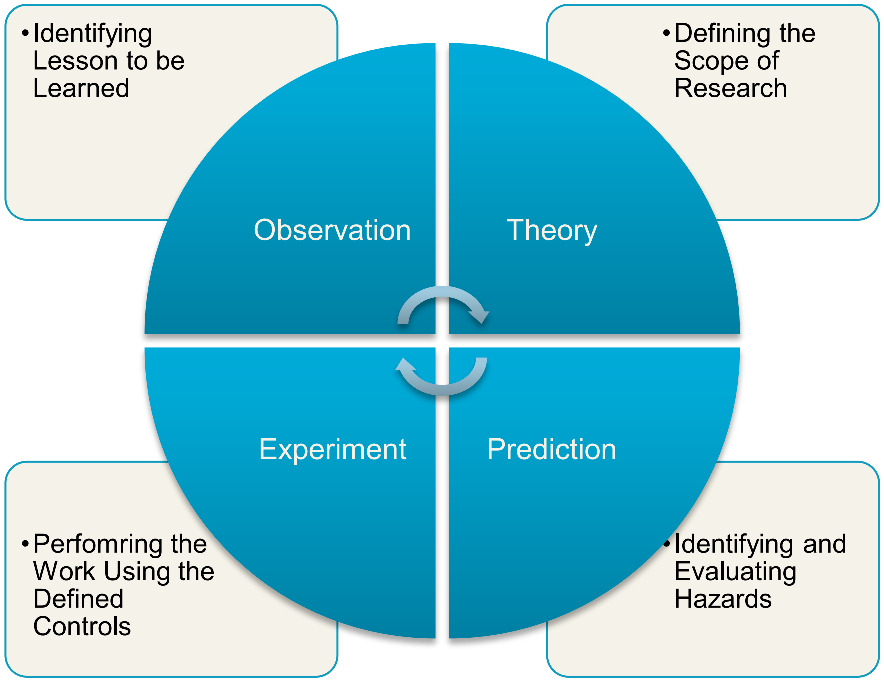
Recognizing that the degree of hazard can vary widely, Environmental Health & Safety (EHS) has sought to assist UNL's academic community with a streamlined system for conducting chemical hazard risk assessments. The goals of the system are:

- Emphasize the synergy between the scientific method of design and the risk assessment process.
- Define chemicals by class and categorize each class by risk.
- Develop safe operating procedures (SOP) to serve as the baseline risk assessment/hazard mitigation plan for most classes of chemicals.
- For each class of chemical, identify those categories that pose an exceptional risk and recommend additional oversight practices in the form of a comprehensive and project-specific risk assessment that is reviewed by a responsible faculty member or supervisor.

Experimental Design & Hazard Analysis/Risk Assessment Process

As noted in the ACS guide, the scientific method allows scientists to methodically plan for, perform, and evaluate the results of experiments. Similarly, the risk assessment process is designed to anticipate hazards, evaluate the level of risk associated with each hazard, selecting mitigation measures to reduce risks, and modifying the risk mitigation plan in response to unexpected hazards that arise during the course of the work. The risk assessment process aligns with and complements the scientific method.

The Figure below, drawn from the ACS guide, illustrates the relationship between the most basic elements of the scientific process (represented by the circle) and the basic elements of the risk assessment process (in the corresponding boxes).



The risk assessment process requires consideration of both the inherent physical and health hazards of a chemical, as well as the hazards posed by associated processes/procedures/ manipulations.

Chemical Classes

Under the Globally Harmonized System (GHS), chemicals are classified according to both physical and health hazards. Chemical classes and categories established under the GHS system are summarized in the following table. Under the GHS system, the relative degree of hazard of chemicals within a certain class (e.g., flammable liquid) is reflected by categories, divisions, or types. For example, a category 1 flammable liquid has a lower flash point and boiling point (greater degree of danger) than a category 4 flammable liquid.

