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Management Procedures for Organic Peroxide Forming Chemicals and other Explosive Chemicals

For assistance, please contact EHS&RM at 575-646-3327

If you identify old explosives or old organic peroxide forming chemicals, immediately contact Environmental Health Safety & Risk Managment (EHS&RM) at 575-646-3327.

A. INTRODUCTION

All explosive chemicals should be identified and carefully managed. There are two main classes of explosive chemicals:

1) **Standard Explosive Chemicals:** These consist of explosive compounds manufactured for detonation such as dynamite, gunpowder, blasting caps, and fireworks. These compounds are rare on the NMSU campus and relatively stable under normal conditions. If these compounds are not being used for a specific, authorized activity they should be immediately called in for pick up by EHS&RM at 575-646-3327.

2) **Potentially Explosive Chemicals (PECs):** These consist of lab chemicals not intentionally made for detonation but which may explode and/or cause fires if not properly managed. A number of PECs are common on the NMSU campus and should be handled with extra precaution. The main focus of this SOP is to help identify PECs and describe the precautions that should be taken to manage them from purchase through disposal.

Organic Peroxide Forming Chemicals

This is the principal group of PECs that lead to problems in university labs. They are carbon-based chemicals capable of forming potentially explosive peroxide “O-O” bonds. Below is a breakdown of the four main subcategories of organic peroxide forming chemicals; common ones are specifically identified in the appendices.

1) Chemicals that form explosive levels of peroxides without a concentration step (evaporation, distillation, etc.) are listed in **Appendix 1**. These chemicals can be a particular hazard since peroxides can form even without opening the containers. Therefore, only small amounts should be ordered and used as soon as possible. After opening, they **should not be kept for over three months.** When possible, **store these chemicals under a nitrogen blanket**.

2) Chemicals that form explosive levels of peroxides upon concentration are listed in **Appendix 2**. These chemicals typically accumulate hazardous levels of peroxides when evaporated, distilled, contaminated, or have their peroxide inhibiting compounds compromised. **After opening, they should not be kept for over 12 months.**

3) Chemicals that may autopolymerize as a result of peroxide accumulation are listed in **Appendix 3**. These chemicals can undergo hazardous polymerization reactions that are initiated by peroxides

that have accumulated in solution. They are typically stored with polymerization inhibitors to prevent these dangerous reactions. Inhibitors can become compromised over time however, and thus **after opening, these chemicals should not be kept for over 12 months**. **Uninhibited chemicals should not be stored over 24 hours**. Uninhibited chemicals should be inhibited with the appropriate compounds before the 24-hour mark is exceeded. **Do not store inhibited chemicals in this category under an inert atmosphere** because some of the inhibitors require a small amount of oxygen to work.

4) Chemicals that cannot be placed into the above categories but still have the potential for forming hazardous levels of organic peroxides are listed in Appendix 4. **After opening, they should not be kept for over 12 months**.

The above lists are not all-inclusive. A wide range of organic chemicals can be oxidized by reaction with molecular oxygen to form explosive peroxides. The chemicals listed above are considered PECs in their pure form. However, when they are mixed with other compounds, their hazards can change. When mixed with other compatible chemicals (especially water) their explosive hazard is sometimes decreased through dilution, but not always. Therefore, laboratory workers should consult more experienced laboratory personnel, container labels, chemical Safety Data Sheets (SDSs), books such as "Hawley's Chemical Dictionary," or a list of Common Peroxide Moieties (See **Appendix 5**) if the hazards of a chemical are not well known or the chemical is suspected to form organic peroxides. It must be kept in mind that there are no "complete lists" of organic peroxide forming chemicals. All peroxide forming chemicals should be identified and carefully managed to best protect the health and safety of all laboratory co-workers.

B. BEST PRACTICES FOR MANAGING ORGANIC PEROXIDE FORMING CHEMICALS

Disclaimer: *There are significant uncertainties about the hazards and safe handling procedures for peroxide forming organic chemicals. Also, there are no definitive data about the concentration at which organic peroxides pose a hazard and several common peroxide detection methods may not detect all types of unstable peroxides. The steps outlined below are simply recommended "best management procedures" recommended by experts and followed at other universities to help prevent potential explosions. Individuals using the material have the primary responsibility for determining what procedures are best suited for their individual situations. The resources identified at the end of this procedure should be consulted before carrying out potentially hazardous experiments in the laboratory.*

HANDLING PROCEDURES

1) **Receipt and Dating Organic Peroxide Forming Chemicals**: Containers must be dated and labeled "Potentially Explosive Peroxide" immediately upon receipt of organic peroxide forming chemicals. The containers also must be dated when first opened and annotated with the required disposal date according to the category of organic peroxide (see category information above).

