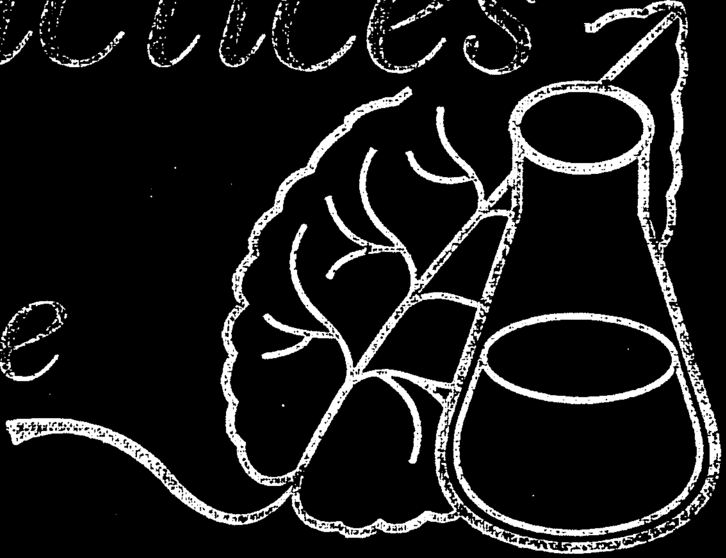
Prudent Practices in the Laboratory



Handling and Disposal of Chemicals

NATIONAL RESEARCH COUNCIL

and chemical treatment of mixed waste. Under certain conditions, regulators may allow such activities without a permit or may temporarily waive the storage or treatment permit requirements. Most regulators allow separation or treatment of chemical and radioactive components in the waste collection container or as part of a process without a RCRA permit.

Within the context of these changes, attention is being directed at promising technologies for the treatment of multihazardous waste. At this time, it cannot be determined if and when these technologies will be available, or if they will be developed for use in the laboratory or on a commercial scale. Nevertheless, they deserve careful attention, as do other approaches that will surely be developed in the near future, including the following:

- Ultraviolet peroxidation is being reviewed by the National Institutes of Health as a method to treat laboratory aqueous mixed waste containing low concentrations of organics. The process, though still under development, is expected to treat a wide range of organics and sterilize the waste.
- Wet oxidation and supercritical fluid oxidation (for aqueous solutions containing 1 to 10% organics) are being developed to destroy the chemical constituents in mixed waste.
- Biodegradation has been used successfully to treat soil, sludge, and other contaminated waste streams containing up to 1% organic waste. Laboratory-scale bioreactors are commercially available.
- Plasma torch, thermal desorption, molten salt pyrolysis, vitrification, and arc or hearth pyrolysis followed by incineration have all been used to treat mixed waste.

7.D PROCEDURES FOR THE LABORATORY-SCALE TREATMENT OF SURPLUS AND WASTE CHEMICALS

Concerns about environmental protection, bans on landfill disposal of waste, and limited access to sewer disposal have encouraged the development of strategies to reduce hazardous waste from laboratories. Many management methods are considered in earlier chapters of this book (see Chapter 4, section 4.B, and Chapter 5, section 5.B). The small-scale treatment and deactivation of products and by-products as part of the experiment plan is one approach that can be used to address the problem at the level of the actual generator, the laboratory worker. However, unless there is a significant reduction in risk by such action, there may be little benefit in carrying out a procedure that will simply produce another kind of waste with similar risks and challenges for disposal. Furthermore, the question of what constitutes "legal" treatment within the laboratory is still unresolved.

Nevertheless, there is often merit for such in-laboratory treatment. Below are some procedures of general use at the laboratory scale. Additional procedures can be found in the earlier edition of this book (*Prudent Practices for Disposal of Chemicals from Laboratories*; NRC, 1983) and other books listed in the bibliography. More specific procedures for laboratory treatment are increasingly being included in the experimental sections of chemical journals and in publications such as *Organic Syntheses* and *Inorganic Syntheses*.

Safety must be the first consideration before undertaking any of the procedures below. The procedures presented here are intended to be carried out only by, or under the direct supervision of, a trained scientist or technologist who understands the chemistry and hazards involved. Appropriate personal protection should be used. With the exception of neutralization, the procedures are intended for application to small quantities, that is, not more than a few hundred grams *Because risks tend to increase exponentially with scale larger quantities should be treated only in small batche unless a qualified chemist has demonstrated that the procedure can be scaled up safely.* The generator must ensur that the procedure eliminates the regulated hazar before the products are disposed of as nonhazardou waste. In addition, if the procedure suggests disposa of the product into the sanitary sewer, this strateg must comply with local regulations.

(See Chapter 6, section 6.F, for further information o protective clothing and also Chapter 5, section 5.C.2.6.

