



# Safe Operating Procedure

(Revised 11/22)

## HAZARDS OF FLAMMABLE GASES, LIQUIDS & AEROSOLS & RISK MINIMIZATION

### Background

The Globally Harmonized System (GHS) of classification and labeling of chemicals has separate classifications for flammable gases, liquids, and aerosols. However, all have similar hazards and are therefore included in this Safe Operating Procedure (SOP).

While the definitions below are somewhat abbreviated, the Globally Harmonized System (GHS) defines flammable gases, liquids, and aerosols as follows:

- *A flammable gas is a gas having a flammable range with air at 20° C and a standard pressure of 101.3 kPa (1 atmosphere). There are two categories for flammable gases: category 1 gases are those that are ignitable at 13% or less, by volume, in air with a flammable range of at least 12% (e.g., Hydrogen); all other flammable gases are assigned to category 2 (e.g., Ammonia).*
- *A flammable liquid means a liquid having a flashpoint of not more than 93 C.*

Category/Example	Criteria	
	Flashpoint	Initial Boiling Point
<b>1 (Ether)</b>	< 23° C (< 74° F)	≤ 35° C (≤ 95° F)
<b>2 (Acetone)</b>	< 23° C (< 74° F)	> 35° C (> 95° F)
<b>3 (Charcoal Lighter Fluid)</b>	≥ 23° C and ≤ 60° C (≥ 74° F and ≤ 140° F)	NA
<b>4 (Diesel Fuel)*</b>	> 60° C and ≤ 93° C (> 140° F and ≤ 199° F)	NA

*\*Category 4 materials are considered "combustible liquids"*

- *A flammable aerosol is any non-refillable receptacle designed to eject components at least one of which is a flammable gas, liquid, or solid. There are two categories of flammable aerosols. The categories are based on technical criteria such as heat of combustion, ignition test distance, flame height and flame duration. These specifics are not important for the purposes of this SOP. Examples of flammable aerosols include spray paints, adhesives, etc.*

With the exception of Category 4 combustible liquids, flammable gases, liquids and aerosols will be identified with the flame pictogram shown below. In addition, Section 2 of the Safety Data Sheet (SDS) will include one or more of the hazard statements indicated below.



- H220 Extremely flammable gas (Category 1)
- H221 Flammable gas (Category 2)
- H224 Extremely flammable liquid and vapor (Category 1)
- H225 Highly flammable liquid and vapor (Category 2)
- H226 Flammable liquid and vapor (Category 3)
- H222 Extremely flammable aerosol (Category 1)
- Flammable aerosol (Category 2)

## Flashpoint

Flash point is defined as the minimum temperature to which a liquid must be heated to produce enough vapor to allow a vapor flash to occur in the presence of an ignition source. In other words, if a liquid is at a temperature below its flash point, insufficient vapor is generated to allow combustion. For example, ether's flash point is  $-40^{\circ}\text{C}$  ( $-40^{\circ}\text{F}$ ). It can be ignited and will burn in most environments. In contrast, diesel fuel has a flash point of  $41^{\circ}\text{C}$  ( $105^{\circ}\text{F}$ ). It will not ignite at typical room temperatures and will actually extinguish lit matches placed on it. However, diesel fuel spilled on black asphalt on a hot day where the temperature of the asphalt is much greater than  $41^{\circ}\text{C}$  can be easily ignited. Thus, the fire hazard of a flammable liquid requires consideration of the temperature of the flammable liquid in relationship to its flashpoint.

Most flammable gases have flashpoints so low that the term has little meaning for helping to evaluate their hazard. For example, hydrogen's flashpoint is  $-150^{\circ}\text{C}$  ( $-238^{\circ}\text{F}$ ).

The flashpoint of an aerosol is sometimes determined by the propellant used. If the propellant is a flammable gas, flashpoints mirror those of flammable gases. If the propellant is air, then the other contents of the container will determine the flashpoint. If the propellant is a freon (chloro and/or fluoro carbons), the propellant might either raise the flashpoint or eliminate it. Once the freon dissipates, the other contents of the container will determine the flashpoint.

While a match cannot ignite a liquid directly if the liquid is below its flashpoint, if the liquid is distributed through a matrix, like paper, a match can locally heat enough of the paper to vaporize the liquid and ignite it. This is why candles have wicks. Other circumstances that can affect flashpoint include container color and sources of radiant heat. Radiant heat sources such as the sun or infra-red heaters warm dark surfaces more than lighter ones. A black container of solvents can be significantly warmer than the air temperature around it. Just like black asphalt is much warmer than the air temperature on sunny days.

