Safe Method of Use 24

Use of Protective Barriers for Potentially Explosive Reactions - Blast Shields and Fume Cupboard Sashes

Purpose: This Safe Method of Use applies to **principal investigators (PIs), sector managers, designated laboratory person (DLPs)**, technical staff and students who use laboratories within the University of Auckland.

General Guidelines

- While every care must be taken to ensure chemical reactions do not proceed in an uncontrolled manner, some chemical reactions carry a risk (however small) of becoming uncontrolled resulting in splash or burst hazard or in rare cases an explosion.
- There are two main sources of protective barrier available to protect laboratory personnel in such events – a blast shield and the fume cupboard sash.
- Blast shields can be moved into the fume cupboard for the duration of the experiment.
- Fume hood sashes are designed to be lowered to provide a physical barrier between reaction in the fume hood and laboratory personnel.
- Laboratory workers Student/Staff) shall **wear** and have accessible to full face shields when;
  - ➢ blast shields have to be removed to manipulate glassware
  - ➢ At any time where the Lab workers face may be exposed to an explosive reaction even with a blast shield in place.
  - ➢ Safety Glasses shall be worn in addition to a full face mask.
  - ➢ Tongs or other handling equipment should be used to manipulate glassware if there is any doubt over the stability/volatility of the synthesis & its potential to explode.
- Prior to conducting the experiment Laboratory workers shall consult the experimental procedure & adhere to any **"Cautions"** particularly where Blast Shields are recommended. They shall also consult closely with their supervisor.

Protective Barriers and their Use

A. Blast Shields

Use of blast shields is mandatory at all times for the following reactions:

1. Reactions where there is a clearly stated explosion hazard for either reactants or products have a (e.g. IBX) or where reactants /products are those listed in Appendix 1 – Explosive and Potentially Explosive Chemicals

2. Any reactions involving diazonium compounds, diazomethane, highly nitrated compounds and when heating organic peroxides.
3. Reactions involving strong oxidising agents in quantities greater than 2 litres
4. Reactions involving strong reducing agents (such as Lithium Aluminium hydride) in quantities greater than 2 litres.

B. Fume hood sashes

Fume hood sashes must be lowered to fullest extent when the following procedures are left unattended:

1. Reactions involving organolithiums, chlorination intermediates, butadiene, nitration intermediates, organic sulfates, polymerization reactions
2. Large scale distillations.

Any faults or observed lack of airflow in the fumehood when the fume hood sashes are lowered must be reported to the Laboratory Manager immediately.

Appendix 1 – Explosive and Potentially Explosive Chemicals

Explosive chemicals can release tremendous amounts of destructive energy rapidly. If not handled properly, these chemicals can pose a serious threat to the health and safety of laboratory personnel, emergency responders, building occupants, chemical waste handlers, and disposal companies. For example, an explosion of old isopropyl ether killed a laboratory worker when he attempted to remove a glass stopper from the container. In another instance, tetrazole exploded inside a hazardous waste incinerator, causing major damage and costly repairs.

Potentially explosive chemicals (PECs), which include peroxidizable organic chemicals. Most chemicals that are used in research and teaching laboratories are stable and non-explosive at the time of purchase. Over time, some chemicals can oxidize, become contaminated, dry out, or otherwise destabilize to become PECs (e.g., isopropyl ether, sodium amide, and picric acid). See Appendix I—Explosive and Potentially Explosive Families— for examples.
Unlike known explosives, which are designed to be stable under normal conditions, PECs are particularly dangerous because they may explode if they are subjected to heat, light, friction, or mechanical shock.

Common Laboratory PECs

There are many PECs used in academic research laboratories.

The following are some commonly used chemicals that can become an explosion hazard under certain conditions:

• Organic chemicals that form peroxides through exposure to air or light (see Appendix II — Peroxide Forming Chemicals)
• Hydrated picric acid that becomes dry or becomes contaminated with metals that form metal picrate salts
• Sodium amide that reacts with air or moisture to form superoxides, as evidenced by yellow or brown discoloration
• Certain alkyl nitrates (e.g., butyl nitrate or propyl nitrate) that become contaminated with nitrogen oxides
• Certain normally stable perchlorates (e.g., pyridium perchlorate or tetraethylammonium perchlorate) that become unstable at elevated temperatures

Note: Most explosions occur while purifying or distilling mixtures. Therefore, use extreme caution before concentrating or purifying any mixture that may contain an explosive chemical (e.g., a peroxide forming chemical or perchlorate).

