"Superacids" Safety Guidelines

☠WARNING☠: Superacids can pose a serious threat to the health and safety of laboratory personnel, emergency responders and waste handlers if not stored, handled and disposed of properly, because of their corrosive and toxic (acute and chronic) properties. Consequently, it is essential to thoroughly understand the properties of superacids and follow all safety protocols to properly store and handle them. Accidental exposures must be treated immediately in order to limit the extent and seriousness of the injury.

1) Purpose and Scope

This document discusses the properties and hazards of most common superacids that may be handled or stored at Concordia University, and how to appropriately protect yourself from potential superacid exposures. Currently, three commercially available single-molecule Brønsted superacids (*i.e.*, trifluoromethanesulfonic acid, chloro- and fluorosulfonic acid) are within scope of these Guidelines.

This document also details emergency procedures for dealing with accidental contact with a superacid, including first aid treatment information.

Note that EHS must be informed of the use or handling of all mixtures involving superacids, whether prepared in-house (*e.g.*, Magic acid) or purchased from commercially available sources.

2) Definition of Superacids

According to a widely accepted description by Gillespie,[1] extremely strong Brønsted (protic) acid systems that are from hundreds to millions of times stronger than 100% sulfuric acid are termed "**superacids**".[2] This class of chemicals can also encompass Lewis (electron acceptor) acids as well as their conjugate pairs. Most common primary superacids include:

- perchloric acid ($HClO_4$, see also: EHS-DOC-010 – Perchloric Acid Safety Guidelines),
- trifluoromethanesulfonic acid (CF_3SO_3H, triflic acid, or TfOH),
- halogenosulfonic acid (XSO_3H, where X = F or Cl), and
- higher perfluoroalkanesulfonic acids ($C_nF_{n+2}SO_3H$).

Superacidity can also be obtained with the use of binary superacids consisting in a mixture of Brønsted superacids (*e.g.*, Hydrogen Fluoride – Fluorosulfuric acid or Hydrogen Fluoride – Triflic acid) or conjugate Brønsted-Lewis superacids (e.g Fluorosulfonic acid – Antimony pentafluoride (1:1) or "Magic acid").

Superacids can resist oxidation and reduction, and show high thermal stability, which make them useful as catalysts in a broad range of organic and inorganic reactions. Their field of application also covers the pharmaceutical industry with the development of drug derivatives (*e.g.*, antibiotics, proteins, glycosides, steroids).

Superacids present major health and physical hazards. They present both acute and chronic toxicity, and are susceptible to react violently in the presence of water, moisture, or other organic chemicals. They are exceptionally corrosive, except for the carborane superacid H-($CHB_{11}X_{11}$; X=Halogen atom) derivatives for which relative "gentleness" has been observed due to the remarkable stability of the corresponding conjugate bases.[3]

3) Properties of Common Superacids

	Trifluoromethanesulfonic acid (Triflic acid)	Fluorosulfonic acid	Chlorosulfonic acid
Formula	CF_3SOOH	FSO_3H	$ClSO_3H$
CAS #	1493-13-6	7789-21-1	7790-94-5
Physical aspect	Light yellow liquid	Colourless liquid	Liquid
Physical Properties			
Molecular weight (g/mol)	150.07	100.07	116.52
Boiling point (@ 760 mmHg)	162°C	165.5°C	151-152°C
Vapour density (*vs* air = 1)	5.2	3.45	4
Density (@ 25°C)	1.696	1.726	1.750
H_0 (Hammet acidity function)[a]	−14.1	−15.1	−12.8

[a] H_0 is a measure of acidity that is used for very concentrated solutions of strong acids, including superacids, taking into account the activity and the thermodynamic activity coefficients of the species in the medium. It is widely used to extend the measure of Brønsted-Lowry acidity beyond the dilute aqueous solution for which the pH scale is useful. On this scale, pure H_2SO_4 has a H_0 value of −12.

