Acutely Toxic Gases (ATGs)

H280 H330 H331 H332 H333

Areas with blue text indicate that information must be provided or modified by researcher prior to the SOP approval.

This SOP is not a substitute for hands-on training.

Print a copy and insert into your laboratory SOP binder.

Department:	[Chemistry]
Date SOP was written:	[Tuesday, September 20, 2016]
Date SOP was approved by PI/lab supervisor:	[ ]
Principal Investigator:	[Name: R. Cohen] [Signature: _____]
Internal Lab Safety Coordinator or Lab Manager:	[Name: Tamara Sparks] [Lab Phone: 303-921-9783] [Office Phone:]
Emergency Contact:	[Name: Tamara Sparks] [Phone Number:]
Location(s) covered by this SOP:	[Hildebrand B49,B70,B74,B76]

1. Purpose

This SOP covers the precautions and safe handling procedures for the use of Acutely Toxic Gases (ATGs).

For a list of ATGs covered by this SOP and their use(s), see the "List of Chemicals". Procedures described in Section 12 apply to all materials covered in this SOP.

If you have questions concerning the applicability of any recommendation or requirement listed in this procedure, contact the Principal Investigator/Laboratory Supervisor or the campus Chemical Hygiene Officer at ucbcho@berkeley.edu.

2. Acutely Toxic Gases Information

Before working with any Acutely Toxic Gases (ATGs), review the UC-Berkeley EH&S publication ***Toxic Gas Program on the EH&S website***. If you have questions about Toxic Gas Program requirements, contact EH&S at 642-3073.

3. Potential Hazards/Toxicity

Toxic gases are gases that may cause significant acute health effects at low concentrations. Health effects may include severe skin or eye irritation, pulmonary edema, neurotoxicity, or other potentially fatal conditions.

The Globally Harmonized System of Classification and Labeling of Chemicals (GHS) designates ATGs by one or more of the following H codes:

H280 Contains gas under pressure; may explode if heated
H330 Fatal if inhaled
H331 Toxic if inhaled
H332 Harmful if inhaled
H333 May be harmful if inhaled

ATGs may also have other hazardous properties in addition to acute toxicity (e.g. corrositivity, pyrophoricity). Safe use requires assessing all potential hazards.

It is the Principal Investigator's responsibility to ensure activity-specific laboratory procedures and/or processes are taken into account when using this Chemical Class SOP.

Please, review the SDS of any chemical before use (see Section 11 – SDS Location).

4. Engineering Controls

Use the engineering controls listed below unless other lab-specific information is included in the Protocol/Procedure section.

- Work with ATGs must be conducted in a fume hood unless other controls are designated in the lab-specific Protocol/Procedure section. Sash height must be kept low to avoid escaping fumes and provide a physical barrier.
- Indoor storage of all gas cylinders in this program must be in a mechanically ventilated, lockable area. Examples of mechanical ventilated areas include exhausted gas cabinets, fume hoods, and special fire code compliant gas storage rooms.
- All cylinders and gas cabinets must be clearly labeled with content and hazard information.
- All regulators, valves, piping, tubing and fittings must be chemically compatible with the gases being used. Regulators must be compatible with the size and type of gas cylinder being used and rated for full cylinder pressure. Consult your gas supplier for approved regulators, valves, piping, tubing, and fittings.
- Cylinders must be stored upright, with tank valves securely closed and valve protection cap in place, and firmly secured to prevent falling or being knocked over.
- Some ATGs have poor warning properties. If a particular ATG falls into this category and work with this gas will be done routinely or larger quantities will be employed, install a continuous electronic warning sensor with alarm if available. Insure that the fume hood is operating properly and keep the sash as low as possible at all times. A ventilation monitor is required on the hood.

5. Personal Protective Equipment

At a minimum, the following PPE must be worn at all times.

Eye and Face Protection

A. ANSI Z87.1-compliant safety glasses with side shields, or chemical splash goggles.
   - Ordinary prescription glasses will NOT provide adequate protection unless they also meet ANSI standard and have compliant side shields.

B. If the potential for explosion/splashing exists, and adequate coverage is not provided by the hood sash, a face shield must be worn.

