Dunbar Research Group
Basic Information Guide
and Group Policies

MAJOR WORK POLICIES FOR OFFICE ASSISTANTS

- **No shorts. Casual attire is acceptable but must be moderately professional**
- **Keep desk and area around your desk neat and organized**
- **No papers or debris are to be placed on the floor**
- **Absences must be reported to Supervisor and documented in LeaveTRAQ**
- **No personal phone calls unless for family emergency purposes**
- **Listening to phone calls or music with earphones is not permitted**
- **No work time is to be used for personal internet use and home related busy work**
- **Sending emails at work related to religious, political or lifestyle or other personal opinions is strictly prohibited**

Work hours are from 8 AM to 5 PM (8 AM to 4 PM and 9 AM to 5 PM without lunch)

MAJOR WORK POLICIES FOR STUDENTS AND POSTDOCTORAL RESEARCH ASSOCIATES

- **No shorts or open-toed shoes**
- **Keep desk and area around your desk neat and organized**
- **No papers or debris are to be placed on the floor**
- **Absences must be reported to Supervisor (documented in LeaveTRAQ for postdocs)**
- **No personal phone calls unless for family emergency purposes**
- **Listening to phone calls or music with earphones is not permitted**
- **No work time is to be used for personal internet use and home related busy work**
- **Sending emails at work related to religious, political or lifestyle or other personal opinions is strictly prohibited**

Working hours are ~60 hours per week which includes evenings and weekends. This includes working at the bench, collecting data on instruments, analyzing data, writing in your notebook, writing papers and reports.

First day

See Mayela

1. She will give the employee
   - Group Package (please bring flash drive to have it installed)
   - Group address list

2. Give to Mayela
   - Key request (form located at http://www.chem.tamu.edu/department/forms/operations/key_request.pdf)
   - Stockroom Card request (form located at http://www.chem.tamu.edu/department/forms/operations/shops.pdf)
   - Security access request (form located at http://www.chem.tamu.edu/department/forms/operations/security.pdf)

If not an American Citizen,

1. Employee is required to see either Kathy Sands or Sheila Robinson at International Faculty and Scholarship Services located at Bizzel Hall room 354 to 'check in'. Requires passport, visa, and pink IAP-66 form.
2. Employee needs to go to the Social Security Office to apply for a Social Security Number (SSN) which is required before salary can be paid by TAMU. SSN will take two weeks to process. Requires passport, visa, and pink IAP-66 form.

All employees:

3. Required to see Judy Ludwig in Room 120, Chemistry Department.
   (paperwork, safety video, e-mail account etc.)
4. Meet with Dunbar Group Laboratory Safety Coordinator to go over group rules and regulations
   and to receive our training. There is a checklist for Dunbar training to use for this purpose.

Safety

1. DRESS CODE: No shorts or open toed shoes permitted when working in the labs.
2. EYE PROTECTION must be work in the lab areas. Lab coats are highly recommended.
3. WASTE: Dispose of waste properly **(DO NOT DISPOSE OF CYANIDE-CONTAINING WASTE IN ACID). ALL CYANIDE WASTE INCLUDING SOLUTIONS AND SOLIDS MUST BE TREATED WITH BLEACH PRIOR TO ANY SUBSEQUENT DISPOSAL OR CLEANING OF GLASSWARE** Use Appropriate Containers (i.e. base should not be put in glass containers). Do not store acids and organic wastes in the same area. If you are not sure if a bottle is actually the correct one DO NOT ADD YOUR WASTE! IF YOU ADD ORGANICS TO ACID OR VICE VERSA THERE WILL BE A VIOLENT REACTION THAT WILL LEAD TO AN EXPLOSION IF THE BOTTLE IS TIGHTLY CAPPED.
   Each container MUST have a Hazardous Waste label on it. This includes your personal waste bottles in your own hood.
   See the person in charge of Dunbar group waste disposal if you have questions.
4. CLEANLINESS IS EXPECTED IN COMMUNITY AREAS. Your own areas should be reasonably tidy. Monthly cleaning days are for heavy cleaning and for backing up your files. LAB CLEAN-UP IS MANDATORY WITH EXCUSES ONLY IN THE CASE OF ILLNESS OR TRAVEL.
5. For new group members, if you have questions, ask a senior member of the group. Do not attempt to operate equipment, solvent stills, or anything unfamiliar to you without proper orientation. DO NOT USE PERCHLORATES WITHOUT PRIOR APPROVAL OF KRD.

Laboratory Guidelines

1. Everyone is requires to keep a neat, detailed notebook (including spectra) with a carbon page for making copies. The copies will be collected at the end of every semester and archived in the computer/journal room. See the Dunbar Group Laboratory Notebook Guide.
2. Weekly Research Group Meetings and Literature Group Meetings are not optional. Any absences from the meetings must be approved by Kim. No exceptions.
3. Weekly research Reports are due every Monday with the exception of the Christmas Holidays which span two weeks. No exceptions regardless of teaching and writing. If you are traveling and were not in the lab that week, you may miss a report for that period.
4. All glassware is community except: personal Schlenkware and special glassware you always use. All other items such as frits, beakers, Erlenmeyers, roundbottoms, condensers, recrystallizing dishes etc., should be used and cleaned immediately, and put back in the proper place by the person who used it.
5. A) If you receive a new chemical notify the person in charge of Chemical Location and Inventory
   B) If you use up all of a chemical, notify the person in charge of Chemical Location and contact the ordering individual (this includes the drybox, organic and inorganic shelves).
6. After instruments use, SIGN THE LOGBOOK and write any messages regarding problems etc. DO NOT let any other groups use the instruments without prior permission by KRD and supervision.
7. If you have crystals, write your name and the compound on the crystal queue sheet according to the procedure that the group has been following with the forms. All data are to be permanently archived on the CDs and stored in the computer room. Be sure to complete the x-ray data form.