4) Hazards and Hazard Classification

This section presents the hazards associated with Trifluoromethanesulfonic acid (Triflic acid), Fluorosulfonic acid and Chlorosulfonic acid. In order to provide a broader view of the dangers, both WHMIS 2015 and NFPA ratings are presented.

Most superacids can :

- react violently with water, acids, bases, strong oxidizing agents, metal carbonates, hydroxides, oxides, amines, alcohols, ketones, nitro compounds;
- react violently with most polar organic solvents; and
- attack many metals (including metal storage containers), forming flammable hydrogen gas. As such, they can represent extreme explosion hazard.

a) Trifluoromethanesulfonic acid[4]

WHMIS 2015 signal word: DANGER

Classification:

- Corrosive to Metals	Category 1
- Acute Oral Toxicity	Category 4
- Skin Corrosion/Irritation	Category 1
- Serious Eye Damage/Eye Irritation	Category 1A
- Specific Target Organ Toxicity (Single Exposure) *Respiratory System*	Category 3

NFPA 704 (Standard System for the Identification of the Hazards of Materials for Emergency Response):

Health Hazard: 3 – Extreme DANGER (Brief exposure may cause serious temporary or moderate residual injury)
Fire hazard: 1 – Flash point above 200°F (Must be heated in order to ignite)
Reactivity: 0 – Stable (Normally stable even when exposed to fire)

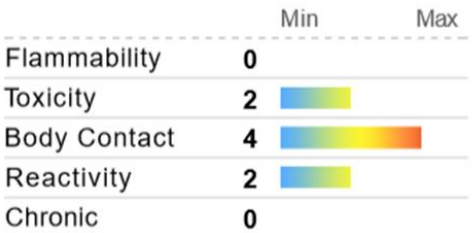
b) Fluorosulfonic acid[5]

WHMIS 2015 signal word: DANGER

Classification:

- Corrosive to Metals	Category 1
- Acute Toxicity (inhalation)	Category 4
- Skin Corrosion/Irritation	Category 1
- Serious Eye Damage/Eye Irritation	Category 1A
- Specific Target Organ Toxicity (Single Exposure) *Respiratory System*	Category 3

NFPA 704 (Standard System for the Identification of the Hazards of Materials for Emergency Response):



Health Hazard: 3 – Extreme DANGER (Brief exposure may cause serious temporary or moderate residual injury)
Fire hazard: 0 – Will not burn

Reactivity: 2 – Violent chemical change (Changes violently at elevated temperature and pressure or reacts violently with water or forms explosive mixtures with water)

~~**W**~~: Reacts with water in a dangerous or unusual way

Strongly reacts with water to form HF and H_2SO_4.

c) Chlorosulfonic acid[6]

WHMIS 2015 signal word: DANGER

Classification:

- Corrosive to Metals	Category 1
- Skin Corrosion/Irritation	Category 1
- Serious Eye Damage/Eye Irritation	Category 1A
- Specific Target Organ Toxicity (Single Exposure) *Respiratory System*	Category 3

NFPA 704 (Standard System for the Identification of the Hazards of Materials for Emergency Response):

	Min	Max
Flammability	0	
Toxicity	0	
Body Contact	4	
Reactivity	2	
Chronic	0	

0 = Minimum
1 = Low
2 = Moderate
3 = High
4 = Extreme

NFPA 704 diamond

Health Hazard: 4 – Extreme DANGER (Very brief exposure may cause death or major residual injury)

Fire hazard: 0 – Will not burn

Reactivity: 2 – Violent chemical change (Changes violently at elevated temperature and pressure or reacts violently with water or forms explosive mixtures with water)

~~**W**~~: Reacts with water in a dangerous or unusual way

OX: Substance is a strong oxidizer

Can contain HCl, H_2SO_4 and SO_3 as decomposition by-products.