## Flammable Range

Unlike flashpoint, flammable range is as important to determining hazards for gases and aerosols as it is for liquids. Flammable range is the percentage of vapor/gas in air necessary for combustion to occur. The lowest percent that will burn is known as the lower explosive limit (LEL) or lower flammable limit (LFL), and any amount below that is said to be "too lean" to burn. The highest percentage of vapor that will burn is known as the upper explosive limit (UEL) or upper flammable limit (UFL), and any amount above that is said to be "too rich" to burn.



Compare the three following flashpoints and flammable ranges:

Chemical	Flashpoint	Flammable Range
Hydrogen	< -150° C (-238° F)	4% to 74%
Ether	-40° C (-40° F)	1% to 48%
Ammonia	132° C (270° F)	15% to 25%

Hydrogen has by far the widest flammable range. It will ignite and burn in air at any concentration between 4% and 74%. Coupled with its extremely low flashpoint, this chemical poses a significant fire risk. At the other end, ammonia has a flammable range that begins at a relatively high concentration of 15% and is only 10% wide. It has a flashpoint well above conditions normally found in a lab or the environment. By definition it is a flammable gas but it does not pose near the fire hazard of either hydrogen or ether. Instead, the toxic nature of ammonia is its real hazard. Hence, the pictograms associated with gaseous ammonia are the compressed gas, skull and cross bones, and corrosives.

## Ignition (Auto-Ignition) Temperature

Ignition temperature is defined as the minimum temperature to which a material must be heated to cause the production of free radicals (bond breakage). If this process occurs in the presence of oxygen or some oxidizing agent, combustion will take place. This differs from flashpoint in that with ignition temperature there is no direct source of ignition (e.g., flame, spark, etc.). Typically, flammable liquids that have low boiling and flash points have relatively high auto-ignition temperatures. This is what allows many solvents to be distilled. They vaporize or boil off before they reach their auto-ignition temperature.

Conversely, some combustible liquids, like cooking oil, have auto-ignition temperatures at, below, or near their relatively high boiling and flash points. These types of materials will not boil off before they reach an auto-ignition temperature.

## Ignition Sources

The most common examples of ignition sources are open flames, sparks (electrical, static, or friction), and heated objects. A common match burns between 680° and 980° C (1500° and 1800° F). Sparks/arcing from electricity begin with static electricity at around 1010° C (2000° F) and increases from there. Sparks from friction depend on the material producing it. Sparks from the most common metal available, steel, are in the range of 1370° C (2500° F). The point of this is that the temperature of any of these ignition sources is hot enough to ignite nearly any flammable gas, liquid or aerosol.

## Gas/Vapor Density

The importance of gas/vapor density is whether the gas/vapor is lighter or denser than air. If lighter than air, they will rise; denser than air and they will fall. Hydrogen, acetylene, ammonia, methane, ethylene, and carbon monoxide are the most common flammable gases that are lighter than air. Other gases, liquids, and aerosols are either as dense as or denser than air. Those that are denser than air tend to pose the greatest risk as the gases/vapors can concentrate on a floor and flow away from the



source to locations where there are ignition sources. Once ignited, a wave of flame flashes back to the source and sets it on fire.

### Other Hazards

The container types for all three classes of flammables are subject to rupture if subjected to excess heat. Compressed gas cylinders are fitted with pressure relief valves, which provide a measure of protection. Though excess heat can be an issue for liquids, it tends to be a greater one for aerosols as these tend to be packaged in lightly constructed containers that are already under pressure. Aerosol cans left in vehicles on hot days have ruptured violently.

Flammable gases, liquids, and aerosols can also be toxic or corrosive, or exhibit other physical or health hazards. Corrosivity is often associated with aerosols used as cleaners since they often also contain sodium or potassium hydroxide. Some solvents, like ether, can have narcotic effects leading to unsafe work practices. Some flammable liquids can form dangerously explosive peroxides on storage.

### Mitigating the Risks of Flammable Gases, Liquids, and Aerosols

First and foremost, conduct a general hazard analysis/risk assessment of the work to be conducted and verify that a written, comprehensive project-specific risk/assessment with additional oversight is not in order, as described in the companion EHS SOP, ***Chemical Hazard Assessment & Risk***