Laboratory Courtesy and Security

1. Avoid personal phone calls on office phones and lengthy calls in any case
2. Avoid eating computer room or at your desk. Eat in the conference room
3. Avoid walking back and forth in the computer room when people are working.
4. Keeping Mayela's office door locked after she leaves.
5. Lock all outside lab doors in the evening and MAKE SURE THE door is actually closed as we have problems with the doors not latching.

Work Absences (non-Business related)

ABSENCES PLANNED IN ADVANCE:

STUDENTS: If you want to request some time off, you must fill out the Dunbar group leave form and have it signed by me BEFORE you leave. If I am traveling you must contact me first. I have a cell phone and I check e-mail frequently on my Blackberry when traveling.

POSTDOCS AND OFFICE ASSISTANTS: You MUST fill out the LEAVE TRAQ form provided by Human Resources. You must check the appropriate box- vacation, personal time etc., ASK ME BEFORE filling going online and having me find out by e-mail first. This is just standard courtesy and I am usually able to accommodate. I do not, however, want you to expect that all absences will be automatically approved.

UNEXPECTED ABSENCES DUE TO ILLNESS OR PERSONAL BUSINESS:

ALL DUNBAR GROUP STUDENTS AND EMPLOYEES:
YOU MUST CALL ME AT HOME 690-7536 or cell 324-6761. Leave a message if I do not answer. THIS IS NOT TO BE SUBSTITUTED BY AN E-MAIL or A CALL TO MAYELA OR CHARLENE. You can e-mail me as well but it does not mean you do not have to call.

POSTDOCS AND OFFICE ASSISTANTS:
You MUST fill out a LEAVE TRAQ request for a sick day or a personal/vacation day. No exceptions.

ABSENCES RELATED TO BUSINESS TRAVEL

All persons attending a conference or giving a talk, seminar etc., must fill out an official travel form before leaving. This is true for the KRD as well as everyone else. Doing so insures that the University will have documentation of your or my whereabouts if a situation arises. Insurance is also an issue. When you are on University Business, it does not fall into any of the aforementioned categories. The form MUST BE filled out with where you are going and why (what is your role: attendee or presenter with title of your presentation).

Dunbar Research Group
Guide to Keeping a Research Laboratory Notebook

Q: What is the purpose of the laboratory notebook?
A: To record daily progress in research and provide details of experiments, and to document when and how they were preformed. Include details of yields, colors, and methods of characterization.

Q: What type of notebook does the group use? Is it acceptable to use an electronic notebook format?
A: Regular style carbon paper. No electronic notebooks are acceptable.

Q: Where and how does the group archive spectral data? Do I need to archive all spectral data regardless of quality? What if the data is of a known compound?
A: In their notebooks and in files for each compound/project. Yes, archive all spectral data but not for every new batch of starting material.

Q: Where and how do I archive chemical samples? Do I need to archive every compound that I make?
A: In the dry box and with your advsior before you go. Yes, you need to archive every compound (where it is, what it is, notebook pages that say how and when it was prepared).

The items that must be included in a notebook for this research group.

1. Date (obviously this is very important!)
2. Experimental set up, appropriate level of detail for reproducibility in your absence by a non-expert, reactions: times, colors, temperatures, obviously quantities, work-up, yields. Use the adage – More is better than less!
3. Cross-referencing of related work/page numbers
4. List of common chemicals in an index or table of contents (formula weights, densities, etc.)
5. Table of Contents/Index of reactions – so people can find what they need later
6. Best to tape copies of spectra, magnetic plots (hard data) to make your point
7. Please practice good Penmanship! If no one can read it, what is the point?
8. Make sure the carbon sheet is not terribly worn such that it is not transferring to the yellow sheets.
9. Crystallography and SQUID experiments as well as any detailed set of experiments must be documented in the notebook. If you require comprehensive NMR, spectroscopic, mass spectral or computational studies on a regular basis, these data must also be recorded meticulously. *Either keep a separate notebook for these data or incorporate them into your regular notebook.*

THE MAIN POINT IS:
HAVE A SYSTEM THAT YOU AS WELL AS OTHERS FIND INFORMATIVE AND USEFUL FOR REPRODUCING RESULTS.

Crystallography program references for Group Papers

PLATON/PLUTON – (a) A. L. Spek, Acta Crystallogr., Sect A 1990, 46, C34. (b) PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, A.L. Spek, 1998.

SAINT – SAINT, Program for area detector absorption correction, Siemens Analytical X-Ray Instruments Inc., Madison, WI 53719, USA 1994-1996

SADABS – G.M. Sheldrick, SADABS, Program for Siemens area detector absorption correction, University of Göttingen, 1996.

