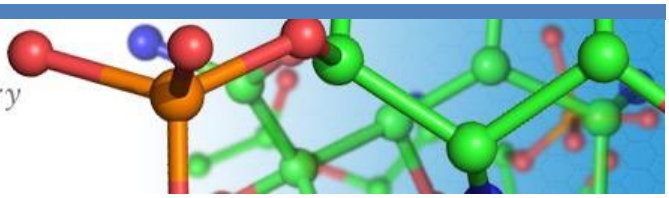
UNM | Department of Chemistry & Chemical Biology



Standard Operating Procedure
Safe Handling of Azido Compounds

Facility:	Chemical Research Laboratory 368 Riebsomer Dept. of Chemistry & Chemical Biology
Lab Director:	Brian Gold 372 Riebsomer Office Phone: 321-298-4734 (cell)
Scope:	This SOP details the safe handling practices of organic and inorganic azides.
Last Revision:	2/16/2021

1. Purpose:

The purpose of this document is to provide the information necessary to safely use organic and inorganic azides in the Gold laboratory and to comply with safety requirements of the Department of Chemistry and Chemical Biology at UNM and the OSHA Standards.

2. Hazard Identification:

Sodium Azide (CAS: 26628-22-8) & other (organic) azido compounds

- *Explosion Hazard* – Sodium azide poses a high explosion hazard when exposed to heat, rapidly decomposing to release nitrogen gas above the melting point (275 °C). Exposure to heavy metals or metal surfaces generates heavy metal azide salts, which are highly shock-sensitive and may spontaneously detonate. Sodium azide reacts violently with carbon disulfide, bromine, nitric acid, and dimethyl sulfate. Sodium azide reacts with halogenated organics to form explosive organic azides – never use halogenated organic solvents (e.g., dichloromethane). Organic azides pose similar hazards to sodium azide, especially those of C:N ratio < 3.
- *Health Hazard* – Sodium azide is very acutely toxic. Sodium azide may be fatal if inhaled, absorbed through the skin or swallowed. Target organs are eyes, skin, lungs, the central nervous system and the brain, cardiovascular system, and kidneys. Sodium azide in solution is rapidly absorbed through the skin. Sodium azide hydrolyzes in water and acid to hydrazoic acid, a highly toxic, volatile liquid posing a severe inhalation hazard.

3. Engineering & Administrative Controls:

- Azides must be handled appropriately:
  - Only handle/use azides within the chemical fume hood, which is designed to pull air and fumes up and away from the user
  - Blast shields and a fume hood are required for all azides known to be or expected to be explosive (all azides unless data exists to suggest otherwise)
  - Clean areas where azides are used regularly
  - For sodium azide, **avoid halogenated solvents**
  - Avoid contact with metals
    - weigh with plastic or ceramic spatulas – **never use a metal spatula**
    - do not dispose in drain,
    - use specified glassware (new or properly cleaned) to avoid contamination of trace metal species
  - avoid grinding, scratching, strong agitation, or other friction
    - avoid glassware with ground glass joints when possible
    - thoroughly rinse ground glass prior to attaching to other glassware
  - Avoid concentrating when possible
  - Minimal quantities should be used
- Azides must be stored appropriately:
  - Below room temperature
  - Away from acids and other incompatible materials
- All lab personnel who use azido compounds must be trained on their hazards, including being familiar with this SOP and general CCB Chemical Safety Protocols.
- The door to the Gold lab is posted with signage indicating the presence and hazards associated with organic and inorganic azides

4. Personal Protective Equipment (PPE)

- *Hand Protection*: Appropriate gloves must be worn when handling azides. Silver shield gloves under nitrile are recommended for handling azides of high toxicity (https://sps.honeywell.com/us/en/products/safety/hand-protection/gloves/silvershield-ssg)
- *Eye Protection*: Safety glasses or splash goggles must be worn when handling azides.
- *Skin and Body Protection*: A lab coat must be worn when handling azides. Blast shields and a fume hood are required for all azides known to be or expected to be explosive (all azides unless data exists to suggest otherwise)

5. Waste Disposal

Under no circumstances should you pour sodium azide solutions down the drain. Reaction with lead or copper pipes can build up highly explosive azide salts. Dispose of all used or unwanted material, including dilute solutions, through DRS.

- All aqueous solutions suspected of containing azides should be tested for azides, and deactivated, according to the following procedures:[1]

- The following colorimetric testing can be used to detect sodium azide (NaN3) in your used solution: a drop of the solution is placed in the depression of a spot plate and treated with 1-2 drops of dilute hydrochloric acid and 1 drop of ferric chloride solution. Let the spot plate be gently heated. If the mixture turns red, it is an indication of the presence of hydrazoic acid, which means that sodium azide is in the solution.
- **DEACTIVATION OF SODIUM AZIDE:** Sodium azide is among the P-listed hazardous wastes regulated by the EPA. As a discarded commercial chemical product, off specification species, container residues, or spill clean-up material, it must be managed as a hazardous waste. Dilute solutions (5% or less) managed as part of your experiment protocol can be destroyed by reaction with nitrous acid.

$$2\ NaNO_2 + H_2SO_4 \rightarrow 2\ HNO_2 + Na_2SO_4$$
$$2\ NaN_3 + 2\ HNO_2 \rightarrow 3\ N_2 + 2\ NO + 2\ NaOH$$

The operation must be carried out in a chemical hood due to the formation of nitric oxide. An aqueous solution containing no more than 5% sodium azide is arranged into a three-necked flask equipped with a stirrer, a dropping funnel, and an outlet with plastic tubing to carry nitrogen oxides to the laboratory chemical hood flue. A 20% aqueous solution of sodium nitrite containing 1.5 g (about 40% excess) of sodium nitrite per gram of sodium azide is added with stirring. A 20% aqueous solution of sulfuric acid is then added gradually until the reaction mixture is acidic to pH paper.