There is an additional group of chemicals that should be considered although they are not necessarily heat-, light-, friction-, or shock-sensitive. These chemicals give off gaseous degradation by-products that may cause over-pressurization of the container and explode. They can degrade over time and should be incorporated into a safety and handling system that will prevent them from becoming explosive hazards.

Explosive and Potentially Explosive Chemical Families

Acetylene or acetylide compounds: N-Chloro-3-aminopropyne Propiolic acid Propynethiol	*Diazo compounds* 2-Buten-1-yl diazoacetate Diethyl diazomalonate Dinitrodiazomethane
Organic Azides Diazidomethyleneazine Picryl azide Vinyl azide Acetyl azide Cyanodiazoacetyl azide Phenylphosphonic azide chloride	*Diazonium carboxylates, perchlorates, salts, sulfates,* *tetrahaloborates, and, triiodides* Benzenediazonium-2-carboxylate 4-Aminobenzenediazonium perchlorate 6-chloro-2,4-dinitrobenzenediazonium sulfate 2-Nitrobenzenediazonium tetrachloroborate 4-Toluenediazonium triiodide
Acyl hypohalites Acetyl hypobromite Hexafluoroglutaryl dihypochlorite	*Difluoroaminoalkanols* 1,1-Difluorourea Perfluoro-N-cyanodiaminomethane
Alkyl nitrates Ethylidene dinitrate Glyceryl trinitrate Propyl nitrate	*Fluoro—nitro compounds* 1-Fluoro-1,1-dinitrobutane Fluorodinitromethyl azide
Alkyl perchlorates Hexyl perchlorate Ethyl perchlorate 1-Chloro-2-propyl perchlorate	*Fulminating metals* Lead fulminate Gold fulminate Silver fulminate
Allyl trifluoromethanesulfonates	*Furazan N-oxides*

2-Chloro-2-propenyl trifluoromethanesulfonate	Dicyanofurazan N-oxide 4-Oximino4,5,6,7-tetrahydrobenzofurazn N-oxide
Amminemetal oxosalts Ammonium hexanitrocobaltate Bis(1,2-diaminoethane) diaquacobalt (III) perchlorate Trihydrazine nickel (II) nitrate	*Hydroxooxodiperoxochromate salts* 1-Ammonium hydroxooxodiperoxochromate Potassium hyroxooxodiperoxochromate
Aromatic nitrates Picric acid Trinitrobenzene Picryl sulfonic acid Trinitroresorcinol	*Iodine Compounds* Calcium 2-iodylbenzoate Iodobenzene 2-Iodylvinyl chloride
Azides Hydrogen azide	*Isoxazoles* 3-Aminoisoxazole 3,5-Dimethylisoxazole
Aziridines 1-Bromoaziridine	*Metal Azide Halides* Chromyl azide chloride Molybdenum diazide tetrachloride Tungsten azide pentachloride
Azocarbaboranes 1,1-‘Azo-1,2-dicarbadecaborane	*Metal Azides* Aluminum azide Bis(cyclopentadienyl)tungsten diazide oxide Mercury (I&II) azide Lead azide
N-Azolium nitroimidates Benzimidazolium 1-nitroimidate 4-Nitroamino-1,2,4-triazole 2-(N-Nitroamino)pyridine N-oxide	*N-Metal Derivatives* Cadmium nitride Dibutylthallium isocyanate Sodium amide
Perchloramide Salts Barium perchloramide Mercury (II) N-perchloryl benzylamide Silver perchlorylamide	*Metal Fulminates* Mercury (II) fulminate Sodium fulminate Tripropyllead fulminate
Metal Halogentates Lead bromate	*Perchloryl Compounds* 2,6-Dinitro-4-perchlorylphenol Perchloryl fluoride N-Perchloryl piperidine
Metal Hydrides Stibine (Antimony hydride)	*Peroxyacid salts* Calcium peroxodisulfate Potassium tetraperoxomolybdate Tetramethylammonium pentaperoxodichromate
Metal Nitrophenoxides Lithium 4-nitrothiophenoxide Potassium 4-nitrophenoxide	*Peroxy and Iodoxy acids* Benzenperoxyselennic acid Peroxyacetic acid Peroxyformic acid o-Iodoxybenzoic acid (IBX)
Metal Oxides Bis (1-chloroethylthallium chloride) oxide Magnesium chloride trioxide	*Peroxycarbonate esters* O-O-tert-Butyl isopropyl monoperoxycarbonate Diallyl peroxydicarbonate Dimethyl peroxydicarbonate
Metal Oxohalogenates Ammonium iodate Lead acetate–lead bromate	*Phosphorus esters* Diethyl phosphite Dibenzyl phosphorchloridate
Metal Oxometallates Bis (benzene) chromium dichromate	*Nitroso Compounds* Dinitrosylnickel Ethyl N-methyl-N-nitrosocarbamate

