Research
Research Laboratory & Safety Services

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Use of Hazardous Gases
Standard Operating Procedure

1. Purpose

This standard operating procedure (SOP) details the requirements for ordering, storing, using, and disposing of **toxic, highly toxic, pyrophoric, corrosive, or commonly abused gases.** These will be referred to as hazardous gases for the remainder of this SOP.

2. Scope

Laboratories must be registered with and obtain approval from Research Laboratory & Safety Services (RLSS), before ordering, acquiring, and/or using the gases detailed in the following section. These gases have the potential to endanger people or property in the case of an accidental release and are therefore heavily controlled. The guidance provided in this document is highly generalized, and there may be additional or different requirements for each gas dependent upon the specific research objective/design. It is for this reason that RLSS must review all orders and authorize the use of these gases in UA laboratories. After registration and order approval, the safe use and storage of hazardous gases will be reviewed during routine safety inspections.

3. Hazardous Gases

The gases listed in Tables 1 are considered hazardous gases in accordance with this SOP and require prior approval by RLSS before ordering and delivering to laboratories. These examples are not all inclusive; other gases may be added depending on the hazards presented by their storage or use.

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Table 1. Corrosive, toxic, highly toxic, toxic gases with poor warning properties, reproductive toxins, pyrophoric compressed gases, and compressed gases which are known carcinogens.

Compressed Gas	Chemical Formula	Corrosive	Toxic	Highly Toxic	Reproductive Toxin	Toxic with Poor Warning Properties	Pyrophoric	Carcinogenic
Ammonia	NH_3	X						
Arsine	AsH_3			X		X		X
1-3- Butadiene	C4H6				X			X
Boron trichloride	BCl_3	X						
Boron trifluoride	BF_3	X						
Carbon monoxide	CO				X	X		
Carbonyl fluoride	CF_2O	X	X					
Carbonyl sulfide	COS	X	X					
Chlorine	Cl_2	X	X					
Cyanogen	$(CN)_2$		X					
Cyanogen chloride	ClCN			X		X		
Deuterium chloride	DCl	X	X					
Diborane	B2H6			X			X	
Dichlorosilane	SiH_2CL_2						X	
Dimethylamine	C_2H_7N		X					
Ethylene oxide	C_2H_4O				X	X		X
Fluorine, ≥1%	Fl_2			X				
Germane	GeH_4			X			X	
Hydrogen bromide	HBr	X						
Hydrogen chloride	HCl	X						
Hydrogen cyanide	HCN			X				
Hydrogen fluoride	HF			X				
Hydrogen selenide	H_2Se			X			X	
Hydrogen sulfide	H_2S					X		
Methyl bromide	CH_3Br					X		
Methyl mercaptan	CH_4S	X	X					
Monomethylamine	CH_3NH_2	X						

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Compressed Gas	Chemical Formula	Corrosive	Toxic	Highly Toxic	Reproductive Toxin	Toxic with Poor Warning Properties	Pyrophoric	Carcinogenic
Nitric oxide ("nitrous")	NO			X		X		
Nitrogen dioxide	NO_2	X	X					
Nitrosyl chloride	NOCl	X	X					
Phosgene	$COCl_2$			X		X		
Phosphine	PH_3			X			X	
Phosphorus pentafluoride	F_5P	X						
Selenium hexafluoride	SeF_6	X	X					
Silane, ≥1.37%	SiH_4						X	
Silicon hexafluoride	SiF_6	X	X					
Silicon tetrafluoride	F_4Si	X	X					
Stibine	SbH_3			X		X	X	
Sulfur dioxide	SO_2	X						
Sulfuryl fluoride	F_2O_2S					X		
Trimethylamine	C_3H_9N	X						
Vinyl chloride	C_2H_3Cl					X		X

4. Order and Delivery

To begin the order process of a hazardous gas, complete and submit the Hazardous Gas Order Request on the RLSS website. This form **must** be completed for all orders, whether initial, reorders, and/or orders of backup cylinders. After receipt of the request, RLSS will assess the hazards presented by the gas, as well as the control measures available in the laboratory. Assessments usually include a visit to the laboratory, though re-orders may only require a phone call to ensure equipment and processes have not changed. RLSS may request the assistance of technical experts (i.e. University Fire Marshall, hazardous gas experts, etc.) in these assessments.