SHELXS-97 – G.M. Sheldrick, SHELXS – 97, Program for crystal structure determination, University of Göttingen, 1997.

SHELXTL – G.M. Sheldrick, SHELXTL, An integrated system for solving refining and displaying crystal structures from diffraction data (Revision 5.1), University of Göttingen, 1985.

SHELXL – 97 – G.M. Sheldrick, SHELXL – 97, Program for refining crystal structures, University of Göttingen, 1997.

Lab Safety

1. WEAR EYE PROTECTION AT ALL TIMES!!!!
2. Emergency phone number – call 911 or use red emergency phones in the hall
3. First Aid Kits are located in rooms 2310 and 2312.
4. Fire extinguishers – are located in rooms 2310 and 2312 (note their location)
5. Eyewashes and showers are provided. Located in rooms 2312 and 2310
6. Wire all tubing onto water taps and condensers and do not let a long reflux go overnight if you are not prepared to check every couple of hours. Water pressure changes dramatically from very low to high and if you have the water turned up high and the pressure shoots up, the hose may pop off.
7. Never allow a reaction to continue with unusually harsh stirring or with a bouncing stirring bar.
8. **Remember: liquid N_2 condenses O_2 and this will happen in traps that are open and immersed in an LN_2 containing dewar. If you see a blue color in your traps, walk away and let everything evaporate.** ***Liquid O_2 is shock sensitive.***
9. **Cyanide chemistry must be treated in a special manner.** ***No acid cleaning of cyanide glassware or disposal of cyanide waste is to be done until after the glassware and compounds are treated with bleach. Hydrogen cyanide is a deadly posion and, if inhaled, must be treated immediately with the amyl nitrite antidote in our safety location in the lab before calling 911. Know where this is located.***
10. Watch your fellow labmates – if they are employing unsafe practices, it is your responsibility to stop it or report it to your advsior!
11. Check the Material Safety Data Sheets (MSDS) before using an unfamiliar chemical.
12. Be careful with any new reactions.
13. Test the reactivity of unknown compounds before working-up or disposing of them.
14. Secure all gas tanks with clamps and straps and do not treat "empty" tanks with any less respect than those that contain pressurized gases.
15. Clean up Hg spills immediately.
16. Be very careful with certain classes of compounds, especially:
    - Diazo compounds
    - Perchlorate salts (ClO_4^-)
    - Na/K alloy or other alkali metals
    - HF and other fluorides
    - Metallic dusts
    - Peroxides
    - Piranha solution (H_2SO_4/H_2O_2) used to clean frits- use only in a hood with protective gear (lab coats, long gloves, safety googles and preferably a face shield)
    - Li reagents
    - Grignard reagents
17. Secure all gas inlets and stoppers onto flasks with copper wire and rubber bands or plastic clips that are specific for this purpose.

Accidents happen when you least expect them!

Glassclad 18

Glassclad is used to make glass surfaces hydrophobic. If you coat your Schlenkware with this reagent, you DO NOT need to store your glassware in the oven.

Information on use and procedure for coating glassware to make it hydrophobic:

Company: Hülls America Inc. (there may be other vendors)
Bartram Road
Bristol, PA 19007
(215) 781-9255 (Fax) 215-785-1226

Catalog #	Amount	Name
PS 200	450 mL	Glassclad 18
	(100 mL = $6.00)	

Typical properties of Glassclad 18 (PS 200)

% active	20
Flashpoint	10°C
Specific Gravity (25°C)	0.88
Solidification Point	-30°C

Application methods

Glassclad 18 is most frequently used as a dilute aqueous solution containing 0.1% - 10% of reactive silicone pre-polymer. A 0.2% solution of active chemical can be easily prepared by adding one part by weight of the product (as supplied) to 99 parts of water while stirring. The following procedure is typical:

1. Thoroughly clean glass with an alkaline detergent. A 2-3% sodium hydroxide solution is fine. All detergent or alkali should be removed with a final rinse.
2. Prepare a 1% solution of Glassclad 18 in water. Ordinary tap water but not "hard water" is acceptable.
3. Immerse the glass or vitreous surface in the solution for 5-10 seconds ensuring that all surfaces are wetted by the solution. Agitation of the solution or the part generally results in more uniform deposition. After immersion, remove the object and thoroughly rinse with water to remove excess Glassclad 18 from the surface.
4. Cure Glassclad 18 coatings by bringing the surface temperature to 100°C for 3-5 minutes. Room temperature cure may be accomplished by air drying for 24 hours if relative humidity is 65% or less.
5. Each liter of solution will coat approximately 80 one liter breakers or 800 15 cm test tubes. (Approximately 250 m^2 of the surface area.)

STABILITY OF GLASSCLAD 18 AND SOLUTIONS

Aqueous solutions of Glassclad are not stable indefinitely and may turn cloudy and precipitate after standing for several days. The solution stability can be optimized by adjusting the pH of the solution to 4.5-5.