Skin and Body Protection

1. Gloves are required when handling hazardous chemicals.
   - Refer to specific chemical SDS for information on glove selection.
   - For additional information on glove selection, go to: http://ehs.berkeley.edu/hs/63-laboratory-safety/94-glove-selection-and-usage.html
2. Lab coats are required when handling hazardous chemicals in the lab. Select the type of lab coat according to the hazards at the specific workplace.
3. Long pants, closed-toe/closed-heel shoes, covered legs, and ankles.

Respiratory Protection

Respiratory protection is normally not required for UC Berkeley laboratory activities. Any lab personnel considering the use of a respirator must contact EH&S for a workplace assessment.

6. First Aid Procedures and Medical Emergencies

In the event of an injury, notify your supervisor immediately and EH&S within 8 hours.

Go to the Occupational Health Facility (Tang Health Center, on campus); if after hours, go to the nearest emergency room (Alta Bates, 2450 Ashby Ave in Berkeley); or

Call 911 (from a cell phone: 510-642-3333) if:

- ***it is a life threatening emergency; or***
- ***you not are confident in your ability to fully assess the conditions of the environment and/or the condition of the contaminated/injured person, or you cannot be assured of your own safety; or***
- ***the contaminated/injured person is not breathing or is unconscious.***

Please remember to provide a copy of the appropriate manufacturer SDS (if available) to the emergency responders or physician. At a minimum, be ready to provide the identity/name of any hazardous materials involved.

In case of skin contact

If skin contact occurs, and/or skin or clothing are on fire, immediately drench in the safety shower with copious amounts of water for no less than 15 minutes to remove any remaining contaminants. If possible to do so without further injury, remove any remaining jewelry or clothing.

In case of eye contact

Rinse thoroughly with plenty of water using an eyewash station for at least 15 minutes, occasionally lifting the upper and lower eyelids. Remove contact lenses if possible.

If inhaled

Move into fresh air.

7. Special Handling, Storage, and Disposal Requirements

Lab-specific information on handling and storage may be included in the Protocol/Procedure section.

Precautions for safe handling

- Do not drag, roll, slide or drop cylinders. A suitable hand truck, to which the cylinder is secured, must be used for cylinder movement.
- When transporting gases outside the lab, the protective cap must be in place and must cover the valve.
- Never attempt to lift a cylinder by its cap.
- Secure cylinders at all times while in use and during transport.
- Once cylinder has been connected to process, open valve slowly and carefully. If experiencing difficulty opening cylinder valve, discontinue use and contact supplier. Do not attempt to force freeing "frozen" or corroded valves.
- Regulators and valves must be kept free of moisture. Systems must be purged with dry inert gas (e.g. helium, nitrogen, argon, etc.) before the product is introduced and when system is out of service.

Conditions for safe storage

- It is essential that all ATGs be stored separately from all chemicals with which they may react. Ensure segregation of incompatible chemicals per guidance within EH&S guidelines. Also, follow any substance-specific storage guidance provided in Safety Data Sheet (SDS) documentation.
- All compressed gas cylinders must be stored upright with valve cover caps in place. Damage to a valve can cause the cylinder to become a dangerous projectile. Cylinders must be properly secured with two non-combustible restraints to prevent them from falling at all times.

Disposal

- All empty gas cylinders must be labeled as empty; however, empty cylinders may still contain some toxic gas, so must remain in exhausted enclosures or fire code compliant gas storage rooms. Depleted gas cylinders must be returnable to the vendor according to their guidelines.

8. Chemical Release

Chemical Release Dial 911

- Accidental Release – Help contaminated or injured persons. If conditions and time permit, close any open valve. Evacuate the release area. Avoid breathing vapors. Eliminate sources of ignition. Keep others from entering this area (e.g., use caution tape, barriers, etc.). *Notify supervisor and EH&S immediately.*
- Contact with body or clothes – Remove clothing and rinse body thoroughly in emergency shower for at least 15 minutes. Seek medical attention. *Notify supervisor and EH&S immediately.*
- Contact with Eyes – Immediately rinse eyeballs and inner surface of eyelid with water for 15 minutes using an eyewash station by forcibly holding the eye open. Seek medical attention. *Notify supervisor and EH&S immediately.*

9. Cleaning and Decontamination

Lab-specific information on decontamination may be included in the Protocol/Procedure section.