	Potassium nitrosodisulfate
Metal Perchlorates Chromyl perchlorate	*N–S Compounds* Disulfur dinitride Potassium sulfurdiimidate Tetrasulfur tetranitride Thiotrithiazyl nitrate
Metal Peroxides Many transition metal peroxides are dangerously explosive.	*Organolithium Reagents* o-Trifluoromethyl phenyllithium m-Bromo phenyllithium
Metal Peroxomolybdates 2-Potassium tetraperoxomolybdate 2-Sodium tetraperoxomolybdate	*Organomineral Peroxides* Bis(triethyltin) peroxide Diethylhydroxotin hydroperoxide
Metal Picramates Palladium picramate Uranyl picramate	*Oximes* Bromoacetone oxime Hydroxycopper glyoximate Potassium cyclohexanehexone 1,3,5-trioximate
Nitroaryl Compounds N-Chloro-4-nitroaniline	*Oxosalts of Nitrogenous Bases* Ammonium tetranitroplatinate (II) Diamminepalladium (II) nitrate 1,2-Diammonioethane nitrate
Nitrogenous Base Nitrite Salts Methylammonium nitrite	*Ozonides* trans-2-Butene ozonide Ethylene ozonide (1,2,4-trioxolane) Trifluoroethylene ozonide
aci-Nitroquinonoid Compounds Sodium 1,4-bis(aci-nitro)-2,5-cyclohexadienide	*Perchlorate Salts of Nitrogenous Bases* Pyridinium perchlorate Teteraethylammonium perchlorate
aci-Nitro Salts Ammonium aci-nitromethanide Dipotassium aci-dinitromethanide Thallium aci-phenylnitromethanide	*Triazoles* 3-Diazo-5-phenyl-3*H*-1,2,4-triazole 4-Hydroxy-3,5-dimethyl-1,2,4-triazole 1,2,3-Triazole
Picrates Nickel picrate (anhydrous) S-7-Methylnonylthiouronium picrate Sodium picrate	*Poly(dimercuryimmonium) Compounds* Poly(dimercuryimmonium picrate) Poly(dimercuryimmonium permanganate) Poly(dimercuryimmonium trinitrobenzoate)
Polymerization (violent) Acrylic acid Ethylene oxide Vinyl acetate	*Polynitroalkyl Coumpounds* Dinitroacetonitrile Hexanitroethane Potassium trinitromethanide
Polynitroaryl Compounds 5,6-Dinitro-2-dimethyl aminopyrimidinone 4-Nitro-1-picryl-1,2,3-triazole 2,4,6-Trinitrotoluene	*Silver Compounds* Silver nitride (fulminating silver) Disilver ketenide Phenylsilver Silver azide Silver Osmate
Strained-Ring Compounds 2-Azatricyclo[2.2.102,6]hept-7-yl perchlorate Dicyclopropyldiazomethane Prismane	*Tetrazoles* 5-Aminotetrazole Silver and mercury salts of 5-nitrotetrazole Tetrazole

Ideal use and set up of a Blast Shield. Note that the combination of fully lowered fume hood sash and Blast Shield assist in containing any potential explosion.