2) **Storage of Organic Peroxide Forming Chemicals**: Keep all PECs away from ignition sources such as open flames, hot surfaces, sparks, heat, and direct sunlight. Store them in tightly closed original containers to protect them from evaporation or possible contamination. Protect them from shock, friction, and do not shake the container. Ensure they are stored away from incompatible materials such as oxidizers (for exact incompatibility information consult the specific Safety Data Sheet). When

possible, store most of organic peroxide formers under inert gas except for chemicals that may autopolymerize as a result of peroxide accumulation.

3) **Use of Organic Peroxide Forming Chemicals**: Extreme care should be taken when opening and pouring organic peroxide formers. The cap and threads on the container should be wiped down with a damp towel after use. This is to prevent the deposition of peroxides around the cap area that could detonate simply from the friction of turning the cap. Most peroxide explosions occur during purification or distillation procedures. Therefore, before distilling a PEC or mixture of PECs, follow the designated peroxide testing procedures outlined below.

ORGANIC PEROXIDE TESTING PROCEDURES

WARNING: *Never test containers of unknown age or origin. Old containers may contain hazardous levels of peroxides, or peroxides may have crystallized on the cap threads, both of which present serious hazards when opening the bottle for testing. EHS&RM should be immediately notified in this situation and the suspect container should not be handled by anyone in the laboratory.*

1) The best method to test for peroxides involves semi-quantitative analysis using peroxide detection dip strips. These can be purchased from many of the major scientific and laboratory supply vendors. The peroxide strips are similar to the use of pH paper and a simple instruction sheet accompanies the strips. **If a test strip indicates a peroxide concentration above 10 ppm, the chemical should not be used and should be immediately turned in to EHS&RM for disposal**.

Note: Some test strips will detect hydroperoxides and most higher peroxides, but some polyperoxides may be poorly detected. Thus use of test strips is not always 100% effective at identifying dangerous levels of peroxides.

2) Modifications to the dip strip testing method are required to test low volatile organic compounds. For water-miscible chemicals, add three drops of water to one drop of a chemical to be tested. Wet the dip strip, wait until the color stabilizes, and then multiply the result by 4. For water-immiscible chemicals, add three drops of a volatile ether to one drop of a chemical to be tested. Wet the dip strip, wait until the color develops, and then multiply the result by 4.

3) Peroxide testing strips have a limited shelf life. Refrigeration is not recommended once the test strip container has been opened because water condensing on the strips reduces their effectiveness. The strips should be stored in as dry an environment as possible.

4) Chemicals that reach their expiration dates can be regularly tested. If they reveal a peroxide concentration below 10 ppm they can still be used. **Post-expiration date chemicals should be tested every six months and test dates and results annotated on the bottle**. Once a 10 ppm or greater peroxide level is detected, chemicals should be sent to EHS&RM for disposal.

5) **All peroxide forming chemicals to be distilled must be tested for peroxide content. If there are any measurable peroxides they should not be distilled**. When distilling peroxide forming chemicals, volume reductions should not exceed 80%. The remaining 20% of the chemical should remain in the distillation column to prevent the apparatus from drying out. **Distilling peroxides to dryness guarantees explosions**. If possible, a nonvolatile organic compound such as mineral oil should be added to the distillation mixture. The oil will remain behind and dilute any potential peroxides. During distillation, the solution must only be stirred mechanically or with inert gas; air or

other oxygen-containing mixtures can cause peroxide formation. **PECs without peroxide inhibitors should not be distilled**.

HANDLING OLD ORGANIC PEROXIDE FORMING CHEMICALS

When old peroxide chemicals are identified, **leave them in place and call EHS&RM for disposal**. Some of the **chemicals could be too dangerous even to move**. A quick look at the containers is helpful in revealing the dangerous situations (use of a flashlight as a light source can be helpful to peer through bottles). If crystals, solid masses, cloudiness, string-like formations, layers, or discoloration are observed, then there are likely very high levels of peroxides and everyone in the lab should be warned not to touch the chemicals until EH&S has evaluated the situation. Warning signs should be posted. **Never attempt to force open a rusted or stuck cap on a container of a PEC. Never scrape or scrub glassware or containers with oily or crusty residues that have been used with peroxide-forming compounds**.