After RLSS assessment, all hazardous gases **must** be ordered through the University's Cryogenics & Compressed Gas Facility (UA Cryo), in the smallest practical quantity, and lowest concentration for its intended application. Gas cylinders must be ordered with restricted flow orifices, whenever possible. **Their use, storage, and disposal must be in accordance with any and all relevant regulations and/or applicable industry standards (e.g. Compressed Gas Association Standards and guidelines).**

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After assessment, RLSS will approve, conditionally approve*, or disapprove each request in a formal, written letter to the laboratory and UA Cryo.

*May authorize the order but not the delivery of a gas until corrective measures have been resolved

5. Quantity Limits

Regulatory quantity limits often apply to these gases. These limits may be applicable to the lab itself, a storage unit, the floor of a building, or the entire building itself.

5.1 Building Quantity Limits: The University of Arizona adheres to the International Fire Code (IFC), which limits the quantities of hazardous gases allowed per building by "control areas." A control area is generally considered to be the floor of a building, though it can be a smaller area within a building floor.

During the order assessment process, RLSS will ensure that the desired hazardous gas order will not exceed the building's IFC storage and/or use limits. The IFC quantity limits for hazardous gases are summarized in Table 2. These quantities may vary if the building meets certain requirements; RLSS and the University Fire Marshall must be consulted for these unique situations.

Table 2. International Fire Code (IFC) Hazardous Gas Quantity Limits*

Material	Storage (standard cubic feet)	Use-Closed System (standard cubic feet)
Flammable Gas	1000	1000
Oxidizing Gas	1500	1500
Pyrophoric Gas	50	10
Unstable (Reactive) Gas	10 – 250	10 - 250
Corrosive Gas	810	810
Highly Toxic Gas	20	20
Toxic Gas	810	810

*Limits are based on cylinder maximum internal water volume, as per the IFC.

5.2 Storage Unit Limits: In addition to the IFC limits, the National Fire Protection Agency (NFPA) limits the amount of gases with an NFPA Health Rating of 3 or 4 that may be stored in a chemical fume hood. The following rules should be adhered to when storing such gases.

- Gases with a health rating of 3 or 4 in lecture bottles may be stored in a certified chemical fume hood.
- Gases with a health rating of 3 or 4 in gas cylinders larger than a lecture bottle should be stored in a certified gas cabinet, not a chemical fume hood.

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6. Gas Cylinder Storage and Transport

6.1 Storage:

- Incompatible gases (e.g. oxygen and acetylene) must be separated by a distance of ≥20 feet, or a noncombustible partition extending ≥18 inches above and to the sides of the cylinders. Gases that are incompatible must not be stored within the same gas cabinet, fume hood, or exhausted enclosure. The room in which hazardous gases are stored must be ventilated and at negative pressure to any public areas.
- Hazardous gases must be stored in an approved, ventilated device such as a gas cabinet or chemical fume hood that are fitted with an alarm-installed airflow monitoring device. Some medical or research devices that require hazardous gases (e.g. optical lasers) are not ventilated but are manufactured to prevent exposure; these are also acceptable for the storage of hazardous gases upon a case-by-case approval by the RLSS. Specific requirements exist for each type of storage device, unless otherwise noted by the RLSS.
  - Gas cabinets must:
    - Be constructed of not less than 12-gauge steel,
    - Connect to a local exhaust system,
    - Operate at a negative pressure in relation to surrounding areas,
    - Function with an average face velocity of ≥200 linear feet per minute (fpm), with ≥150 fpm at any point,
    - Have self-closing doors, limited access ports, and/or non-combustible windows to give access to equipment controls, and
    - Pass the gas through filters/scrubbers before releasing it out of the cabinet.
  - Chemical fume hoods must:
    - Operate at a negative pressure in relation to surrounding areas, and
    - Function with an average face velocity of ≥200 fpm, with ≥150 fpm at any point.
  - Approved medical/research devices must:
    - Conform to all manufacturer specifications unless modifications are approved by RLSS,
    - Utilize appropriate control measures (i.e. ventilation, scrubbers, filters, etc.),
    - Be controlled by a manual or automatic emergency failsafe, and
    - Be used in accordance to the setup, maintenance, and operational protocols developed by the laboratory and approved by RLSS.

If gases with a NFPA health rating of 3 or 4 in a cylinder larger than a lecture bottle must be stored in a chemical fume hood, the following additional control measures are required:

- Gas monitors must be affixed to the chemical fume hood to monitor ambient air concentrations of the hazardous gas and alarm at hazardous concentrations.
- The gas piping must have readily accessible manual or automatic fail-safe emergency shutoff valves installed at the point of use and the source (e.g. the cylinder).