All lines or ducts carrying purged or exhausted emissions of gases must be connected to a mechanical exhaust system that discharges to a safe location (i.e., presents no potential for re-entrainment into any building supply air intake or occupied area). Construction of the exhaust ducts must be chemically resistant to degradation by the gas in use. Significant emissions of corrosive or toxic gases require an emission control device (*e.g.*, scrubber, flare device, adsorbent) before the purged gas can be vented into the exhaust duct system. Refer to ***Toxic Gas Program.***

10. Hazardous Waste Disposal

Label Waste

- All empty gas cylinders shall be labeled as empty

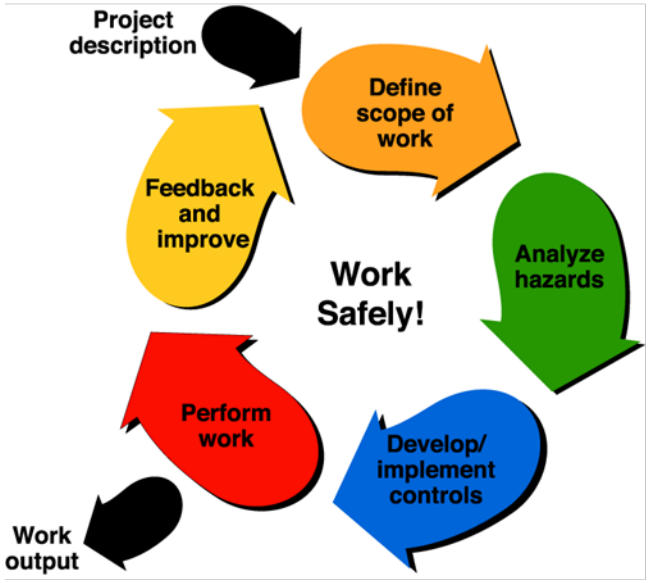
Dispose of Waste

- Depleted gas cylinders should be returnable to the vendor according to their guidelines.
- Contact EH&S at 642-3073 if you need assistance.

11. Safety Data Sheet (SDS) Location

SDS can be accessed online at http://ucsds.com

-Take Ownership of Your Safety-



Before starting any work, ask yourself:

1- What will I be doing?
2- Do I know what the hazards are?
3- Do I have everything I need to do the job safely?
4- Am I doing the job safely?
5- What can we do better?

12. Protocol/Procedure – Acutely Toxic Gases (ATGs)

Section 12 must be customized to your specific needs. Delete any procedure that does not apply to your laboratory.

Procedure/Use	Scale	Engineering Controls/Equipment	PPE (eye, face, gloves, clothing)	Procedure Steps and Precautions
1. a)Laser induced fluorescence instrument calibratation .with nitrogen dioxide. 1.b) Chemiluminescence instrument calibration with nitric oxide. 1.c) Fumigate chamber	5-15 sccm (standard cubic centimeters per minute) from 5-6 ppm cylinder < 500 ppb after dilution	See procedure.	**Eye protection**: Wear ANSI Approved tight-fitting safety goggles or safety glasses with side shields. **Clothing**: Wear lab coat; full length pants or equivalent; and close-toed, close-heeled shoes.	Before purchasing, check that complete failure of cylinder would not result in ambient concentrations that would exceed safety thresholds (10 ppm for nitrogen dioxide or 25 ppm for nitric oxide). Check cylinder is secured with two chains prior to removing cap. Room must be well ventilated before using cylinder. Cylinder must not be in contact with a heat source or in direct sunlight. Check regulator is correctly attached with no leaks. Attach gas line to instrument NO_2 in- port and check for leaks. Open cylinder slowly for use. Use valve on cylinder to stop gas flow when finished, as well as closing the regulator
Notes	Any deviation from this SOP requires approval from PI.			