KNOWN ORGANIC PEROXIDE CHEMICALS

There are numerous chemicals produced that are pure organic peroxides. A number of these chemicals are easy to identify however because they contain the phrases "**peroxide**" or "**peroxy**" in their nomenclature. These chemicals are extremely explosive and should be handled as outlined in previous sections. Some are "wetted" and should not be allowed to dry out, e.g., **benzoyl peroxide** and **picric acid**. Others are temperature sensitive and often unstable at room temperature. Special explosive proof refrigerators with backup power supplies must be in place before purchasing such temperature sensitive chemicals. EH&S should also be contacted in advance of obtaining temperature sensitive chemicals. Unless specifically instructed by the chemical manufacturer however, do not refrigerate organic peroxide forming chemicals since some develop higher peroxide levels upon cooling. The best rule of thumb is to review the SDS on each individual chemical.

C. OTHER TYPES OF POTENTIALLY EXPLOSIVE CHEMICALS (PECs)

Below are additional categories of PECs that can lead to serious explosions or fires.

1) **Explosive and Potentially Explosive Chemical Families:** Many non-peroxide chemicals are also explosive hazards. **Appendix 6** identifies a number of other common explosive/potentially explosive chemical families and specific examples that are known "problem compounds."

2) **Spontaneous Combustibles**: These chemicals ignite when exposed to air or water and can lead to explosions. Extreme care should be used in handling/storing these materials. Often these types of chemicals must be stored under oil or inert gas. Common campus examples are metallic sodium and potassium, both of which must be stored under oil.

3) **Oxidizers**: These chemicals can be considered PECs when combined with organic materials. Often just mixing can result in a fire or explosion. Examples of oxidizers include salts containing nitrates, chlorates, and most "per" prefixed chemicals such as permanganates, persulfates, and peroxides. (In fact, organic peroxide chemicals are dangerous because they are compounds with both oxidizer and organic components.) These compounds must be stored separately from flammable materials such as acetone, alcohol, or other volatile organic solvents.

4) **Perchloric Acid**: Is a PEC that requires very careful handling. Overall, perchloric acid is a strong oxidizer often used for the hot digestion of a variety of materials. **When used for digestions, it must be used in specifically designed perchloric acid hoods**. If at all possible, perchloric acid should be used cold. Anhydrous perchloric acid is unstable at room temperature and will decompose violently. Commercial perchloric acid is 72%. Do not store or use organic materials like solvents in a perchloric acid hood. If a vacuum is needed for perchloric acid work a water aspirator must be used instead of a mechanical pump since the latter contains hydrocarbon oils, which if contaminated with perchloric acid, can lead to explosive mixtures. Perchloric acid should be inspected for contamination. If the acid is discolored it must immediately be turned in for disposal. If a spill occurs, even if it is small, consult your supervisor immediately. Do not attempt to clean it up without supervision. When in doubt, call EHS&RM or 911.

5) **Chemical Over-Pressurization Risks**: Some chemicals give off gaseous degradation by-products that can lead to over-pressurization of containers and possible explosions- especially when heated or when incompatible chemicals are mixed together. Containers that are bulging clearly reveal an over-pressurization hazard. If a container is bulging contact EHS&RM for guidance.

D. DISPOSAL OF POTENTIALLY EXPLOSIVE CHEMICALS

1) Complete an NMSU Waste/Material Tracking Form
2) Call Environmental Health Safety & Risk Management at 575-646-3327 for a chemical pickup (pickup service available for Las Cruces campus only).

1. CHEMICAL SPILLS

1) Spills of potentially explosive chemicals must be dealt with carefully.
2) The chemical SDS should be immediately consulted to establish the nature of the hazard and proper spill cleanup procedure.
3) Determine whether personnel responsible for the cleaning up the spill have the expertise and protective equipment necessary to safely clean it up.
4) If there is any question about how to safely cleaning up the spill immediately contact EHS&RM at 575-646-3327 or dial 911.
5) All cleanup materials should be bagged, labeled and handled as hazardous waste. Do not throw cleanup materials into regular trash.

