safety in the chemical laboratory

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Identifying and Dealing With Hazardous Materials and Procedures in the General Chemistry Laboratory

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Chemistry deals with many substances which can pose hazards in handling: corrosive chemicals, irritants, oxidizers, carcinogens, and other toxic substances. Sometimes hazards can be reduced or essentially eliminated by aqueous dilution, as with acids and bases, but for many other hazardous materials dilution will not necessarily reduce or remove any harmful effects.

Information on alternatives to hazardous chemicals is lacking in the literature. In over a dozen books dealing with laboratory and chemical safety which were consulted, there are few, if any, suggestions; and such an authority as OSHA will not recommend specific substitutes on the grounds that they must be decided on a case-by-case basis: one substitution does not fit all situations.

Not all laboratory hazards are chemical in nature; many are also a result of either poorly planned or outdated procedures or both. Although textbooks are constantly being reviewed and updated, laboratory manuals generally do not enjoy so much attention. Many set-ups and procedures used in current laboratory manuals have remained unchanged for years.

A survey of some popular freshman chemistry laboratory manuals (*1*) turned up many questionable procedures:

Hazard 1: Determination of the solubility of a substance in a nonpolar solvent using benzene, a known carcinogen, which causes leukemia in some persons (*2*, *3*).

Alternative: Use solvents such as toluene, petroleum ether, cyclohexane, and 1,1,2-trichloro-1,2,2-trifluoroethane. In each case, consult the current OSHA list of suspected carcinogens and available safety manuals for possible hazards. If a hazardous solvent must be used, it is suggested that semi-micro quantities be used with monitoring and adequate venting.

Hazard 2: The use of benzene as a solvent in the preparation of rhombic sulfur where the procedure calls for boiling the benzene-sulfur mixture under a fume hood "for a minute or two" to effect solution of the sulfur, and later to concentrate the solution. At the end of the procedure is the warning:

"Note: Do not breathe the fumes of benzene or get any on your skin."

Alternative: Use another solvent such as toluene, or one selected from a solubility chart of sulfur (*4*) which will produce the desired results. Place the appropriate warning at the beginning of the procedure.

Hazard 3: Determination of the boiling point of a volatile liquid for compound identification or thermometer calibration using liquids such as acetone, carbon tetrachloride, ethanol, hexane, and other flammable or toxic liquids with venting directly to the atmosphere.

Alternative: Using a stopper equipped with tubing to direct the vapors into a drain or fume hood. A better alternative is a micro boiling point apparatus of the type shown in Figure 1. Such a set-up utilizes readily available apparatus with sample sizes in the range of 0.1–0.3 mL (*5*).

Hazard 4: Fractional crystallization of potassium dichromate, $K_2Cr_2O_7$, with insufficient warning regarding the hazards of handling hot dichromate solutions or contact with dichromate dust due to spattering. Also, reduction products of chromium(VI) are probably carcinogenic.

Alternative: Substitute sodium nitrate, $NaNO_3$, benzoic acid, C_6H_5COOH, or another salt exhibiting solubility characteristics similar to potassium dichromate. Chemical tests can be used to test the purity of the recrystallized component.

Hazard 5: An analysis of coal where the coal is heated in a closed crucible for determination of volatile matter with no provision for venting the products of this destructive distillation (aromatic compounds, phenols, and heterocyclics).

Alternative: Work in a fume hood or use an alternative venting apparatus with a cold trap. An alternative venting apparatus is an inverted funnel placed above the crucible and attached to a water aspirator. Such a set-up can be an effective means for collecting the gaseous products of a reaction but is often inadequate; the small inside diameter of the funnel stem will limit the vapor flow. If adequate ventilation cannot be provided, this experiment

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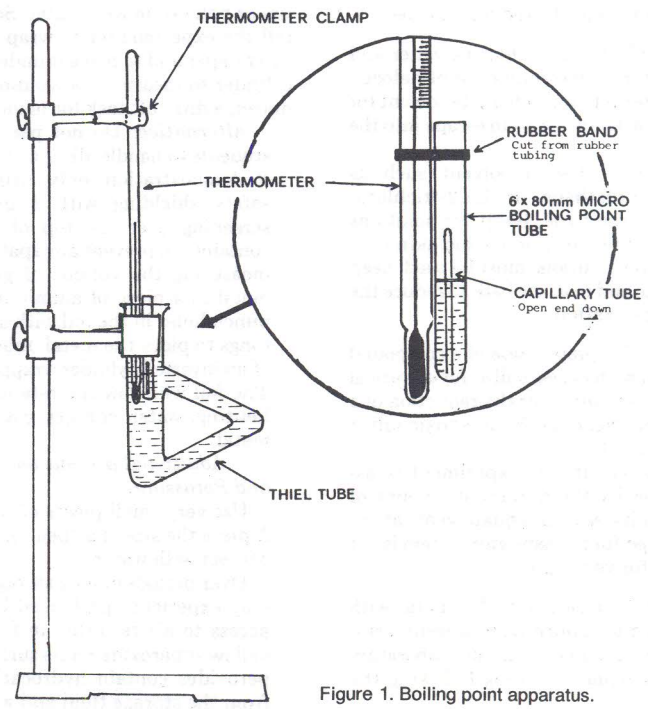

