UNIVERSITY OF VICTORIA
Occupational Health, Safety and Environment

Chemical Safety – Special Hazards

Safe Work Procedure (SWP – 004)

AZIDES

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REVISION HISTORY

	Revision Date	*Author*	*Position*
1.	May 18 2022	Paraskevi Lagaditis	OHSE consultant

DOCUMENT APPROVAL

Approved by: Laboratory Safety Committee

Jody Spence	May 18, 2022
Chair, Laboratory Safety Committee	*Date Approved*

**This revision replaces all previous versions of this document. If a copy is printed, it is the users' responsibility to verify the copy is the most current version of the document.*

University of Victoria

PURPOSE

To provide guidance and instruction of the safe use and handling in laboratories of azides. In addition to this general Safe Work Procedure (SWP), each lab must develop a lab-specific work procedure unique to the experiments and activities being performed. The Lab SWP must be reviewed by OHSE (see Procedures, #7).

SCOPE

The SWP applies towards the handling and disposal of azides, such as sodium azide (NaN_3, the most commonly used commercial source of azide) or organic azides.

TRAINING

The following training is required to be completed prior to working with azides:

- WHMIS
- Lab Safety for Lab Workers
- Lab SWP with documented signoff by the individual and their supervisor.

Refresher training in the General and Lab SWP must be provided when:

- There has been an extended timeframe of inactivity, or
- There has been an incident or injury, or
- 2 years has elapsed since the original training.

REGULATION AND POLICY

The University of Victoria will follow WorkSafeBC Occupational Health and Safety Regulation Part 30.19 & 30.20 and the University of Victoria Occupational Health, Safety & Environment Department.

RESPONSIBILITY

It is the responsibility of personnel undertaking activities with special hazards to complete all required training and adhere to these safe work procedures, including any additional lab or job-specific procedures.

It is the PI's or supervisor's responsibility to ensure that individuals working with special hazards have been trained prior to commencing work and have demonstrated competency in safely performing all duties associated with the special hazard in accordance with these procedures.

MATERIALS

- Waste containers for solid or solution waste dedicated to inorganic azides are labeled with "azide contaminated waste" to ensure no other incompatible materials (in particular acids, halogenated solvent or heavy metal salts) are added and potentially cause an explosion.
- Waste bags labeled as "azide contaminated waste" to collect all contaminated material (e.g. gloves, weigh boats/paper etc) used to handle inorganic azides.
- Blast shields should be used when handling or preparing azides

HAZARD

Inorganic and organic azides are explosive compounds with the slightest addition of energy from external sources (heat, light, pressure).

Sodium azide

- NaN_3 is a solid and is stable at room temperature; however, NaN_3 will violently decompose when in contact with incompatible materials or if it is heated above 275 °C.
- NaN_3 is also highly toxic when absorbed through the skin or ingested orally. Azide toxicity is analogous to cyanides such that they also form strong complexes with hemoglobin and block oxygen transport in the blood.
- NaN_3 is reactive with water and concentrated solutions can lead to the formation of potentially explosive hydrazoic acid (HN_3) and emits toxic vapors.

Organic azides

- Olefinic, aromatic, or carbonyl azides are less stable than aliphatic azides.
- General methods to determine the safety of organic azides:
    - Carbon to nitrogen (C/N) ratio provides a means to estimate the stability of organic azides
        - Formula: (number of carbon atoms, $\#_C$ + number of oxygen atoms, $\#_O$) / (number of nitrogen atoms, $\#_N$)
    - **Never isolate organic azides with C/N < 1**; these species must be synthesized only *in situ* as transient reaction intermediates AND as the limiting reagent. These experiments must be limited to < 1 g scale.
    - Organic azides with C/N ratios between 1 and 3 can be safely synthesized; **however**, they should be stored as solutions (< 1 M concentration) below room temperature (fridge or freezer). These experiments must be limited to < 5 g scale.
    - Rule of six: six carbons (or other atoms of about the same size) per azide group render organic azides relatively safe to use. These experiments must be limited to < 20 g scale unless a specific risk assessment is carried out, including safety evaluation of the specific azide via analytical methods (TGA, DSC, shock test).