2. EMPTY CONTAINER HANDLING PROCEDURE

1) Empty containers of peroxide forming chemicals can still pose a significant hazard.
2) Immediately after the last amount is removed from the container triple rinse the container and collect the rinsate for disposal as hazardous waste
3) If after triple rinsing, the container is deemed to be free of residue, remove the label and and discard the container as regular trash.
4) If the container cannot be satisfactorily rinsed, it must be turned into EHS&RM as hazardous waste.
5) **Do Not** attempt to open or rinse old chemical containers that contained a PEC.

G. TRAINING

All personnel who work with potentially explosive chemicals need to be trained in the proper storage, use, and disposal of these dangerous chemicals. This SOP provides only basic training; personnel should discuss specific questions with their supervisor or EHS&RM staff.

APPENDIX 1

Chemicals That Form Explosive Levels of Peroxides without a Concentration Step

These chemicals can be a particular hazard since peroxides can form even without opening the containers. Therefore, only small amounts should be ordered and used as soon as possible. After opening, they should not be kept for over three months. When possible, store these chemicals under a nitrogen blanket.

Butadiene (When Stored as a Liquid Monomer)	Potassium amide (Inorganic Peroxide Former)
Chloroprene (When Stored as a Liquid Monomer)	Sodium amide (Inorganic Peroxide Former)
Diisopropyl ether	Sodamide (Inorganic Peroxide Former)
Divinyl acetylene	Tetrafluoroethylene (When Stored as a Liquid Monomer)
Divinyl ether	Vinylidene chloride
Isopropyl ether	

APPENDIX 2
Chemicals that Form Explosive Levels Of Peroxides upon Concentration

These chemicals typically accumulate hazardous levels of peroxides when evaporated, distilled, contaminated, or have their peroxide inhibiting compounds compromised. After opening, they should not be kept for over 12 months.

Acetal
Acetaldehyde
Benzyl alcohol
Butadiyne
2-Butanol
Cellosolves
Chlorofluoroethylene
Cumene
Cyclohexene
Cyclohexanol
2-Cyclohexen-1-ol
Cyclooctene
Cyclopentene
Decahydronaphthalene
Decalin
Diacetylene
Dicyclopentadiene
Diethyl ether
Diethylene glycol
Diglyme (Dimethyl ether)
Dioxanes
Ethyl ether
Ethylene glycol dimethyl ether
Ethylene glycol ether acetates
Furan
Glyme
4-Heptanol
2-Hexanol
Isopropyl alcohol
Isopropylbenzene
Methyl acetylene
3-Methyl-1-butanol
Methyl cyclopentane
Methyl isobutyl ketone
4-Methyl-2-Pentanol
4-Methyl-2-Pentanone
2-Pentanol
4-Penten-1-ol
1-Phenylethanol and 2-Phenylethanol
2-Propanol
Tetrahydrofuran
Tetrahydronaphthalene
Tetralin
Vinyl ethers

APPENDIX 3
Chemicals that may Autopolymerize as a Result of Peroxide Accumulation

These chemicals can undergo hazardous polymerization reactions that are initiated by peroxides that have accumulated in solution. They are typically stored with polymerization inhibitors to prevent these dangerous reactions. Inhibitors do become compromised over time however, and thus after opening, these chemicals should not be kept for over 12 months. Uninhibited chemicals should not be stored over 24 hours. Uninhibited chemicals should be inhibited with the appropriate compounds before the 24-hour mark is exceeded. Do not store inhibited chemicals in this category under an inert atmosphere because some of the inhibitors require a small amount of oxygen to work.

Acrylic acid
Acrylonitrile
Butadiene
Chlorobutadiene
Chloroprene
Chlorotrifluoroethylene
Dibenzocyclopentadiene
9,10-Dihydroanthracene
Indene
Methyl methacrylate
Styrene
Tetrafluoroethylene
Vinyl acetate
Vinyl acetylene
Vinyl chloride
Vinyl pyridine

APPENDIX 4

Other Organic Peroxide Forming Chemicals

A list of chemicals that cannot be placed into the categories listed in Appendices 1-3 but still have the potential for forming hazardous levels of organic peroxides are listed below. After opening, they should not be kept for over 12 months.