Figure 1. Boiling point apparatus.

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should be eliminated.

Hazard 6: Demonstrating the Law of Multiple Proportions by heating copper(II) bromide, $CuBr_2$. The decomposition product of the reaction, bromine, commonly is directed into a flask of water with a delivery tube above the water surface. Inevitably some toxic bromine vapors escape directly into the atmosphere and water is a poor solvent for bromine.

Alternative: This experiment probably should be eliminated. If one insists on performing such a procedure, a suggested apparatus is shown in Figure 2. In this

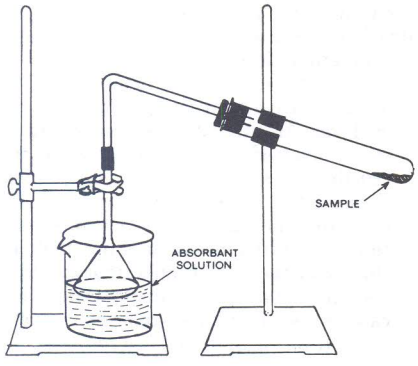

Figure 2. Method for collecting irritating vapors.

set-up, the delivery tube is replaced by an inverted funnel with the open end slightly below the liquid surface and the water in the beaker is replaced with an absorbant solution such as 1 *M* sodium hydroxide. At the conclusion of the reduction, there is still the problem of safely disposing of residual bromine in the reduction tube.

Hazard 7: The use of chlorine water and bromine water in determination of halogen activity. Water is not an adequate solvent for halogens allowing the gases to escape into the atmosphere.

Alternative: Use a solvent such as 1,1,2-trichloroethane or 1,2,2-trichloro-1,2,2-trifluoroethane. Keep the solutions in a well vented area and avoid skin contact. If water solutions must be used, keep them dilute and in an ice bath to reduce the rate of vaporization.

Hazard 8: The preparation of a compound using a metal with excess sulfur for empirical formula determination, or the reduction of a sulfide by heating. In both cases toxic sulfur oxides are formed.

Alternative: If this experiment is assigned, specify the minimum amount of sulfur and insist on adequate ventilation. (An inverted funnel-aspirator system is not adequate for venting.)

Hazard 9: The reaction of a metal with sulfur, ignited by a burning magnesium ribbon, on asbestos paper in the open laboratory with the inadequate warning following the procedure:

"(Exercise reasonable care, and do not get too close, because the mixture burns rapidly.)"

Alternative: Perform this experiment only as a demonstration, in a fume hood with adequate shielding. Warn the students not to look directly at the burning magnesium.

Hazard 10: Heating potassium chlorate, $KClO_3$, for analysis or determining the molar volume of oxygen. This experiment is an explosion hazard.

Alternative: For determination of the molar volume of oxygen, the reduction of a 3% solution of hydrogen peroxide with manganese dioxide, MnO_2, is a safer alternative. Another possibility is the reduction of copper oxide using burner gas (*6*) or an oxidation of steel wool (*7*).

Hazard 11: The analysis of a Drano®-type drain cleaner (consisting of sodium hydroxide and aluminum) by reacting it with 6 *M* sodium hydroxide producing an extremely caustic solution (Final concentration will exceed 7 *M*).

Alternative: The hazard can be reduced by adding water to the drain cleaner, but the reaction time may be longer and still produces a caustic solution and flammable hydrogen. Take the proper precautions: wear safety goggles (not visitor specs) and wear rubber gloves.

Hazard 12: Preparation of a sodium hydroxide solution, for later dilution for acid-base titrations, by dissolving 50 g of sodium hydroxide in 50 mL of water. This results in a highly exothermic reaction forming an extremely caustic solution with a concentration of 25 *M*.

Alternative: Have the students dilute a 6 *M* stock solution of sodium hydroxide to prepare the base solution for standardization. Wear safety goggles and rubber gloves when handling 6 *M* sodium hydroxide.