PROCEDURE

1. Handling

a. Always wear personal protective equipment (nitrile gloves, safety glasses and laboratory coat) when handling azides.
b. Use a blast shield to set up experiments with azides behind of or use a face shield.
c. Handle only in a fume hood.
d. Use the smallest amount of azide possible for your experiment. Follow scalability guidelines given above based on the type/structure of the azide being prepared/reacted.
e. Ensure the following are not present in the fume hood while handling sodium azide:
    i. Heavy metals or their salts (including barium, lead, and copper)
    ii. Acids
    iii. Halogenated solvents (such as dichloromethane or chloroform)
    iv. Bromine
    v. Dimethyl sulfate
f. Use plastic or ceramic spatulas and avoid metal spatulas to handle azides.

g. Avoid scratching solid azides.
h. Never expose organic azides to ground glass joints – use rubber septa or specialized glassware.
i. Never use elevated temperature for purification, such as distillation or sublimation; limit purification to extraction or precipitation, or low temperature vacuum transfer.
j. Avoid grinding, scratching, strong agitation or otherwise causing friction with azides.
k. Do not use a rotary evaporator to concentrate azide containing solutions for materials with CN < 4.
l. Only dilute sodium azide solutions (0.1 – 2 %) are permitted for preservation purposes.

2. Storage

a. Ensure all stored azides are labeled with received, open and/or synthesized dates.
b. Do not store azides on opens shelves or counters or on metal shelves.
c. Store synthesized organic azides below room temperature and in amber bottles.
d. Store in tightly closed containers in a cool, well-ventilated area away from heat, air, light and moisture.
e. Store away from metals, acids, carbon disulfide, bromine, dimethyl sulfate, and halogenated solvents.

3. Spills

a. Follow OHSE's general spill response instructions.
b. Do not attempt to clean up any spill if not trained. Seek assistance or call Campus Security (250-721-7599)
c. Specific steps for small azide spills in the fume hood.
    i. Solution (250 mL or less):
        - Confine spill to small area with absorbent pads.
        - Clean surfaces with a pH > 9 buffer solution.
        - Wipe surfaces with absorbent pads.
        - Collect all materials and label all containers or bags used in the clean-up for disposal through the hazardous waste system indicating the material is "azide contaminated waste".
        - Keep the waste containers or bags in a fume hood until hazardous waste pick-up day.
    ii. Solid (250 g or less):
        - Cover gently solid spills with paper towels or absorbent pads.
        - Wet the covering with a pH > 9 buffer solution to prevent raising dust.
        - Wipe up the wetted towels or pads.
        - Clean surfaces with a pH > 9 buffer solution.
        - Wipe surfaces with absorbent pads.
        - Collect all materials and label all containers or bags used in the clean-up for disposal through the hazardous waste system indicating the material is "azide contaminated waste".
        - Keep the waste containers or bags in a fume hood until hazardous waste pick-up day.

d. Specific steps for large (more than 250 mL or 250 g) azide spills in the fume hood or any spill outside the fume hood

    i. Secure the area and warn others.
    ii. Immediately evacuate the area.
    iii. Post “do not enter” signs on the doors of the lab.
    iv. Contact Campus Security at 250-721-7599.

e. Complete a Department Incident & Hazard Report Form to document and review the spill incident.

4. Decontamination

a. Decontaminate work surfaces and glassware with pH > 9 buffer solution
b. Collect all washings into a labeled waste container “azide contaminated waste”
c. Decontaminate finally with 70% ethanol.

5. First Aid and Emergencies

a. Call 911 to summon an ambulance if there is a medical emergency.
b. Call Campus Security at 250-721-7599 for first aid.
c. If material has contacted the eyes, use emergency eyewash and flush for at least 15-20 minutes.
d. For skin contact, flush affected area with running water for at least 15-20 minutes.

6. Waste Disposal

a. Never dispose dilute aqueous azide solutions down the sink.
b. Collect all azide containing solutions, stock materials or washings in a designated bottle/container label “azide contaminated waste”.
c. Affix a green hazardous waste sticker on the containers or bags.
d. Submit an online request for hazardous waste pick-up from OHSE.
e. Store the hazardous waste containers/bags in a fume hood until hazardous waste pick up day.

7. Lab SWP

In additional to this general SWP, each lab that using or preparing azide compounds requires a Lab SWP that includes specific procedures for:

a. Outline of the azides to be used or prepared.
b. Maximum permitted scale of the reaction.
c. Storage details.
d. Designated areas to conduct experiments and signage.
e. Experiment details including specifics of labware required.
f. Spill containment and response.
g. Emergency first aid response.

REFERENCES

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