7.D.1 Acids and Bases

Neutralization of acids and bases (corrosives) is generally exempt from a RCRA treatment permit. However, because the products of the reaction are ofte disposed of in the sanitary sewer, it is important t ensure that hazardous waste such as toxic metal ior is not a part of the effluent.

In most laboratories, both waste acids and wast bases are generated, and so it is most economical t collect them separately and then neutralize one wit the other. If additional acid or base is required, sulfur or hydrochloric acid and sodium or magnesiu hydroxide, respectively, can be used.

If the acid or base is highly concentrated, it is prude to first dilute it with cold water (adding the acid base to the water) to a concentration below 10%. Th the acid and base are mixed, and the additional wat is slowly added when necessary to cool and dilute t neutralized product. The concentration of neutral sa disposed of in the sanitary sewer should generally be below 1%.

7.D.2 Organic Chemicals

7.D.2.1 Thiols and Sulfides

Small quantities of thiols (mercaptans) and sulfides can be destroyed by oxidation to a sulfonic acid with sodium hypochlorite. If other groups that can be oxidized by hypochlorite are also present, the quantity of this reagent used must be increased accordingly.

Procedure for oxidizing 0.1 mol of a liquid thiol:

$$\mathrm{RSH} + 3\mathrm{OCl}^- \rightarrow \mathrm{RSO_3H} + 3\mathrm{Cl}^-$$

Five hundred milliliters (0.4 mol, 25% excess) of commercial hypochlorite laundry bleach (5.25% sodium hypochlorite) is poured into a 5-L three-necked flask located in a fume hood. The flask is equipped with a stirrer, thermometer, and dropping funnel. The thiol (0.1 mol) is added dropwise to the stirred hypochlorite solution, initially at room temperature. A solid thiol can be added gradually through a neck of the flask or can be dissolved in tetrahydrofuran or other appropriate nonoxidizable solvent and the solution added to the hypochlorite. (The use of tetrahydrofuran introduces a flammable liquid that could alter the final disposal method.) Traces of thiol can be rinsed from the reagent bottle and dropping funnel with additional hypochlorite solution. Oxidation, accompanied by a rise in temperature and dissolution of the thiol, usually starts after a small amount of the thiol has been added. If the reaction has not started spontaneously after about 10% of the thiol has been added, addition is stopped and the mixture warmed to about 50 °C to initiate this reaction. Addition is resumed only after it is clear that oxidation is occurring. The temperature is maintained at 45 to 50 °C by adjusting the rate of addition and using an ice bath for cooling if necessary. Addition requires about 15 minutes. If the pH drops below 6 because of generation of the sulfonic acid, it may be necessary to add some sodium hydroxide or additional bleach because hypochlorite is destroyed under acidic conditions. Stirring is continued for 2 hours while the temperature gradually falls to room temperature. The mixture should be a clear solution, perhaps containing traces of oily by-products. The reaction mixture can usually be flushed down the drain with excess water. The unreacted laundry bleach need not be decomposed.

(Because sodium hypochlorite solutions deteriorate on storage, it is advisable to have relatively fresh material available. A 5.25% solution of sodium hypochlorite has 25 g of active chlorine per liter. If determination of the active hypochlorite content is justified, it can be accomplished as follows. Ten milliliters of the sodium hypochlorite solution is diluted to 100.0 mL, and then 10.0 mL of this diluted reagent is added to a solution of 1 g of potassium iodide and 12.5 mL of 2 M acetic acid in 50 mL of distilled water. Using a starch solution as indicator, titrate the solution with 0.1 N sodium thiosulfate. One milliliter of titrant corresponds to 3.5 mg of active chlorine. A 5.25% solution of sodium hypochlorite requires approximately 7 mL of titrant.)

Calcium hypochlorite may be used as an alternative to sodium hypochlorite and requires a smaller volume of liquid. For 0.1 mol of thiol, 42 g (25% excess) of 65% calcium hypochlorite (technical grade) is stirred into 200 mL of water at room temperature. The hypochlorite soon dissolves, and the thiol is then added as in the above procedure.

Laboratory glassware, hands, and clothing contaminated with thiols can be deodorized by a solution of Diaperene®, a tetraalkylammonium salt used to deodorize containers in which soiled diapers have been washed.

Small amounts of sulfides, RSR′, can be oxidized to sulfones ($\mathrm{RSO_2R'}$) to eliminate their disagreeable odors. The hypochlorite procedure used for thiols can be employed for this purpose, although the resulting sulfones are often water-insoluble and may have to be separated from the reaction mixture by filtration.