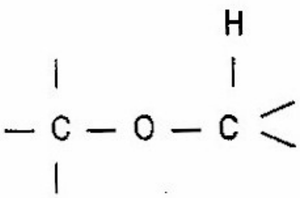
4-Vinyl cyclohexene	B-Methoxypropionitrile
p-Chlorophenetole	Buten-3-yne
Triethylene glycol	Chloroacetaldehyde diethylacetal
(2-Ethoxyethyl)-o-benzoyl benzoate n-Butyl phenyl ether	Chloroethylene
1-(2-Chloroethoxy)-2-phenoxyethane	Chloromethyl methyl ether
1-(2-Ethoxyethoxy)ethyl acetate tert-Butyl ethyl ether	Cyclopropyl methyl ether
1,1,2,3-Tetrachloro-1,3-butadiene	Di(1-propynyl) ether
1,1-Dimethoxyethane Bis(2-methoxyethyl) ether	Di(2-propynyl) ether
1,2-Bis(2-chloroethoxyl)ethane	diacetate
1,2-Dibenzyloxyethane Benzyl methyl ether	Diallyl ether
1,2-Dichloroethyl ethyl ether Bis(2-n-butoxyethyl) phthalate	Diethoxymethane Bis(chloromethyl) ether
1,2-Diethoxyethane Bis(2-chloroethyl) ether	Diethoxymethane Bis(chloromethyl) ether
1,2-Diethoxyethane Bis(2-chloroethyl) ether	Diethyl acetal
1,2-Diethoxyethane Bis(2-chloroethyl) ether	Diethyl acetal
1,2-Epoxy-3-isopropoxypropane	Diethyl ethoxymethylenemalonate
1,2-Epoxy-3-phenoxypropane	Diethyl fumarate
1,3,3-Trimethoxypropene	Diethylketene
1,3-Dioxepane	Dimethoxymethane Bis(2-methoxyethyl) phthalate
1,5-p-Methadiene	Dimethylketene
1-Ethoxy-2-propyne	Di-n-propoxymethane o-Bromophenetole
1-Ethoxynaphthalene	dipropionate
1-Octene	Ethyl vinyl ether
1-Pentene	Ethyl-b-ethoxypropionate
2,2-Diethoxypropane Bis(2-ethoxyethyl) adipate	Isoamyl benzyl ether
2,2-Diethoxypropane Bis(2-ethoxyethyl) adipate	Isoamyl ether
2,4-Dichlorophenetole	Isobutyl vinyl ether
2,4-Dinitrophenetole	Isophorone
2,5-Hexadiyn-1-ol	Isopropyl 2,4,5-trichlorophenoxyacetate
2-Bromomethyl ethyl ether	Limonene
2-Ethoxyethyl acetate	m,o,p-Diethoxybenzene Bis(4-chlorobutyl) ether
2-Ethylacrylaldehyde oxime	Methoxy-1,3,5,7-cyclooctatetraene
2-Ethylbutanol	Methyl p-(n-amyloxy)benzoate
2-Ethylhexanal	m-Nitrophenetole
2-Methoxyethanol	n-Amyl ether
2-Methoxyethyl vinyl ether	n-Butyl vinyl ether

2-Methyltetrahydrofuran	n-Hexyl ether
3,3-Dimethoxypropene Bis(2-methoxymethyl) adipate	n-Methylphenetole
3-Bromopropyl phenyl ether	n-Propyl ether
3-Ethoxypropionitrile	n-Propyl isopropyl ether
3-Methoxy-1-butyl acetate	o,p-Ethoxyphenyl isocyanate
3-Methoxyethyl acetate	o,p-Iodophenetole
4,5-Hexadien-2-yn-1-ol	o-Chlorophenetole p-(n-Amyloxy) benzoyl chloride
Acrolein	Oxybis(2-ethyl acetate)
Allyl ether	Oxybis(2-ethyl benzoate)
Allyl ethyl ether	p-Bromophenetole
a-Phenoxypropionyl chloride	p-Dibenzyloxybenzene Benzyl ethyl ether
B,B-Oxydipropionitrile	p-Di-n-butoxybenzene Benzyl-1-napthyl ether
B-Bromophenetole	p-Ethoxyacetophenone
B-Chlorophenetole Allyl phenyl ether	Phenoxyacetyl chloride
Benzyl ether	Phenyl-o-propyl ether
Benzyl n-butyl ether	p-Phenylphenetone
Bis(2-(methoxyethoxy)-ethyl) ether	Sodium 8,11,14-eicosatetraenoate
Bis(2-ethoxyethyl) ether	Sodium ethoxyacetylide
Bis(2-ethoxyethyl) phthalate	tert-Butyl methyl ether
Bis(2-methoxyethyl) carbonate	Tetrahydropyran
Bis(2-phenoxyethyl) ether	Triethylene glycol
B-Isopropoxypropionitrile	Vinylene carbonate