Procedure/Use	Scale	Engineering Controls/Equipment	PPE (eye, face, gloves, clothing)	Procedure Steps and Precautions
2. Leak Detection with nitrogen dioxide	Small bubbles when placed in water < 6 *ppm*	See procedure.	**Eye protection**: Wear ANSI Approved tight-fitting safety goggles or safety glasses with side shields. **Clothing**: Wear lab coat; full length pants or equivalent; and close-toed, close-heeled shoes.	Before purchasing, check that complete failure of cylinder would not result in ambient concentrations that would exceed safety thresholds (10 ppm for nitrogen dioxide or 25 ppm for nitric oxide). Check cylinder is secured with two chains prior to removing cap, near experimental area. Room must be well ventilated before using cylinder. Cylinder must not be in contact with a heat source or in direct sunlight. Check regulator is correctly attached with no leaks. Attach micro gas line to cylinder with valve. Open valve slowly. Direct micro line opening at connection points in gas line setup for a minimum of 10s in order to test for leaks into the system. Use valve on cylinder to stop gas flow when finished, as well as closing the regulator. Replace cylinder in two-chained storage area when finished.
Notes	Any deviation from this SOP requires approval from PI.			

Procedure/Use	Scale	Engineering Controls/Equipment	PPE (eye, face, gloves, clothing)	Procedure Steps and Precautions
3. Ozone reaction with nitric oxide in instrument	Up to 160 sccm	See procedure.	**Eye protection**: Wear ANSI Approved tight-fitting safety goggles or safety glasses with side shields. **Clothing**: Wear lab coat; full length pants or equivalent; and close-toed, close-heeled shoes.	Check that complete failure of exhaust or housing of ozone generator would not result in ambient concentrations that would exceed safety thresholds (0.1 ppm average over 8 hours). Room must be well ventilated. Ensure exhaust lines are secure and there are no leaks. Check the Oxygen SOP for additional hazards if oxygen tank is used to produce ozone.
Notes	Any deviation from this SOP requires approval from PI.			

Procedure/Use	Scale	Engineering Controls/Equipment	PPE (eye, face, gloves, clothing)	Procedure Steps and Precautions
4. Calibrate ozone monitors in BEACON Instrument	Up to 300 ppb O_3 (about 2-3 times the ambient range)	See procedure.	**Eye protection**: Wear ANSI Approved tight-fitting safety goggles or safety glasses with side shields. **Clothing**: Wear lab coat; full length pants or equivalent; and close-toed, close-heeled shoes.	Check that complete failure of exhaust or housing of ozone generator would not result in ambient concentrations that would exceed safety thresholds (0.1 ppm average over 8 hours Room must be well ventilated. Ensure exhaust lines are secure and there are no leaks.
Notes	Any deviation from this SOP requires approval from PI.			

Procedure/Use	Scale	Engineering Controls/Equipment	PPE (eye, face, gloves, clothing)	Procedure Steps and Precautions
5. Calibration of CO sensors	1 slpm from 100ppm CO in inert gas cylinder mixed with air or nitrogen	See procedure.	**Eye protection**: Wear ANSI Approved tight-fitting safety goggles or safety glasses with side shields. **Clothing**: Wear lab coat; full length pants or equivalent; and close-toed, close-heeled shoes.	Before purchasing, check that complete failure of cylinder would not result in ambient concentrations that would exceed the safety threshold (25 ppm). Check that regulator is properly installed will no leaks. Attach CO mixture gas line to diluter along with air line, attach output lines to calibration chamber. Connect calibration chamber exhaust to fume hood exhaust. Leak check all connections. Open cylinder slowly for use. Use valve on cylinder to stop gas flow when finished, as well as closing the regulator.
Notes	Any deviation from this SOP requires approval from PI.			