***Minimization***. General risk mitigation measures are as follows:

- Conduct a thorough literature search, including review of Safety Data Sheets to understand the properties (e.g., flammable range, flash point, ignition temperature, etc.) of the flammable materials to be used and how they may be relevant to your intended work/processes/procedures/apparatus.
- Follow general safe chemical handling practices as described in the EHS SOP, ***General Guidance for Chemical Ordering, Receipt, Distribution, Use and Storage***.
- When possible, substitute products with higher flash and boiling points for products with lower flash and boiling points. Limit purchases and storage to the smallest quantity feasible. Order flammable and combustible liquids in the smallest, feasible container size. Numerous containers of smaller quantities are generally less hazardous than large quantities in a single container. Avoid glass or use coated-shatter proof containers, if possible.
- Keep containers of flammable/combustible liquids tightly closed at all times when not in use. Store away from light and heat sources.
- National Fire Protection Association (NFPA) Standards establish maximum amounts of flammable and combustible liquids that can be stored in a building or unit (generally an area with 2-hour fire separation from adjacent spaces) based on the type of occupancy and class of liquid. As a general rule, strive to limit storage to a maximum of 60 gallons and store within a rated flammable liquid storage cabinet that meets specific design criteria, including a three-point latch system on the doors, a 2" raised seal to retain spilled liquids, and markings that state



“Flammable – Keep Fire Away.” Venting of cabinets is not generally recommended. Bungs must be securely fastened in un-vented cabinets.

- Storage must be in a manner as to not impede egress from the storage location (e.g., stored away from aisles and exit doors).
- Store flammable liquids requiring cooling in tightly closed containers within refrigerators and/or freezers that meet specific design criteria, including no internal ignition sources. Manufacturers of flammable liquid refrigerators/freezers must prominently mark these types of devices to indicate that they are intended for flammable/combustible liquid storage.
- Transport breakable bottles in buckets or some other form of protective secondary containment.
- Observe all specific safety precautions established for the laboratory/procedure.
- Wear appropriate PPE. See EHS SOP, **Personal Protective Equipment for Chemical Exposures**. Non-flammable lab coats provide the best protection in a laboratory setting. Avoid wearing synthetic apparel that will melt, even when worn under a flame-resistant lab coat.
- Know how to use a fire extinguisher and have a dry chemical or carbon dioxide extinguisher readily available. See EHS SOP, **Fire Safety – General Prevention and Extinguishers** and EHS web-based training, **Fire Extinguisher Training** for more information.
- Observe strategies for reducing the risk of laboratory fires. See related presentations from the Laboratory Safety Colloquium series on the EHS web page: **Flammable – Toxic – Corrosive Gas Safety** and **Preventing Laboratory Fires**.
- Use flammable liquids that do not form peroxides, if possible. If a peroxide-forming solvent is necessary, follow the guidance in the EHS SOP, **Use and Storage of Peroxide Forming Chemicals**.
- If working with compressed gas cylinders, observe the safety precautions detailed in the EHS SOP, **Gases Under Pressure Hazards & Risk Minimization**.
- Verify the accessibility and operability of a safety shower and appropriately classed and sized fire extinguisher in the immediate work area.
- Conduct work on the smallest scale possible.
- Thoroughly evaluate and strictly control sources of ignition, including those that may come into play only in the event of a spill or other emergency/mishap.
- Identify and eliminate sources of static discharge. Sources of static include clothing, use of plastic, and transfer of materials between containers. Low humidity environments also increase the potential for static. Ground and bond containers, particularly those that are  $\geq 4$  L during transfer operations to prevent ignition via static electricity. Bonding means connecting two containers, whereas grounding means connecting the containers to a ground wire or cable. Avoid the buildup of static electricity when transferring between plastic containers by avoiding the free-fall of liquids; pour carefully in a steady stream down the sides of the container.
- Dispensing/transferring and heating operations must be performed in a manner that limits the accumulation of flammable vapor/air mixtures to less than 25% of the Lower Explosive Limit (LEL). This is usually accomplished by using the smallest volumes possible, and conducting the operation in a fume hood or other mechanically ventilated space.
- Do not use an open flame to heat flammable/combustible liquids; use steam baths, heating mantles, and other similar safer methods. Heat flammable/combustible liquids in ovens,



furnaces, environmental chambers, and other heated enclosures only if the equipment is designed to prevent internal explosion.

- Only those chemicals involved in the operation should be in the vicinity of the work being done. Bottles/containers from which they were dispensed and other chemicals need to be stowed away from the procedure being conducted.
- Treat all reaction products containing flammable liquids as flammable liquids. In one reported incident, a reaction product that had not been dried of solvent ignited when the person handling it moved it near an ignition source. The same applies to contaminated media such as paper towels.
- Unattended operations involving flammable/combustible liquids are strongly discouraged. If absolutely necessary, engineering controls, in the form of override controls, automatic shutdown devices, over-temperature shutoff switches on electrically heated constant temperature baths, cooling fan interlocks, etc. are required, along with routine physical surveillance.

Do not distill flammable/combustible liquids prone to peroxide formation. Prior to conducting a distillation operation, ensure that the equipment was designed for such use, the apparatus is set-up in a properly functioning fume hood, and glass equipment is free from cracks, chips, scratches or other defects.