Hazard 13: The reaction of metallic sodium or potassium with water. Some manuals tell the experimenter to wrap the metal in filter paper and to place it under an inverted cylinder to measure the volume of gas produced, a difficult task for novices.

Alternative: Do not permit freshman students to handle alkali metals. Do this as a demonstration only using adequate safety shielding with a piece of wire screening over the top of the reaction container to prevent any spattering. When measuring the volume of gas, wrap the metal in a piece of aluminum or tin foil, punch holes in the foil with a pin, and use tongs to place the metal under the mouth of an inverted cylinder wrapped with tape. The foil will slow the rate of reaction by limiting water contact with the active metal.

Additional precautions with Sodium and Potassium

Use very small pieces of sodium metal. A piece the size of a "pea" can explode on contact with water.

Over periods of long storage, potassium may experience prolonged but restricted access to air resulting in formation of a yellow superoxide on its surface. Such superoxides contain hydrocarbon residues from the storage fluid and will result in a violent explosion on percussion or cutting of the metal (*2*, *3*). If the presence of potassium superoxides are suspected, seek assistance for proper disposal.

Hazard 14: Heating a liquid in a beaker on a ring support. This is a common cause of burns and/or cuts due to unsupported beakers falling from the ring supports.

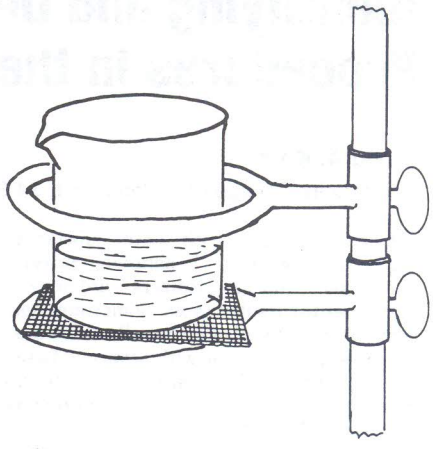

Figure 3. Technique for safe heating of beakers on a ring support.

Alternative: Always use a second ring around the beaker to prevent the beaker from falling off the ring support (see Fig. 3). Manuals always call for the clamping of flasks; the same should apply to beakers.

Hazard 15: Poor wording of the experimental procedure such as: "Add . . . sulfur acid, and then . . . potassium permanganate solution to . . . sodium oxalate solution." Students generally add reagents in the order listed without reading the entire procedure first. This can result in exothermic or violent reactions.

Alternative: Always list all reagents in the experimental procedure in the order in which they are to be added to the reaction container.

Summary

Hazards such as these are relatively widespread and most are encountered relatively early in the chemistry course when the students have limited laboratory experience.

Perhaps the greatest single hazard of most laboratory manuals is their lack of safety instructions. Generally, when instructions are included, they are given in the body of the procedure *following* the hazardous operation and are often read by the student after that step has been completed. At this writing, the author has found only two laboratory man-

uals that devote a section to "Safety Precautions" *preceeding* the experimental procedure (*8*), a practice that should be universally followed.

Overall, the best alternatives to hazards in the chemistry laboratory are simple safety practices and common sense. Use small containers of any potentially hazardous material, using dropping bottles when possible. Volatile substances (including halogens, hydrocarbons, etc. . . .) should be kept in a vented area as well as used and disposed of in vented areas. Safety equipment such as goggles, face shields, safety shields, gloves, aprons, proper tongs, etc . . . should be readily available. Most importantly, take the time to teach safety practices to your students in addition to actively practicing safety yourself. This means that you, too, must be wearing eye protection at all times in your laboratory.

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(3) Sax, N. I., "Dangerous Properties of Industrial Materials," 5th Ed., Van Nostrand Reinhold Co., New York, **1979.**

(4) Hampel, C. A. (*Editor*), "The Encyclopedia of the Chemical Elements," Reinhold Book Corp., New York, **1968,** p. 671.

(5) This set-up is a modification of that found in Shriner, R. L., Fusion, R. C., and Curtin, D. Y., "The Systematic Identification of Organic Compounds," 5th Ed., John Wiley and Sons, Inc., New York, **1964,** pp. 37–8. A complete procedure is available from the author on request.

(6) Zidick, C., and Weismann, T., J. CHEM. EDUC., **50,** 717 (1973) and modification by Katz, D. A., J. CHEM. EDUC., **52,** 204 (1975). **NOTE:** This procedure should be performed using heavy wall ignition tubes. Standard test tubes may melt and rupture during the reduction.

(7) Katz, D. A., Melucci, R. C., and Slavin, D. G., "Determination of a Chemical Formula," unpublished. Copy available from author on request.

(8) These manuals are:

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