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Hazardous gas ventilated devices are certified annually by Facilities Management. RLSS can perform function checks but the responsibility to certify and/or repair devices that do not meet the criteria detailed in this SOP lies with Facilities Management.

6.2 Transport: RLSS does not recommend the transport of any hazardous gas cylinders by laboratory workers. Contact RLSS and Risk Management Services (RMS) if transport within a building, across campus, and/or to a secondary location is required to ensure workers are compliant with DOT regulations and all relevant safety requirements.

7. Piping, Tubing, Valves and Fittings

The piping, tubing, valves, and fittings used to carry a hazardous gas must be made of adequate strength and durability, and of material compatible with the gas itself. The piping system must not be located within corridors, within any route of egress, or within a concealed space. Connections between segments must either be welded or brazed unless the connections are within a ventilated enclosure or other safety measures have been approved by the RLSS. The following requirements also apply to any piping, tubing, valves, and fittings carrying hazardous gases.

- Piping must be labeled to identify the hazardous gas being carried and the direction of flow.
- Piping, tubing, valves, and fittings must have backflow-prevention or check valves when the backflow of hazardous materials could create a hazardous condition (e.g. acetylene, hydrogen).
- Excess flow control must be provided within the ventilated enclosure if the hazardous gas is carried in the piping at >15 pounds per square in gauge (psig).
- If the gas piping is made of low melting point materials (i.e. aluminum, copper, some brass alloys, or non-metallic materials), they shall be:
    - protected by isolation from fire exposure by fire-resistive construction,
    - isolated from fire exposure by gas cabinets,
    - protected from fire exposure by an automatic fire-extinguishing system,
    - located so that any release resulting from failure of the piping systems will not unduly expose persons, buildings or structures, or
    - provided with a readily accessible shutoff valve or valves which will shut off the source of gas to the piping system in the event of leakage.

8. Release and Disposal

Highly toxic, toxic, and corrosive gases must be trapped, neutralized, or condensed to avoid contaminating vacuum pumps or discharging substantial quantities to exhaust air. Report any unplanned discharge/release of hazardous gases to RLSS at 520-626-6850 and Risk Management Services at 520-621-1790.

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Hazardous gases must be purchased in returnable cylinders whenever possible. Disposal or returns to the manufacturer should be coordinated through the UA Cryo**. Lecture bottles of gases are not returnable** and must be collected by Risk Management Services for disposal.

9. Equipment Maintenance

Equipment, machinery, and instruments associated with hazardous gases must be maintained in operable condition; SOPs should describe required maintenance (e.g. cleanings, filter replacements, etc.). Broken equipment, malfunctioning apparatus, or ventilated equipment out of certification must be immediately removed from service until it is replaced, repaired, or recertified. Contact Facilities Management for repairs and recertification. Ventilated equipment, piping, and other systems related to the storage and use of toxic or corrosive gases must not be modified without approval by RLSS.

10. Training and Hazard Communication

Beyond the OSHA and RLSS required trainings for hazardous chemical workers, laboratory personnel working with hazardous gases must be familiar with the hazards of the gas, proper handling procedures and emergency procedures detailed within the gas's Safety Data Sheet (SDS) **RLSS also requires the development of an SOP for all hazardous gases, to be included in the Laboratory Chemical Hygiene Plan (LCHP) that will be made available to all workers via the RLSS User Dashboard; please see the RLSS website for an SOP template. RLSS will work with each lab to develop the laboratory's hazardous gas SOP.** General safety information regarding the hazardous gas use and storage areas should be included in the Approval's Laboratory-Specific Training for hazardous chemical workers that do not use the hazardous gas.

Every cylinder of hazardous gas in possession must be entered into the Approval's hazardous chemical inventory within the RLSS User Dashboard. An SDS will be available to all laboratory workers from the RLSS User Dashboard for any hazardous gas entered into this inventory. Laboratory personnel should be aware of the location of the SDS's, and refer to a gas's SDS before use. Individual gas cylinders must also be labeled with the name of the gas, the manufacturer name and address, and a GHS-compliant label warning of the gas's main hazard (e.g. Toxic, Corrosive, etc.).

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11. Definitions

CGA: Compressed Gas Association

Corrosive Gas: A gas that can cause visible destruction of, or irreversible alterations in, living tissue (e.g., skin, eyes, or respiratory system) by chemical action.