5) Health Hazards

a) Triflic acid and chlorosulfonic acid

***Skin exposure*:** Direct contact with skin can cause **severe pain and burns** with potential delayed tissue destruction. Entry into the bloodstream through, for example, cuts, abrasions, puncture wounds or lesions, may produce systemic injury with harmful effects.

***Eye exposure*:** Any eye contact must be taken seriously. Severe ocular lesions may appear 24 hours or more after direct contact. Repeated or prolonged contact with vapours/mists may cause severe eye irritation with discomfort, tearing, or blurring of vision.

***Inhalation*:** The material is **extremely destructive** to the tissue of the mucous membranes and upper respiratory tract (trachea and lung). Inhalation of quantities of liquid mist may be extremely hazardous, even lethal due to spasm, extreme irritation of larynx and inflammation of bronchi, chemical pneumonitis and pulmonary oedema.

***Ingestion*:** Oral acute toxicity generates **immediate pain** and evident difficulties in swallowing and speaking. Death may also be rapid and often results from asphyxia, circulatory collapse or aspiration of even minute amounts.

***Chronic toxicity*:** Long-term exposure to respiratory irritants may result in disease of the airways involving difficult breathing and related systemic problems. Prolonged or repeated exposure may cause inflammation of the mouth and gums, ulcerative changes, and erosion of the teeth.

All the hazards abovementionned can apply to chlorosulfonic acid, but due to the presence of decomposition by-products such as sulfuric acid, hydrochloric acid and sulfur trioxide, chronic toxicity ("Carcinogenic to humans"), acute poisoning and further corrosiveness considerations must be added.

b) Fluorosulfonic acid

All the hazards abovementioned (severe eye burns, destruction of trachea and lung, oral acute toxcicity and long term illnesses) can also be attributed to flurosulfonic acid, in solution or as pure chemicals. **Hydrofluoric acid (HF) is one of the hazardous decomposition products of fluorosulfonic acid. Therefore, hazards related to HF's acidic properties and HF's ability to release toxic fluoride anions inside the organism are also associated.** The HF molecule is able to penetrate deeply into the skin and soft tissues, resulting in destruction of nerves, blood vessels, tendons and bones which can result in sudden death.

Important: - It is mandatory for users who handle or store HF-generating fluorosulfonic acid (or corresponding mixtures), and the person responsible for the disposal of these chemicals, to refer to the following document : EHS-DOC-008_HF Guidelines.[7] These guidelines specifically discuss the properties and health and safety hazards of HF, and the related emergency procedures for dealing with spill situations or accidental HF contact.

- When using fluorosulfonic acid, calcium gluconate gel MUST be present in the immediate vicinity of the location of use.

6) Safety Precautions for Superacids Use

6.1 General safety precautions for all superacids

Training

Students and employees who handle superacids must have read the corresponding (Material) Safety Data Sheet ((M)SDS) and receive training on the hazards of superacids from their respective department. They must know what to do in the event of a spill or an exposure incident. The list of mandatory trainings shall include:

- *WHMIS for Laboratory Personnel*,
- *Corrosive Substances*,
- *Hazardous Waste Disposal for Laboratory Personnel,* and
- *Hazardous Material Minor Spill Response*.

Three documents must always be kept in the immediate vicinity of the working area:

1) The Standard Operating Procedure (SOP) developed by the student / employee's department;
2) The specific (M)SDS corresponding to the superacid used or developed in the laboratory; and
3) The present document "Superacids" Safety Guidelines.

Engineering controls

All operations involving the use, handling, or transfer of superacids must be carried out in a properly functioning chemical fume hood that has been verified/calibrated in the previous 12 months. Ensure adequate ventilation, especially in smaller areas with less ventilation. Only required materials are to be in the fume hood during operations.

Facility Safety Equipment

Before beginning any work, ensure that eyewash stations are operational and both eyewash stations and safety showers are situated close to the workstation. Ensure that they are clean, accessible and free of obstacles.

Eye Protection

Tight-fitting chemical splash goggles **and** a face shield (20 cm, 8 in. in minimum) **MUST** be worn when handling superacids.