Procedure/Use	Scale	Engineering Controls/Equipment	PPE (eye, face, gloves, clothing)	Procedure Steps and Precautions
6. In-line generation of trace level $ClNO_2$ (using CL_2 + $NaNO_2$)	Cl_2 trace levels in carrier gas from permeation device	All reactions using these materials must be performed in a properly operating fume hood with the sash as low as possible.	**Eye protection**: Wear ANSI Approved tight-fitting safety goggles or safety glasses with side shields. **Face protection**: Face shields are to be used when there is no protection from the hood sash. **Hand protection**: Confirm the compatibility of the gloves you use with the specific ATG. General guidance (unless otherwise specified in the specific SDS): at a minimum, 8 mil minimum nitrile gloves must be used to prevent incidental contact. For gas release or for potential contact with larger quantities, use double nitrile or heavier gauge nitrile or neoprene gloves. Gloves must be inspected prior to use. Remove gloves immediately upon contamination. Wash and dry hands after use. **Clothing**: Wear lab coat; full length pants or equivalent; and close-toed, close-heeled shoes.	Procedure: In the hood, mix approx. 0.2 g of NaNO2 with 2 g of NaCl. Place this in a horizontal 1/2" dia by 8" long teflon tube and moisten the bed until almost a slurry. Install adapter fittings to connect to 1/4" or 1/8" tubing. At the experiment location run a small flow of carrier gas containing trace level Cl2 (a few parts-per-million mixing ratios) over the NaNO2/NaCl bed. The resultant gas stream containing a trace amount of ClNO2 is then diluted to parts-per-billion levels and delivered to the analyzer. Permeation devices contain less than one gram of the pure substance, are permanently sealed, virtually unbreakable, and safe to handle. Our Cl2 device delivers 260 nanograms/minute at 40 degrees C. The device is contained in a gas-tight tube with a small amount of N2 gas continuously flowing.
Notes	Any deviation from this SOP requires approval from PI.			

Procedure/Use	Scale	Engineering Controls/Equipment	PPE (eye, face, gloves, clothing)	Procedure Steps and Precautions
7. In-line generation of trace level HONO (using HCl + $NaNO_2$)	200mL of >8 M HCl diluted	All reactions using these materials must be performed in a properly operating fume hood with the sash as low as possible.	**Eye protection**: Wear ANSI Approved tight-fitting safety goggles or safety glasses with side shields. **Face protection**: Face shields are to be used when there is no protection from the hood sash. **Hand protection**: Confirm the compatibility of the gloves you use with the specific ATG. General guidance (unless otherwise specified in the specific SDS): at a minimum, 8 mil minimum nitrile gloves must be used to prevent incidental contact. For gas release or for potential contact with larger quantities, use double nitrile or heavier gauge nitrile or neoprene gloves. Gloves must be inspected prior to use. Remove gloves immediately upon contamination. Wash and dry hands after use. **Clothing**: Wear lab coat; full length pants or equivalent; and close-toed, close-heeled shoes.	Trace level HCl in carrier gas stream is from a gas-tight glass flask (the generating cell) containing a coiled Teflon tube (1/16" dia., 30" long). The cell is filled with a concentrated (above 8 M) aqueous solution of hydrochloric acid, possessing a gaseous pressure of hydrogen chloride. A carrier gas (nitrogen or clean air) is flown through the Teflon tube to pick up HCl that has diffused through the teflon. In the hood, prepare a filter cartridge with a thin layer of NaNO2 sandwiched between two teflon filter discs. At the experiment location run a flow of carrier gas containing trace level HCl (parts-per-billion mixing ratios) through the NaNO2 filter cartridge. The resultant gas stream containing a trace amount of HONO (parts-per-billion level) is then delivered to the analyzer. Preparation of the HCl solution: Always add acid to water to avoid spattering. Do not add water to acid. Ensure that all glassware is clean and dry before beginning procedure. Determine the amounts of acid and water required for the dilution. Concentrated HCl reagent with a nominal concentration of 12 M (37% by weight) will require only a small amount of

				water. Measure the concentrated acid, and slowly add it to the water. A pipettor, or other means can be used to control the flow of acid, to slowly add the acid into a container of water until the acid has been diluted. Note: if temperature becomes too warm, stop addition immediately. Wait for the solution to cool down before proceeding with addition. When finished, neutralize any remaining acid and dispose of waste following appropriate procedures.
Notes	Any deviation from this SOP requires approval from PI.			