Base Bath Recipe for cleaning glassware

Recipe 1

1. Equal volume of H_2O is added to a mass of KOH pellets (i.t. 1000g KOH/ 1 liter H_2O)
2. Stir together in a large Erlenmeyer flask until all the KOH dissolves
3. Add 95% EtOH until concentration is ~ 100g KOH/ 1 Liter of solution. (i.e. for 1000g KOH and 1 Liter H_2O, add 9 Liters EtOH)

Recipe 2

Add 1kg of KOH to pure *i*-PrOH: add H_2O to dilute as desired. It is not necessary to add H_2O, as the KOH dissolves in the *i*-PrOH, but the lifetime of ground-glass joints will be considerably shortened the more concentrated the base is.

Proper Procedure for cleaning glassware with base:

1. First remove all traces of grease from the joints and stopcocks! Soak the joints in hexanes to achieve this. You will need to get some pipe cleaners to remove the grease from the hole in the stopcock. If you don't comply with this step, the grease will harden in the base bath (turns black) and will be impossible to remove without baking it off at a high temperatures.
2. Only clean beakers, flasks and other reaction glassware with base. Never use base on NMR tubes, E-Chem glassware or other trace impurity sensitive uses.
3. Soak the glassware in the base bath for no longer than 12 hours. If you allow the glassware and particularly the ground glass joints to be in prolonged contact with a strong base solution, the glassware will gradually dissolve. **DO NOT PUT FRITS INTO BASE BATHS!**
4. Rinse the glassware with water from the distilled water tap. This is the one with the white handle. Do not use water from the green or red taps. Water from the latter two is not purified and is unfit for drinking or washing glassware.
5. Place the rinsed glassware in a dilute HCl/H_2O bath for several minutes to hours. If it is in there longer it won't harm the glassware, however.
6. Repeat step 4.
7. Either follow with an acetone rinse or place in the oven directly.

Acid Cleaning of Glassware

Items to include: Frits, EPR tubes, NMR tubes, Electrochemical cells

1. There are bags of oxidizing salts called NO-CHROMIX around the lab (or order some) with directions for preparing a solution of it on the packet. The "solvent" here is sulfuric acid. A bath of this can be used by everyone for cleaning frits and NMR tubes. You can stand the NMR tubes up in a tall beaker or Erlenmeyer and pipet the acid solution into the NMR tubes and soak for as long as you like. I want one person in 2310 and one person in 2312 to be in charge of this bath.
2. Alternatively we use a solution of sulfuric acid and hydrogen peroxide. The method is described as follows and is used for **FRIT CLEANING**:
   The procedure is on the following page:

SULFURIC ACID/30% HYDROGEN PEROXIDE FOR FRITS ("PIRANHA JUICE")

(1) Wear a closed lab coat, safety glasses and long plastic gloves.

(2) Conduct the cleaning in a well ventilated hood with the sash down so that you are just reaching in when you need to add the solutions.

(3) Make certain that all of the glassware (frit, suction flask) is clean and doesn't contain residual organic material such as acetone or any other organic solvents or acids. If you fail to do this, the reaction will be violent and create a serious hazard. **Pre-clean the frits to remove residual solids and soak in water prior to cleaning after any organic solvents have been used to remove traces of compounds. If you are working with cyanide or organocyanide compounds, pre-treat the frit with bleach solution to be certain that all cyanide groups have been oxidized by the hypochlorite solution.**

Procedure:

(1) Attach the frit to a suction filter flask attached to a vacuum in the hood.

(2) Add a small amount of concentrated sulfuric acid so that it covers the surface of the frit.

(3) Add a small volume of hydrogen peroxide and close the sash. The solution becomes very hot and bubbles vigorously. After the mixture has been sitting for a couple of minutes, apply a slight vacuum to pull the solution through the frit.

(5) Give the mixture sufficient time to cool and thorough rinse the frit with copious amounts of water with suction. **DO NOT PULL ACETONE OR ANY OTHER SOLVENT THROUGH THE FRIT INTO THE SAME SUCTION FLASK**. Place the frit in an oven to dry.

Purification of Solvents in the Laboratory
(Unless the Solvent is now being Purified with the MBRAUN Columns)

1. **Hexanes**
   a. Wash the hexanes with sulfuric acid (shake in a large Erlenmeyer flask and let it stand for 24 hours).
   b. Remove the water layer and dry the hexane with $MgSO_4$ for 1-2 days.
   c. Distill the hexanes from Na/K benzophenone ketyl solubilized with tetraglyme (5-10mL) or Na dispersion (Aldrich) benzophenone ketyl.
2. **Pyridine**
   a. Pre-dry the pyridine by storing over KOH pellets.
   b. Distill from BaO (dry pyridine is very hygroscopic!).
3. **Toluene**
   a. Pre-dry the toluene by storing over 4 Å molecular sieves
   b. Distill from Na/K/Ph_2CO ketyl or Na dispersion (Aldrich) benzophenone ketyl.
4. **Benzene**
   a. Pre-dry the benzene over 4 Å molecular sieves.
   b. Stir or shake the benzene with H_2SO_4 (100 mL H_2SO_4/1 liter C_6H_6).
   c. Remove the acid layer and repeat b until the darkening of the H_2SO_4 layer is only slight.
   d. Distill from Na/benzophenone ketyl or Na dispersion (Aldrich) benzophenone ketyl.