Classes of Physical Hazards	Categories, Divisions, or Types
Explosives	Unstable and Divisions 1.1 through 1.6
Flammable Gases	Categories 1 & 2
Flammable Aerosols	Categories 1 & 2
Flammable Liquids	Categories 1 through 4
Flammable Solids	Categories 1 & 2
Self-Reactive Substances	Types A through F
Pyrophoric Liquids & Solids	Type 1

Self-Heating Substances	Categories 1 & 2
Substances Which in Contact with Water Emit Flammable Gases	Categories 1 through 3
Oxidizing Liquids & Solids	Categories 1 through 3
Oxidizing Gas	Category 1
Organic Peroxides	Types A through F
Corrosive to Metals	Category 1
Gases under Pressure	Groups - Compressed, Refrigerated, Liquefied, & Dissolved
Classes of Health Hazards	Categories, Divisions, or Types
Acute Toxicity Oral, Dermal, & Inhalation	Categories 1 through 5
Skin Corrosion	Category 1, Sub-categories 1A, 1B, 1C
Skin Irritation	Category 2
Serious Eye Damage	Category 1
Serious Eye Irritation	Category 2
Respiratory/Skin Sensitization	Category 1; Subcategories 1A & 1B
Germ Cell Mutagenicity	Category 1, Subcategories 1A & 1B Category 2
Carcinogenicity	Category 1, Subcategories 1A & 1B Category 2
Reproductive Toxicity	Category 1, Subcategories 1A & 1B Category 2 Effects via Lactation
Specific Target Organ Toxicity	Single Exposure; Categories 1 - 3
Specific Target Organ Toxicity	Repeated Exposure; Categories 1 & 2
Aspiration Hazard	Category 1

General Hazard Analysis/Risk Assessment

EHS has developed individual SOPs for each of the above chemical hazard classes. Where classes of chemicals share similar hazards, they are combined into a single SOP. For many laboratory operations, the risk assessment process can be as simple as completing the following steps:

1. Reviewing and understanding the Safety Data Sheets (SDSs) for specific chemicals to be used and adhering to stated precautions. Section 2 of the SDS will identify the GHS Chemical Classes, which will facilitate use of EHS SOPs.
2. Reviewing and understanding the general EHS SOPs for the particular classes of chemicals to be used and implementing the risk mitigation measures.
3. Verifying that the chemicals to be used do not pose exceptional risk. Chemicals posing exceptional risk should be used only after conducting a comprehensive and project-specific risk assessment. See EHS SOP, ***Job Safety Assessments***. The completed risk assessment should be reviewed by a responsible faculty member or supervisor (as described in the next section of this SOP). Chemicals posing exceptional risk are as follows:
    - Explosives – Unstable & Divisions 1.1 through 1.3
    - Organic Peroxides – Type A through C
    - Any Pyrophoric
    - Substances in Contact with Water Emit Flammable Gases – Type 1
    - Self-Reactives – Type A though C
    - Acute Toxicity – Category 1
4. Verifying that the intended work will be conducted at laboratory scale.
    Laboratory scale is defined as: work with chemicals in which the containers used for reactions, transfers, and other handling of chemicals are designed to be easily and safely manipulated by one person. Workplaces that use pilot plant, production level or commercial quantities of chemicals are excluded from the definition of "Laboratory."
5. Verifying that procedures/manipulations or scale/rate of reaction to be conducted with the chemicals do not pose unique hazards that could result in death, serious injury (i.e., amputation, loss of vision, permanent disfigurement), or serious property damage. When a hazard is not known, mitigating steps should be implemented as if the hazard is present. See Appendix A for an example of this.
6. Verifying that the person conducting the work has an understanding of lab safety and the skills required to conduct the intended tasks/procedures/manipulations. This is gained by supervised laboratory work and formal classroom study. It includes, but is not necessarily limited to, the following:
    a. Reading and adhering to the laboratory safety manual. Supervisors have the option of creating their own safety manual/chemical hygiene plan or using the EHS Virtual Manual tool (Resources Tab from EHS Home Page).
    b. Completing the following EHS web-based training modules:
        i. Core 1 - Injury and Illness Prevention
        ii. Core 2 - Emergency Preparedness
        iii. Chemical Safety Training (all four modules)
    c. Properly using appropriate Personal Protective Equipment. See EHS SOP, ***Personal Protective Equipment for Chemical Exposures***.
    d. Demonstration of adequate skills for the tasks to be conducted. This is to be assessed by the responsible faculty member or supervisor.

7. Non-chemical related hazards (e.g., laceration by sharp objects, electrical hazards, etc.) have been considered and appropriate risk mitigation measures adopted.
8. If, in the course of the work, additional or unexpected hazards are identified, stop work, evaluate the hazard, and implement additional risk minimization measures before proceeding.

Specific Risk Assessment (Exceptional Risk/Additional Oversight)

There are two situations when a comprehensive and project-specific risk assessment should be conducted and reviewed by the responsible faculty member or supervisor.