Procedure/Use	Scale	Engineering Controls/Equipment	PPE (eye, face, gloves, clothing)	Procedure Steps and Precautions
8. In-line generation of trace level N_2O_5 (using O_3 + NO_2)	0 to 10 parts-per-billion in 10 liters/minute flow of dry air (<0.00002 g/hour)	See procedure.	**Eye protection**: Wear ANSI Approved tight-fitting safety goggles or safety glasses with side shields. **Face protection**: Face shields are to be used when there is no protection from the hood sash. **Hand protection**: Confirm the compatibility of the gloves you use with the specific ATG. General guidance (unless otherwise specified in the specific SDS): at a minimum, 8 mil minimum nitrile gloves must be used to prevent incidental contact. For gas release or for potential contact with larger quantities, use double nitrile or heavier gauge nitrile or neoprene gloves. Gloves must be inspected prior to use. Remove gloves immediately upon contamination. Wash and dry hands after use. **Clothing**: Wear lab coat; full length pants or equivalent; and close-toed, close-heeled shoes.	Check that complete failure of exhaust or housing of ozone generator would not result in ambient concentrations that would exceed safety thresholds (0.1 ppm average over 8 hours Before purchasing, check that complete failure of cylinder would not result in ambient concentrations that would exceed safety thresholds (10 ppm for nitrogen dioxide) Establish a 50 sccm flow of the driest possible air into the photolytic ozone generator. Combine the ozone generator output (roughly 10 parts-per-million O3) with a 10 sccm of 5 ppmv NO2 flow at the entrance of the N2O5 reactor (just a 200 cm3 volume Teflon tube). Dilute the output with 1 to 10 SLPM dry air as required for the instrument. All is at ambient pressure downstream of the flow controllers.
Notes	Any deviation from this SOP requires approval from PI.			

13 - Documentation of Training (signature of all users is required)

- Prior to conducting any work with ATGs, designated personnel must provide training to his/her laboratory personnel specific to the hazards involved in working with this substance, work area decontamination, and emergency procedures.
- The Principal Investigator must provide his/her laboratory personnel with a copy of this SOP and a copy of the relevant SDSs provided by the manufacturer.

I have read and understand the content of this SOP:

Name	Signature	Identifier	Date

Appendix – List of Acutely Toxic Gases (non-exhaustive list)

Chemical Name/Formula	CAS#	Chemical Name/Formula	CAS#
Ammonia NH_3	7664-41-7	Arsenic pentafluoride AsF_5	7784-36-3
Arsine AsH_3	7784-42-1	Boron trichloride BCl_3	10294-34-5
Boron trifluoride BF_3	7637-07-2	Carbon monoxide CO	630-08-0
Cyanogen C_2N_2	460-19-5	Cyanogen chloride NCCl	506-77-4
Chlorine Cl_2	7782-50-5	Diazomethane H_2CN_2	334-88-3
Diborane B_2H_6	19287-45-7	Fluorine F_2	7782-41-4
Germane GeH_4	7782-65-2	Hexaethyltetraphosphate $C_{12}H_{30}O_{13}P_4$	757-58-4
Hydrogen bromide HBr	10035-10-6	Hydrogen Chloride HCl	7647-01-0
Hydrogen fluoride HF	7664-39-3	Hydrogen sulfide H_2S	7783-06-4
Hydrogen selenide H_2Se	7783-07-5	Methyl mercaptan CH_3SH	74-93-1
Nitric oxide NO	10102-43-9	Nitrogen dioxide NO_2	10102-44-0
Nitrogen tetroxide N_2O_4	10544-72-6	Oxygen difluoride OF_2	7783-41-7
Phosgene $COCl_2$	75-44-5	Phosphine PH_3	75-45-5
Phosphorous pentafluoride PF_5	7641-19-0	Selenium hexafluoride SeF_6	7783-79-1
Stibine SbH_3	7803-52-3	Sulfur tetrafluoride SF_4	7783-60-0
Trimethylsilyldiazomethane $(CH_3)_3SiCHN_2$	18107-18-1		

List of Chemicals

Chemical(s)	Chemical(s)	Chemical(s)
CARBON MONOXIDE,CYL.	CHLORINE	HYDROCHLORIC ACID
NITRIC OXIDE	NITROGEN DIOXIDE	Nitrogen dioxide (<1%) /Nitrogen
Ozone	Dinitrogen Pentoxide	