5. **Dichloromethane (methylene chloride)**
   a. Pre-dry the CH_2Cl_2 by storing over 4 Å molecular sieves.
   b. Distill the CH_2Cl_2 from $P_2O_5(P_4O_{10})$.

6. **Tetrahydrofuran (THF)**
   a. Pre-dry the THF by storing over 4 A molecular sieves.
   b. Distill from Na/K benzophenone ketyl or Na dispersion (Aldrich) benzophenone ketyl.
7. **Acetone**
   a. Distill from 4 Å molecular sieves. This does not produce extremely dry acetone. To rigorously dry acetone, see the Chemist's Companion.
8. **Methanol**
   a. Pre-dry the MeOH using 4 Å sieves then set up a 2 L MeOH still as outlined in b-d:
   b. Put 50 mL of MeOH in the flask along with 5g Mg turnings and 0.5g I_2 crystals.
   c. Reflux until I_2 color disappears (H_2 evolution is apparent from rapid bubble formation).
   d. Add 1.5 L of MeOH to this slurry of $Mg(OMe)_2$ and reflux.
9. **Diethyl ether**
   a. Distill "anhydrous" Et_2O from CaH_2. **Be sure the diethyl ether is fresh and free of peroxides!**
10. **Acetonitrile**
    a. Pre-dry the CH_3CN over 3 Å molecular sieves for several weeks before use in the still.
    b. Distill from CaH_2 to remove water and traces of acetic acid that are well-known to contaminate CH_3CN.
    c. Any moisture-sensitive chemistry should use acetonitrile purified by steps a-b and further purified by running it down a column of activated alumina.
11. **Ethanol**
    a. Pour 20 mL of EtOH in a 2 L flask along with 5g Mg turnings and 0.5g I_2.
    b. Reflux mixture until I_2 color disappears
    c. Add the remainder of the EtOH (~ 1.5L) to the $Mg(OEt)_2$ slurry.
12. **Nitromethane**
    Distill from CaH_2. Do not store over molecular sieves.

Preparation of Mn/SiO_2 Drying Column for Schlenk-line purification of Nitrogen or Argon:

1. Silica 60-120 mesh
2. $Mn(NO_3)_2$ 50% solution

Procedure:

1. Wash SiO_2 with 0.1 M HCI (slurry, then filter).
2. Dry SiO_2 at 150-200°C in oven
3. Add the $Mn(NO_3)_2$ solution to the silica (85 mL $Mn(NO_3)_2$ to 100g of SiO_2).
4. **Dry in oven at 150°-200°C in the HOOD**. Caution 1: decomposition of nitrate salts gives off noxious fumes of NO_2 and NO. The silica turns black.
5. Load the material into the column. Heat the column to at least 450°C under a flow of H_2 until the entire column is green. (The color goes from black to brown to green).
6. Pass Argon through at 450°C to remove residual water.
7. Pump on the column at 450°C for several hours to remove last traces of H_2O
8. Ready to hook up to your gas source again.

To Regenerate:
Repeat steps 5-8

Compounds that Form Peroxides During Storage

*When stored as a liquid, the peroxide forming potential increases and certain of these monomers (especially butadiene, chloroprene, and tetrafluoroethylene) should then be considered as List A compounds.

Proper handling and Storage:

- Purchase small quantities of peroxidizable chemicals. This limits amount exposed to air and improves the chance of using before first peroxide formation (see Table above)
- Store peroxide forming compounds in airtight containers in a dark, cool and dry area.
- Label containers with date received, date opened and recommended disposal date.
- Special attention should be given to stored peroxidizable compounds with particles or a crusty conglomerate around the cap. This is caused by evaporation and tends to occur in peroxidizable compounds whose age is not known.
- Any stored peroxidizable compound that has physical characteristics different from those of the pure substance should be classified as waste and disposed of accordingly.

Proper Disposal:
If pure peroxides are found, DO NOT attempt to move the container to remove the lid. Contact ORB+CBS for assistance.
Peroxidizable Compounds

Introduction

What is a Peroxide?

** A peroxide is a compound that contains a bivalent O-O group.

Why are Peroxides Unstable?

**Peroxides are unstable because the two oxygen atoms comprising the peroxide are held together by a weak bond. Factors such as shock, heat, and friction are capable of cleaving this bond.

Why is this cleavage dangerous?

**Each of the two radicals that result from the cleavage of the peroxo group contains a single unpaired electron. Like all free radicals, these two groups are highly reactive. They will react with other radicals and molecules to form new molecules and radicals. An explosion normally results when the destruction of free radicals cannot keep up with their creation.

Peroxides are among the most hazardous chemicals used in laboratories. Their danger is a result of both their instability (many peroxides are more sensitive to shock than are the majority of primary explosives such as TNT) and their high flammability. They are sensitive to heat, friction, impact, and light. In addition, they are highly reactive with strong oxidizing and reducing agents. Chemicals which form peroxides are also a problem because their presence can alter the course and results of a planned reaction.

Many common laboratory chemicals can form peroxides when allowed access to air over a period of time. A single opening of a container can introduce enough air for this impurity to occur. Table 1 shows some common compounds which form peroxides.