1. When the work does not conform to one or more of the conditions listed above.
2. When the work involves a class of chemical that poses exceptional hazard, as listed below.
    - Explosives – Unstable & Divisions 1.1 through 1.3
    - Organic Peroxides – Type A through C
    - Any Pyrophoric
    - Water Reactives – Type 1
    - Self-Reactives – Type A though C
    - Acute Toxicity – Category 1

It is at the supervisor or faculty member's discretion to define how broadly the risk assessment can be written and remain an effective risk minimization tool based on evaluation of unique circumstances (e.g., experience of the laboratory worker, increments or conditions that greatly change the associated hazards or risk, similarity of experiments, etc.). Examples of situations that may be identified as triggers for modifying/re-visiting the risk assessment include: unexpected hazards observed, near-miss incidents, scale-up beyond a pre-determined threshold, introduction of new laboratory workers, changes to apparatus or experimental conditions (e.g., pressure, time, temperature, etc.) beyond a pre-determined threshold, etc.

Guidance for conducting a comprehensive and project-specific risk assessment is provided in the EHS SOP, ***Job Safety Assessments*** and in the referenced ACS publication. Additional guidance is provided in Appendix A.

Appendix A
Notes on Hazard Assessments and Risk Mitigation

When considering hazards, it is sometimes helpful to identify them by type and address each individually. With regard to chemical hazard assessments, these types could be divided into:

1. Chemical hazards; both physical and health. SDSs deal very well with this type of hazard. For example, chemicals that are highly toxic are classified as 'Acute Toxicity – Category 1', explosive, self-reactive and chemical with similar high hazards are classified as well. SDSs contain additional information as well with regard to hazards. In addition to this, a chemical with a high hazard requires specialized techniques or procedures required for the storage, handling and use. A good example of this is the transfer of pyrophoric liquids. The SDS and EHS SOPs will provide some guidance and technical information on the chemical and hazard class but other resources will have to be referenced for handling and use.
2. Equipment/Apparatus hazards. Examples of these are reactions conducted under high pressure, temperature, etc. Like those hazards listed above, these are generally known and can be minimized.
3. Reaction hazards. Of the hazards on this list, reaction hazards are the most difficult to assess. For those reactions described in literature, most provide little, if any, information on reaction hazards such as exothermicity, induction periods or by-products (i.e., toxic gases). In addition to this, researchers often need to use different reactants in order to conduct their research. Exactly how these reactants will react cannot be known.
4. Post reaction hazards. Example of this includes quenching excess reactants. Again, like chemical and technique hazards, these are known and specific and well-defined methods are available to minimize the risks.

Thus, of the four types of hazards listed above, only reaction hazards are difficult to assess and minimize. One method that can be used is to take standardized actions to minimize the reaction hazards that cannot be determined. The following table shows one way this can be approached:

<table>
<tr><th>Hazard Assumed Unless Otherwise Known</th><th>Standard Risk Minimization</th><th>Specific Parameter Risk Minimization</th></tr>
<tr><td>1. Reaction is exothermic</td><td rowspan="4">• Standard PPE
• Work conducted in a fume hood
• Sash closed when possible
• Initial work-up done at the smallest quantity described in the literature</td><td>• Thermometer in reaction vessel
• Dropwise addition of reactant
• Ice bath or other means of cooling immediately available</td></tr>
<tr><td>2. Generation of gases/vapors whether or not toxic</td><td>• Venting reaction vessel/ apparatus</td></tr>
<tr><td>3. Reactants/products/ by-products are air/oxygen/moisture reactive or peroxide forming</td><td>• Work conducted under a nitrogen blanketed reaction vessel in a fume hood or in a nitrogen atmosphere (glove box)</td></tr>
<tr><td>4. Reaction has an induction period</td><td>• Thermometer in reaction vessel
• Dropwise addition of reactant
• Time allowed for induction prior to additon of additional reactant</td></tr>
</table>

		• Ice bath or other means of cooling immediately available
5. Flammable solvents used with equipment or environments that contain ignition sources		None
6. Reactants/reaction/products/byproducts are potentially shock-sensitive/explosive		• Work conducted behind a blast shield • Initial work up <20 mmole
7. Work/reaction unattended or with a constant flow of water		None

Changes that Must Result in a Re-evaluation:

- Scale of reaction has increased
- Concentration of reactant(s) has increased
- New chemical stocks are being used, especially catalysts
- A new but related reactant is introduced

Be aware that other hazards can be present, such as cracked glassware that fails during a reaction or improperly setting the temperature of a heating mantel. These potential hazards should be considered.