Hand Protection

- **Always consult the manufacturer's glove selection guide when selecting gloves for working with superacids.**
- **Gloves must be inspected prior to use, and changed regularly through the experiment (approximately evey 30 minutes, or whenever there is contamination on the gloves or signs of degradation or damage).**
- **It is strongly recommended to double glove if using disposable nitrile gloves: the proper glove removal technique ("doffing" technique, no skin touching the glove's outer surface) must be applied.**

6.2 Trifluoromethanesulfonic acid

Thin Nitrile-rubber disposable gloves (minimum layer thickness of 0.10 mm (**4 mil**)) provide only a good contact barrier in case of potential splash incident. Thicker (10-20 mil) Viton® or Nitrile rubber offer good resistance to triflic acid. If gloves become contaminated with this chemical, remove them immediately, **wash your hands** thoroughly with water and check for any sign of contamination. Contaminated gloves must be disposed of as solid chemical waste.

6.3 Fluorosulfonic and chlorosulfonic acid

Thin disposable gloves (such as 4, 6, or 8 mil blue Nitrile glove) provide a contact barrier only. Thicker (10-20 mil) Viton (fluorinated rubber Vitoject®), PVC or neoprene gloves provide good resistance to acids and specifically to HF. Also 6 mil nitrile inner gloves and 22 mil (nominal) gauge neoprene or SilverShield outer gloves may be used. Nitrile gloves (6 mil) may also be efficient as a layer on top of SilverShield gloves for dexterity. ***Do not use latex gloves***.

Protective Clothing

A closed lab coat with long sleeves and tight wrist, or chemical smock along with a chemically (acid)-resistant apron (neoprene or Viton, PVC) must be worn when handling superacid solutions. **No exposed skin is allowed**; long pants, sleeves, and closed toe shoes/boots must be worn. If necessary, disposable sleeve covers should be worn for added protection in wrist/forearm regions.

Respiratory Protection

Avoid inhalation of vapour or mist at all times. Working under a properly functioning fume hood will protect the user from being exposed to vapours and mists. In the event of a minor spill outside of the fume hood, respiratory protection is mandatory. In that context, the lab personnel intending to use/wear a respirator mask must be trained and fit-tested by EHS prior to proceeding with any clean-up. Only specific cartridges for acid gases (+HF in the event fluorosulfonic acid is used) may be used with **full-face respirators**.[8,9]

Safe Work Practices

- Absolutely no eating, drinking or chewing gum where superacids are used.
- Whenever possible, less hazardous materials should be substituted for superacids.
- Always work in a well-ventilated area when handling superacids or superacid-containing materials.
- Never work alone when using superacids. A "buddy system" should be implemented.
- The area must be equipped with an emergency shower, an eyewash station and a first aid kit.
- **The use of fluorosulfonic acid requires the presence of calcium gluconate gel in the first-aid kit**. This gel must be inspected before each use of these materials or at least monthly to ensure the gel has not been removed and has not reached the expiration date. If the gel has been opened, a new container must be purchased and the old container discarded. No work with HF-generating chemicals can be done with an expired tube of calcium gluconate gel.
- Contaminated work clothing must not be allowed out of the workplace.
- Never add water to superacids.

7) Storage considerations

Due to the hazardous nature of the material, only minimal quantities of superacid should be purchased and stored.

Dry and well-ventilated places are required to store superacids.

Keep superacids stored in their original containers if possible (*i.e.*, PFA/FEP containers for fluorosulfonic acid, and glass bottles for triflic acid and chlorosulfonic acid). In the event triflic acid is sold in ampoules, transfer the unused material under an inert atmosphere and tightly close the compatible container. As a part of hazard communication, containers must be clearly identified with WHMIS 2015-compliant supplier or workplace labels. Secondary polyethylene containment trays should be used and clearly labeled.

Containers which are opened must be carefully resealed under an inert atmosphere, and kept upright to prevent leakage.