Recommendations

1. Laboratory researchers must date containers of peroxide-forming compounds after they are opened. This date should be written legibly on the outside of each container. If desired, the label shown below can also be used.

PEROXIDIZABLE COMPOUND
DATE OPENED _____
DISCARD OR TEST WITHIN 12 MONTHS
AFTER OPENING

2. An inventory should be kept of all peroxide-forming chemicals stored in the laboratory (see table 1). This list should be examined routinely so that chemicals which have reached their recommended storage times can be found. At this time, chemicals which have reached their storage limits should either be tested for the presence of peroxides (see following page) or removed from the lab.
3. Researchers should make sure that containers of peroxide-forming chemicals are tightly sealed.
4. Researchers should keep these materials away from light and heat sources.
5. Peroxidizable compounds should not be kept in the same storage area as chemicals they can react with.

Special Precautions

The properties of diethyl ether make it an especially hazardous material. For instance, it has an extremely low flashpoint (-45°C). At room temperature, its vapors can be ignited by a flame, spark or even by static electricity. Furthermore, the vapor of ethyl ether is more than twice as dense as air and is capable of traveling long distances to a possible source of ignition. Once started, an ether fire is considered more difficult to combat than a gasoline fire.

6. Diethyl ether containers should be stored in a fumehood that has its ventilation turned on. If this suggestion is followed, the fumehood should always be kept free of electrical as well as sparking devices.

Table 1. COMMON PEROXIDE – FORMING CHEMICALS

List A: Severe Peroxide Hazard on Storage with Exposure to Air. DISCARD AFTER 3 MONTHS

Divinyl acetylene
Isopropyl ether
Potassium amide
Potassium metal
Sodium amide
Vinylidene chloride

List B: Peroxide Hazard on Concentration; Do Not Distill or Evaporate Without First Test for the Presence of Peroxides. DISCARD OR TEST FOR PEROXIDES AFTER ONE YEAR

Acetal
Cumene
Cyclohexene
Cyclooctene
Cyclopentene
Decalin (Decahydronaphthalene)
Diacetylene
Diethylene Glycol Dimethyl Ether (Diglyme)
Dioxane
Diethyl ether
Ethylene Glycol Ether Acetates
Ethylene Glycol Monoethers (Cellosolves)
Dicyclopentadiene
Ethylene glycol dimethyl ether (glyme)
Furan
Methylcyclopentane
Methyl acetylene
Methyl i-butyl ketone
Tetrahydrofuran
Tetrahydronaphthalene
Vinyl ethers

List C: Hazard Due to Peroxide Formation or Initiation or Spontaneous Polymerization
DISCARD OR TEST FOR PEROXIDES AFTER ONE YEAR

*Butadiene
*Chlorobutadiene (Chloroprene)
Chlorotrifluoroethylene
Styrene
*Tetrafluoroethylene
Tetracyanoethylene
Vinyl acetate
*Vinyl acetylene
Vinyl chloride
Vinyl pyridine

*The hazard from peroxides of these compounds is substantially greater when they are stored in the liquid phase, and if so stored without an inhibitor they should be considered as in LIST A.

Detection of Peroxides

Technique 1

PURPOSE – To determine whether a substance that has reached/surpassed its recommended period of storage contains peroxides.

CONCEPT – To discern whether or not the iodide ion is oxidized to iodine by peroxides.

EXPERIMENTATION – Add 1mL of the substance to be tested to a freshly prepared solution of 100 mg of sodium or potassium iodide in 1 mL of glacial acetic acid.

RESULTS

Yellow Color: Low concentration of peroxide in the sample
Brown Color: High concentration of peroxide in the sample

USE – This test is capable of discovering the presence of hydroperoxides (ROOH) which are the principal hazard of peroxidizable solvents.

LIMITATION – This test does not detect the peroxides which are difficult to reduce such as dialkyl peroxides (ROOR).

EXPERIMENTATION – ROOR can be detected by a reagent prepared by dissolving 3 g of sodium iodide in 50 mL of glacial acetic acid and adding 2 mL of 37% hydrochloric acid.

RESULTS

Same characteristics as above

Technique 2

Test paper containing a peroxidase is available that detects organic peroxides (including dialykl peroxides) and oxidizing anions (e.g., persulfate, chromate) colorimetrically.

EM Quant Test Strips

EM-Quant TM, MC/B Manufacturing Chemists, Inc., 2909 Highland Ave., Cincinnati, Ohio 45212.