Compressed Gas:

(i) A gas or mixture of gases in a container, having an absolute pressure exceeding 40 psi at 70 0 F (21.10 C) or

(ii) A gas or mixture of gases in a container, having an absolute pressure exceeding 104 psi at 130 0 F (54.40 C) regardless of the pressure at 70 0 F (21.1 0 C) or

(iii) A liquid having a vapor pressure exceeding 40 psi at 100 0 F (37.8 0 C) as determined by ASTM D-323-72.

DOT: U.S. Department of Transportation.

Flammable Gas: A gas that, at ambient temperatures and pressures, forms a flammable mixture with air at a concentration of less than thirteen (13) percent by volume; or forms a range of flammable mixtures with air wider than twelve (12) percent by volume.

Flammable limits: The concentration of flammable vapor in air, oxygen, or other oxidants that will propagate flame upon contact when provided with a source of ignition. The lower explosive limit (LEL) is the concentration below which a flame will not propagate; the upper explosive limit (UEL) is the concentration above which a flame will not propagate. A change in temperature or pressure may vary the flammable limits.

Flashpoint: The minimum temperature at which a liquid gives off a vapor in sufficient concentration to ignite and sustain a flame.

Hazardous Gas: A gas that is included in one or more of the following hazard categories: corrosive, flammable, health hazard, oxidizer, pyrophoric, reactive, or toxic.

Health Hazard: Any chemical for which there is at least one scientific study that shows it may cause acute or chronic health symptoms. This includes chemicals which are carcinogens, toxic or highly toxic, irritants, corrosives, sensitizers, or chemicals that effect target organs including the lungs, kidneys, nervous system, pulmonary system, reproductive system, skin, and/or eyes.

Ignition Source: Anything that provides heat, sparks, or flame sufficient to cause combustion/explosion.

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Incompatible: Materials which could cause dangerous reactions from direct contact with one another.

LEL: (Lower Explosive Limit) LEL is the lowest concentration of a gas or vapor in the air that can produce ignition or explosion. Mass Flow Controller- (MFC) is a device used to measure and control the flow of gases.

SDS: (Safety Data Sheet) Written or printed material about a chemical that specifies its hazards, safe use and other information. It is prepared by the chemical manufacturer, and is required by federal law.

NFPA: National Fire Protection Association.

NFPA Health Rating 3: Materials that can affect health or cause serious injury, during periods of short exposure, even though prompt medical treatment is give; this can be determined using a chemical's SDS.

NFPA Health Rating 4: Materials that can affect health or cause serious injury, during periods of very short exposure, even though prompt medical treatment is given; this can be determined using a chemical's SDS.

Oxidizing gas: A gas that initiates or promotes combustion in materials, either by catching fire itself or by potentially causing a fire through the release of oxygen or other gases.

Oxygen deficiency: A condition that occurs when a breathable atmosphere contains less than 19.5% oxygen. Note: Normal air contains 20.8% oxygen.

Physical hazard: A chemical for which there is scientifically valid evidence that it is a combustible liquid, a compressed gas, an explosive, a flammable, an organic peroxide, an oxidizer, a pyrophoric, an unstable (reactive), or a water-reactive.

Pyrophoric gases: Gases that may spontaneously ignite in air at or below 54 ºC (130 ºF). Specific gases may not ignite in all circumstances or may explosively decompose.

Restrictive Flow Orifice (RFO): A safety device placed in the outlet of a cylinder valve that is intended to limit the release rate of a hazardous gas to a maximum specified range in the event of the inadvertent opening of the valve, or failure of the system downstream of the valve outlet.

STP: Standard Temperature and Pressure or STP is defined as 0 °C (32 °F) and 1 atmosphere of pressure (101.325 kPa or 29.92 inHg).

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Toxic gas: A gas that is poisonous or capable of causing injury or death, especially by chemical means, at room temperature and has:

(i) a median lethal dose (LD(50)) of 50 mg or less per kg of body weight when administered orally to albino rats weighing between 200 and 300 grams each; or

(ii) a median LD(50) of 200 mg/kg of body weight when administered by continuous contact for 24 hours (or less if death occurs within 24 hours) with the bare skin of albino rabbits weighing between two and three kilograms each; or

(iii) a median lethal concentration (LC(50)) in air of 200 PPM by volume or less when administered by continuous inhalation for one hour (or less if death occurs within one hour) to albino rats weighing between 200 and 300 grams each.

UEL: Upper Explosive Limit - The highest concentration of a gas or vapor in air that can produce ignition or explosion.

Unstable (Reactive): An unstable or reactive chemical can go through vigorous polymerization, decomposition or condensation. This process occurs when the chemical