Recommended storage temperatures:

- Triflic acid: **Do not store above temperatures of 25°C.**
- Fluorosulfonic acid: **2–8°C**
- Chlorosulfonic acid: **Do not store above temperatures of 25°C.**

Do not store superacid containers with these incompatible materials: Water, strong bases, strong oxidizing agents, metals, alcohols.

NEVER STORE fluorosulfonic acid in glass containers. This can generate highly toxic fumes of Silicon tetrafluoride (SiF_4) in contact with glass.

8) Spill Considerations

The immediate area of superacid spill must be cleared of all non-response personnel. Depending on the quantity and the location of the spill, an EVACUATION must be considered.

a. Minor (incidental) spills

Spills of superacids or superacid-containing materials can be considered minor (incidental) only if all of the following criteria are met:

- It involves ≤25ml of spilled superacid or superacid-containing material.
- It is not ongoing (leakage/release has stopped) and spilled material can be easily contained.
- Public and non-lab spaces are not implicated or affected by the spill.

In the event of an **incidental (minor) spill**, the user can consider to do the clean-up **only if** the requirements described below are met:

- The user has all necessary safety training and experience using/handling superacid solutions;
- All PPE required to avoid breathing vapors and contact with skin and eyes is available;
- Sufficient spill response materials (compatible/inert sorbent pads, neutralizers, compatible waste container for collected spill materials) are present onsite;
- Access to the spill area is controlled and no further contamination/spill is taking place; and
- **The person responsible for the clean-up is comfortable responding to and cleaning up the spill.**

If one or more of the above criteria are not satisfied, notify Security at **ext. 3717** and request the Hazmat Spill Response Team.

Spill procedure for NON-HAZMAT Team Members (students, lab technicians, workers) in case of any spill (minor or major) of fluorosulfonic acid (located in a fume hood or not): Please refer to EHS-DOC-008_HFguidelines.

Spill cleanup procedure for NON-HAZMAT Team Members (students, lab technicians, workers) in the event of an incidental (minor) spill (*e.g.,* small volumes (≤ 25mL)) **of triflic acid or chlorosulfonic acid located in a fume hood:**

1. Notify personnel from the immediate area to stay away from the spill area.
2. Don all PPE required for cleaning the spill:

- Fully buttoned lab coat, long pants, and closed shoes (no exposed skin),
- Chemical splash goggles,
- Face shield,
- Thick gloves (10-20 mil, neoprene or Viton),
- **If the spill has occurred outside of a fume hood:** a full-face respirator for which the wearer has been fit tested, and appropriate acid gas cartridges.

3. Refer to the approved SOP for specific cleaning instructions. The goal of the spill cleanup should be to ensure a thorough decontamination of affected equipment and surfaces, including the fume hood.

- An inert binding material may be used to absorb the liquid: sand, other inert granular sorbent, or hazmat sorbent pads.
- **If neutralizers are used, heat and gas will often evolve and can cause splattering.** Suitable neutralizers include dilute solutions of weak bases, such as sodium (bi)carbonate. Take proper precautions (PPE) and use appropriate technique for their application: begin at the outer perimeter of the spill, slowly adding neutralizer and working from the edges of the spill inward. To ensure effective neutralization and safe disposal, test with litmus paper or colour-indicating solution until the spilled material is within the neutral range of pH 6-8.

4. After removing the spilled material, the area and affected surfaces must be neutralized. Spray the area lightly with water and test the pH. Continue to clean with water and/or neutralizer until the pH is 6-8.

5. Discard contaminated materials in dedicated solid hazardous waste containers, displaying labels and warnings described before.

6. Advise your PI/supervisor of the event and complete EHS-FORM-042, Injury/Near-Miss Report.

7. **If you do not feel comfortable performing the clean-up, treat the spill as a major (emergency) one**. Refer to section b. below.

b. Major (emergency) spill

Spills of superacids or superacid-containing material must be considered major (emergency) if **any** of the following criteria are met:

- Involves ≥25ml of superacid or superacid-containing material.
- Is ongoing and/or cannot be contained.
- Occurs in or affects a public corridor or other non-lab space.