COMMON WINDOW MATERIALS AND THEIR PROPERTIES
For Infrared Spectroscopy

Material	Range, cm^{-1}	Water Solubility g/100 mL H_2O	Other Properties
NaCl Cuts off at $650cm^{-1}$	50,000-650	35.7	Cleaves and polishes easily. Inexpensive
KBr Cuts off at 400	10,000-400	53.8	Cleaves and polishes easily. Slightly more expensive than NaCl.
CaF_2 Solution Cell	48,000-1250	1.7×10^{-3}	Does not cleave. Difficult to polish. Relatively more expensive than NaCl.
BaF_2	50,000-1,000	0.17	Does not cleave (obtained as sawed blanks). Moderately easy to polish. Relatively more expensive than NaCl.
CsBr	20,000-280	123	Does not cleave. Moderately easy to polish. Soft, easily deformed. Very expensive.
CsI *Best for full range	10,000-200	44	Does not cleave. Moderately easy to polish. Soft, easily deformed. Very expensive.
AgCl Cuts off at $450cm^{-1}$	4,000-450	8.9×10^{-5}	Does not cleave. Moderately easy to polish. Soft, easily deformed. Darkens on exposure to UV radiation.
AgBr	22,000-280	2×10^{-5}	Does not cleave. Moderately easy to polish. Soft, easily deformed. Darkens on exposure to UV radiation. More expensive than AgCl.
Irtran-2	17,000-715	Insoluble	Does not cleave. Difficult to polish. High reflection losses. Very expensive.
KRS-5	20,000-250	Insoluble	Does not cleave. Difficult to polish. Poisonous. High reflection losses. Very expensive.
Polyethylene Best for just FAR-IR	600-1	Insoluble	Does not cleave or polish. Porous to certain substances. Has strong absorption bands in fundamental region, useful throughout far-infrared region.

Properties of Common Solvents

Solvent	M.P. (°C)	B.P. (°C)	Dieletric Constant

H_2O	0.00	100.0	78.5
MeOH	-97.9	64.7	32.6
EtOH	-114.6	78.5	24.3
n-PrOH	-127	97.8	19.7
Iso-PrOH	-85.8	82.5	18.3
n-Hexane	-94.3	69.0	1.90
C_6H_6	5.5	80.1	2.27
$C_6H_5CH_3$	-95	110.6	2.38
CCl_4	-22.8	76.8	2.23
$CHCl_3$	-63.5	61.3	4.70
CH_2Cl_2	-96.7	40.1	8.9
C_6H_5Cl	-45.2	132	5.62
Et_2O	-116.3	34.6	4.22
THF	-65	65.4	7.39
Monoglyme [(CCH_3OCH_2-CH_2OCH_3)]	-69	85.9	3.5-6.8
Diglyme [$CH_3(OCH_2CH_2)_2OCH_3$]	-64	162.0	
EtOAc	-83.6	77.1	6.02
Acetone	-95.4	56.2	20.7
CH_3CN	-45.7	81.6	36.2
C_5H_5N	-41.8	115.5	12.3
CH_3NO_2	-28.5	101.2	38.6
DMF	-61	153	36.7
CS_2	-111.6	46.3	2.64
Heptane		98.42	
Octane		125.66	
Nonate		150.798	

Low-Temperature Slush Baths/ LN_2 and CO_2

System	°C
p-Xylene/N_2	13
p-Dioxane/N_2	12
Cyclohexane/N_2	6
Benzene/N_2	5
Formamide/N_2	2
Aniline/N_2	-6
Cycloheptane/N_2	-12
Benzonitrile/N_2	-13
Ethylene glycol/CO_2	-15
o-Dichlorobenzene/N_2	-18
Tetrachloroethane/N_2	-22
Carbon tetrachloride/N_2	-23
Carbon tetrachloride/CO_2	-23
m-Dichlorobenzene/N_2	-25
Nitromethane/N_2	-29
o-Xylene/N_2	-29
Bromobenzene/N_2	-30
Iodobenzene/N_2	-31
Thiophene/N_2	-38
3-Heptanone/CO_2	-38
Acetonitrile/N_2	-41
Pyridine/N_2	-42
Acetonitrile/CO_2	-42
Chlorobenzene/N_2	-45
Cyclohexanone/CO_2	-46
m-Xylene/N_2	-47
n-Butyl amine/N_2	-50
Diethyl carbitol/CO_2	-52
n-Octane/N_2	-56
Chloroform/CO_2	-61 (-77)
Chloroform/N_2	-63
Methyl iodide/N_2	-66
Carbitol acetate OR Diethylene Glycol Ethyl Ether Acetate/CO_2	-67
t-Butyl amine/N_2	-68
Ethanol/CO_2	-72
Trichloroethylene/N_2	-73
Butyl acetate/N_2	-77
Acetone/CO_2	-77
Isoamyl acetate/N_2	-79
Acrylonitrile/N_2	-82
Sulfur dioxide/CO_2	-82
Ethyl acetate/N_2	-84
Ethyl methyl ketone/N_2	-86
Acrolein/N_2	-88
Nitroethane/N_2	-90
Heptane/N_2	-91
Cyclopentane/N_2	-93
Hexane/N_2	-94
Toluene/N_2	-95
Methanol/N_2	-98
Diethyl ether/CO_2	-100
n-Propyl iodide/N_2	-101
n-Butyl iodide/N_2	-103
Cyclohexene/N_2	-104
Isooctane/N_2	-107
Ethyl iodide/N_2	-109
Carbon disulfide/N_2	-110
Butyl bromide/N_2	-112
Ethyl bromide/N_2	-119
Acetaldehyde/N_2	-124
Methyl cyclohexane/N_2	-126
n-Pentane/N_2	-131
1, 5 – Hexadiene/N_2	-141
i-Pentane/N_2	-160