Caution: The order of addition is essential. If the acid is added before the nitrite, poisonous volatile HN_3 will be generated.

When the evolution of nitrogen oxides is over, the acidic solution is tested with starch-iodide paper; if it turns blue, it means that excess nitrite is present and decomposition is complete. The reaction mixture is then presumably safe enough to be washed down the drain. However, you should treat any chemical as a hazardous waste as though they are not, so it should be poured into a hazardous waste container instead. Note that the solution must be neutralized with dilute NaOH solution to pH 6-9 prior to disposal.

All personnel involved in deactivating sodium azide shall conduct inspections, maintenance, or other activities to ensure that the process does not result in spills, leaks, or emissions into the environment prior to deactivation of the material.

Sink disposal of solutions of azide compounds that have not been deactivated should be avoided whenever possible. If some does get down the drain, please flush copious amounts of water to avoid accumulation of explosive deposits.

- Following deactivation, all aqueous and organic waste solutions containing azides should be kept in separate waste containers and disposed of through EH&S.

6. Emergency Procedures[2]

Accidental Exposure

- *Skin Contact*: Remove contaminated clothing and rinse off affected skin immediately with soap and copious amounts of water for at least 15 min and then seek medical attention.
- *Eye Contact*: Use the eye wash to rinse the eye thoroughly for at least 15 min, occasionally lifting upper and lower eyelids and rolling the eyeballs around and then seek medical attention.
- *Inhalation*: Move into fresh air and seek medical attention immediately.
- *Ingestion*: Rinse mouth with water. Seek medical attention immediately. Provide the medical team with the Safety Data Sheet.

Spills

- Sweep up spills of solid sodium azide carefully, and try to avoid dust formation. Use a cloth dampened with soap water with a pH of 10 if necessary to avoid dust. Place the material into a non-metal container.
- Wipe up solutions with chemical absorbent pads.
- Once cleaned up, wipe the area thoroughly with water with a pH of 9.
- If the spill is outside the hood and too big to handle safely, call 911. Evacuate the area immediately, alerting others. Close the door and prevent people from entering

7. References

1. Northeastern University, EHS. “Sodium Azide”.
2. University of Illinois, Division or Research Safety. “Sodium Azide NaN_3”.
3. University of Wisconsin–Madison, EHS. “Safe Handling of Sodium Azide (SAZ)”.
4. University of Massachusetts, Amherst, EHS. “Sodium Azide and Azide Compounds SOP”.
5. Stanford University, EHS. “Information on azide compounds”
6. Bräse, S., Gil, C., Knepper, K., Zimmermann, V. “Organic Azides: An exploding diversity of a unique class of compounds” *Angew. Chem. Int. Ed*., **2005**, *44*, 5188.
7. Organic Azides: Synthesis and Applications; Bräse, S., Banert, K., Eds.; Wiley-VCH: Weinheim, 2010
8. Scriven, E. F. V.; Turnbull, K. *Chem. Rev.* **1988**, *88*, 297.
9. (a) Hassner, A.; Stern, M.; Gottlieb, H. E.; Frolow, F. *J. Org. Chem*. **1990**, *55*, 2304. (b) Churchill, D. G. *J. Chem. Educ.* **2006**, *83*, 1798. (c) Conrow, R. E.; Dean, W. D. *Org. Process Res. Dev*. **2008**, *12*, 1285.
10. Kolb, H.C., Finn, M.G., Sharpless, K. B. “Click Chemistry: Diverse Chemical Function from a Few Good Reactions,” *Angew. Chem. Int. Ed*., **2001**, *40*, 2004.
11. Center for Disease Control and Prevention. “Facts about sodium azide”
12. National Research Council: *Prudent Practices for Laboratories (Supplemental CD)*. National Academy Press: Washington, DC, 2011.

8. Training Requirements

- New users of sodium azide, or other azido compounds, should be trained by experienced users and/or the PI. This SOP provides a guide, however, researchers should also familiarize themselves with the specific compounds to be used via the SDS and the literature.
- Minimal quantities should be used < 200 mg. Efforts to “scale up” require approval.

Principal Investigator SOP Approval

By signing and dating here, the Principal Investigator certifies that this Standard Operating Procedure (SOP) for Using Azides is accurate and provides information sufficient to safely use azides in the Gold laboratory.

Signature Printed Name/Title Date

By signing and dating here, the Principal Investigator certifies that this Standard Operating Procedure (SOP) for Using Azides

Name	Signature	Date