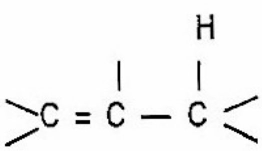
APPENDIX 5
Moieties that can Form Organic Peroxides

These moieties are ranked from highest (1) to lowest (14) risk of forming potentially dangerous peroxide concentrations.

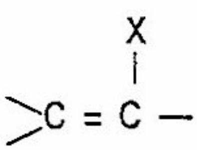
1. Ethers and acetals with α-hydrogen



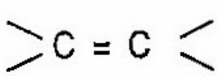
2. Alkenes with allylic hydrogen



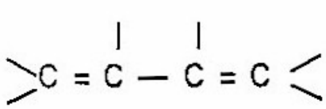
3. Chloroalkenes, fluoroalkenes



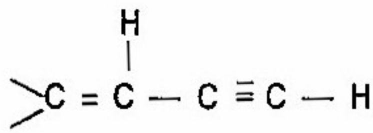
4. Vinyl halides, esters, ethers



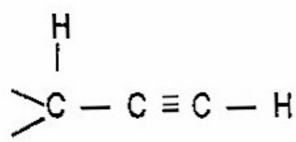
5. Dienes



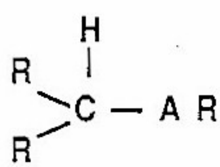
6. Vinylalkynes with α-hydrogen



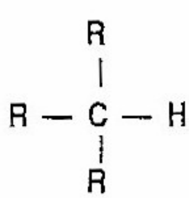
7. Alkylalkynes with α-hydrogen



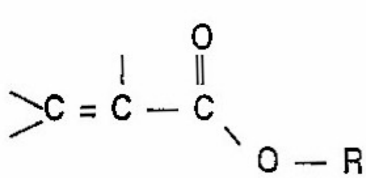
8. Alkylalkynes with tertiary α-hydrogen



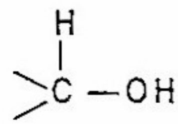
9. Alkanes and cycloalkanes with tertiary hydrogen



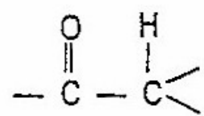
10. Acrylates, methacrylates



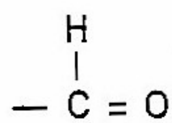
11. Secondary alcohols



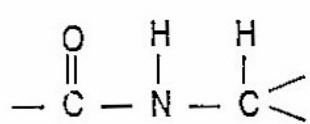
12. Ketones with α-hydrogen



13. Aldehydes



14. Ureas, amides, and lactams with α-hydrogen atom on a carbon attached to nitrogen



APPENDIX 6

Other Common Non-Peroxide Forming Explosive / Potentially Explosive Chemical Families

Many non-peroxide chemicals are also explosive hazards. The list below identifies a number of other common explosive/potentially explosive chemical families and specific examples targeted as “problem compounds.”

Azides:
Lead(II) azide
Silver(I) azide
Sodium Azide
Azo Compounds:
Diazomethane
Azobisisobutylnitrile
Metal Fulminates:
Lead(II) fulminate
Silver(I) fulminate
Metal Acetylides:
Lead acetylides
Silver acetylides

Nitrates:
Propyl nitrate
Pentaerythritol tetranitrate (PETN)
Nitro Compounds:
Cyclonite (RDX)
Dinitrophenol
Dinitrotoluene
Dinitrophenylamine
Nitrocellulose
Trinitrophenol (Picric Acid)
Trinitrotoluene (TNT)
Perchlorates:
Perchloric acid digests
Transition metal perchlorate salts

RESOURCES & REFERENCES

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