DEUTERATED NMR SOLVENTS – HANDY REFERENCE DATA

Compound Mol. Wt.	D^{20}_4	m.p.[a]	b.p.[a]	δ_H (mult)[a]	^JHD	δ_C(mult)[b]	$^JCD(^JCF)$
Acetic Acid – d_4 64.078	1.12	17	118	12.53 (1) 2.03 (5)	2	178.4 (br) 20.0 (7)	20
Acetone – d_6 64.177	0.87	-94	57	2.04 (5)	2.2	206.0 (13) 29.8(7)	0.9 20
Acetonitrile – d_3 44.071	0.84	-45	82	1.93 (5)	2.5	118.2 (br) 1.3 (7)	21
Benzene-d_6 84.152	0.95	5	80	7.15 (br)		128.0 (3)	24
Chloroform-d 120.384	1.50	-64	62	7.24 (1)		77.0 (3)	32
Cyclohexane –d_{12} 96.236	0.89	6	81	1.38 (br)		26.4 (5)	19
Deuterium Oxide 20.028	1.11	3.8	101.4	4.63 (DSS) 4.67 (DSS)			
1, 2-dichloroethane-d_4 102.985	1.25	-40	84	3.72 (br)		43.6(5)	23.5
Diethyl-d_{10} Ether 84.185	.82	-116	35	3.34(m) 1.07 (m)		65.3 (5) 14.5 (7)	21 19
Diglyme-d_{14} 148.263	0.95	-68	162	3.49 (br) 3.40 (br) 3.22 (5)	1.5	70.7(5) 70.0(7) 57.7(7)	21 21 21
Dimethylformamide-d_7 80.138	1.04	-61	153	8.01(br) 2.91 (5) 2.74 (5)	2 2	162.3 (3) 35.2 (7) 30.1 (7)	30 21 21
Dimethyl-d_6 sulphoxide 84.170	1.18	18	189	2.49(5)	1.7	39.5(7)	21
p-Dioxane-d_8 96.156	1.13	12	101	3.53(m)		66.5(5)	22
Ethyl Alcohol-d_4 (anh_ 52.106	.91	<-130	79	5.19(1) 3.55 (br) 1.11(m)		56.8(5) 17.2(7)	22 19
Glyme-d_{10} 100.184	.86	-58	83	3.40 (m) 3.22 (5)	1.6	71.7 (5) 57.8 (7)	21 21
Hexaflouracetone Deuterate 198.067	1.71	21		5.26 (1)		122.5 (4) 92.9(7)	(287) (34.5)
HMPT-d_{18} 197.314	1.14	7	106(11)	2.53 (2 x 5)	2 (9.5)	35.8 (7)	21
Methyl Alcohol-d_4 36.067	.89	-98	65	4.78 (1) 3.30 (5)	1.7	49.0 (7)	21.5
Methyl Chloride-d_2 86.945	1.35	-95	40	5.32 (3)	1	53.8 (5)	27
Nitrobenzene-d_5 126.143	1.25	6	211	8.11 (br) 7.67 (br) 7.50 (br)		148.6 (1) 134.8 (3) 129.5 (3) 123.5 (3)	24.5 (p) 25 26
Nitromethane-d_3 64.059	1.20	-29	101	4.33 (5)	2	62.8 (7)	22
isopropyl Alcohol-d_8 68.146	.90	-86	83	5.12 (1) 3.89 (br)		62.9 (3) 24.2 (7)	21.5 19

				1.10 (br)			
Pyridine-d_5 84.133	1.05	-42	116	8.71 (br) 7.55 (br) 7.19 (br)		149.9 (3) 135.5 (3) 123.5 (3)	27.5 24.5 (8) 25
Tetrahydroforan-d_8 80.157	.99	-109	66	3.58 (br) 1.73 (br)		67.4 (5) 25.3 (br)	22 20.5
Toluene-d_8 100.191	.94	-95	111	7.09 (m) 7.00 (br) 6.98 (m) 2.09 (5)	 2.3	137.5 (1) 128.9 (3) 128.0 (3) 125.2 (3) 20.4 (7)	 23 24 24 (p) 19
Trifluoracetic Acid-d[d] 115.030	1.50	-15	72	11.50 (1)		164.2 (4) 116.6 (4)	(44) (283)
2,2,3-Trifluoroethyl Alcohol-d_3 103.059	1.45	-44	75	5.02 (1) 3.88 (4x3)	2 (9)	126.3 (4) 61.5 (4x5)	(277) 22 (36)

[a] Melting and boiling points (in °C) are those of the corresponding light compound (except for D_2O) and are intended only to indicate the useful liquid range of the materials.

[b] ^1H (of the residual protons) and ^{13}C spectra were determined on HA-100 and XL-100-15 spectrometers, respectively, for the same sample of each solvent containing 5% TMS (v/v). The chemical shifts are in ppm relative to TMS; the coupling constants are in Hz. (Since deuterium has a spin of 1, triplets arising from coupling to deuterium have the intensity ratio of 1:1:1, etc.) The multiplicity br indicates a broad peak without resolvable fine structure, while m denotes one with fine structure. It should be noted that the chemical shifts, in particular, can be dependent on solute, concentration and temperature.

[c] $^2d_F(CFCl_3)$ 76.2 (1) [d] $^2d_F(CFCl_3)$ 77.8 (5), J_{FH} 1.2