Spill procedure for NON-HAZMAT Team Members (students, lab technicians, workers) in case of an emergency (major) spill of superacid (large quantities located in or outside a fume hood):

1. Evacuate and secure the area immediately. Advise and warn coworkers and others in the area.

2. Do not touch the hazardous material.

3. Call Security at **ext. 3717** or **514-848-3717**, providing them with the name of hazardous material, the quantity involved, the related health risks and precautions to be taken. Provide them Safety Data Sheet (SDS) and appropriate documentation.

4. Wait for the arrival of Hazmat clean-up team. Remain nearby (in a safe area) to provide them with details of the spill.

9) Waste considerations

Never put superacids or superacid-contaminated material in regular waste. Liquid and solid chemical wastes generated from superacid-involving experiments are to be stored separately in individual chemically compatible plastic containers provided by EHS, with a sealed lid separated from other chemical waste. The regular Concordia Hazardous Waste management will proceed, including a self-adhering EH&S identification label that will be placed on each container to indicate the volume, the nature, and concentration of the superacids.

To prevent violent exothermic reactions, do not mix aqueous waste with superacid-containing waste. Due to the possible generation of HF, dedicated individual containers should be allowed to accomodate waste of fluorosulfonic acid.

10) Emergency Procedures

All exposure to superacids, at any concentration, must receive immediate first aid and subsequent medical evaluation even if the injury appears minor. The pain can be felt quickly after the exposure. Rapid treatment of the injury is essential since these materials can produce delayed effects and serious tissue damages. **If untreated, permanent damage and disability may result**.

Please refer to EHS-DOC-008 HF Guidelines (Section 7 – Emergency Procedures) in the event of a direct exposure to HF-generating superacids (Fluorosulfonic acid or related mixtures).

1. Evacuate the immediate area where exposure occurred. Exposed/injured persons should proceed immediately to step 2; non-exposed persons should secure the area and prevent others from entering the contaminated zone.

2. Depending on the type of exposure:

a. Skin Contact with triflic acid or chlorosulfonic acid:

i. Remove contaminated clothing as quickly as possible, while preventing further contamination of unaffected skin and/or non-affected areas. Place contaminated clothing in a bag, waste container, or fume hood.

ii. Rinse affected areas with copious amounts of water to remove excess superacid. Non-abrasive soap may be used after the rinsing process.

b. Eye contact with triflic acid or chlorosulfonic acid:

i. Immediately irrigate eyes at eyewash with copious amounts of water, for at least 15 minutes, keeping eyelids apart and away from eyeballs.

c. Inhalation of triflic acid or chlorosulfonic acid:

i. Move victim to fresh air.

ii. **Inhalation of superacid fumes may cause swelling in the respiratory tract up to 24 hours after exposure. Moreover, decomposition products present in chlorosulfonic acid (HCl, H_2SO_4, and SO_3) can worsen the situation.**

d. Ingestion of triflic acid or chlorosulfonic acid:

i. Do not induce vomiting.

3. Call Security at ext. 3717 or 514-848-3717 and request medical assistance for a person who has been exposed. The exposed/injured person may require a non-exposed persons to complete this step for them.
4. Provide the SDS to Security/paramedics.

In all cases of exposures, a copy of the Safety Data Sheet (SDS) must be brought to the emergency room as the treating physician might be unaware of the treatment measures for superacid. All supercid incidents and exposures must be reported to the PI and to Environmental Health & Safety (EHS). An injury/near-miss report must be filled for any incident involving superacid spill or exposure.

Should you have any concerns or additional questions about the use of superacids at Concordia University, please contact EHS:

Email: ehs@concordia.ca
Telephone: 514-848-2424 ext. 4877

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