Small amounts of the inorganic sulfides, sodium sulfide or potassium sulfide, can be destroyed in aqueous solution by sodium or calcium hypochlorite using the procedure described for oxidizing thiols.

$$\mathrm{Na_2S} + 4\mathrm{OCl}^- \rightarrow \mathrm{Na_2SO_4} + 4\mathrm{Cl}^-$$

7.D.2.2 Acyl Halides and Anhydrides

Acyl halides, sulfonyl halides, and anhydrides react readily with water, alcohols, and amines. They should never be allowed to come into contact with waste that contains such substances. Most compounds in this class can be hydrolyzed to water-soluble products of low toxicity.

Procedure for hydrolyzing 0.5 mol of RCOX, $\mathrm{RSO_2X}$, or $\mathrm{(RCO)_2O}$:

$$\mathrm{RCOX} + 2\mathrm{NaOH} \rightarrow \mathrm{RCO_2Na} + \mathrm{NaX} + \mathrm{H_2O}$$

A 1-L three-necked flask equipped with a stirrer, dropping funnel, and thermometer is placed on a steam bath in a hood, and 600 mL of 2.5 M aqueous sodium hydroxide (1.5 mol, 50% excess) are poured into the flask. A few milliliters of the acid derivative are added dropwise with stirring. If the derivative is a solid, it can be added in small portions through a neck of the flask. If reaction occurs, as indicated by a rise in temperature and dissolution of the acid derivative, addition is continued at such a rate that the temperature does not rise above 45 °C. If the reaction is sluggish, as may be the case with less soluble compounds such as *p*-toluenesulfonyl chloride, the mixture is heated before adding any more acid derivative. When the initial added material has dissolved, the remainder is added dropwise. As soon as a clear solution is obtained, the mixture is cooled to room temperature, neutralized to about pH 7 with dilute hydrochloric or sulfuric acid, and washed down the drain with excess water.

7.D.2.3 Aldehydes

Many aldehydes are respiratory irritants, and some, such as formaldehyde and acrolein, are quite toxic. There is sometimes merit in oxidation of aldehydes to the corresponding carboxylic acids, which are usually less toxic and less volatile.

Procedure for permanganate oxidation of 0.1 mol of aldehyde:

$$3RCHO + 2KMnO_4 \rightarrow 2RCO_2K + RCO_2H + 2MnO_2 + H_2O$$

A mixture of 100 mL of water and 0.1 mol of aldehyde is stirred in a 1-L round-bottomed flask equipped with a thermometer, dropping funnel, stirrer, steam bath, and, if the aldehyde boils below 100 °C, a condenser. Approximately 30 mL of a solution of 12.6 g (0.08 mol, 20% excess) of potassium permanganate in 250 mL of water is added over a period of 10 minutes. If the temperature rises above 45 °C, the solution should be cooled. If this addition is not accompanied by a rise in temperature and loss of the purple permanganate color, the mixture is heated by the steam bath until a temperature is reached at which the color is discharged. The rest of the permanganate solution is added slowly at within 10 °C of this temperature. The temperature is then raised to 70 to 80 °C, and stirring continued for 1 hour or until the purple color has disappeared, whichever occurs first. The mixture is cooled to room temperature and acidified with 6 N sulfuric acid. **(CAUTION: Do not add concentrated sulfuric acid to permanganate solution because explosive manganese oxide (Mn_2O_7) may precipitate.)** Enough solid sodium hydrogen sulfite (at least 8.3 g, 0.08 mol) is added with stirring at 20 to 40 °C to reduce all the manganese, as indicated by loss of purple color and dissolution of the solid manganese dioxide. The mixture is washed down the drain with a large volume of water.

If the aldehyde contains a carbon-carbon double bond, as in the case of the highly toxic acrolein, 4 mol (20% excess) of permanganate per mol of aldehyde is required to oxidize the alkene bond and the aldehyde group.

Formaldehyde is oxidized conveniently to formic acid and carbon dioxide by sodium hypochlorite. Thus 10 mL of formalin (37% formaldehyde) in 100 mL of water is stirred into 250 mL of hypochlorite laundry bleach (5.25% NaOCl) at room temperature and allowed to stand for 20 minutes before being flushed down the drain. This procedure is not recommended for other aliphatic aldehydes because it leads to chloro acids, which are more toxic and less biodegradable than corresponding unchlorinated acids.

7.D.2.4 Amines

Acidified potassium permanganate efficiently degrades aromatic amines. Diazotization followed by hypophosphorus acid protonation is a method for deamination of aromatic amines, but the procedure is more complex than oxidation.

Procedure for permanganate oxidation of 0.01 mol of aromatic amine:

A solution of 0.01 mol of aromatic amine in 3 L of 1.7 N sulfuric acid is prepared in a 5-L flask; 1 L of 0.2 M potassium permanganate is added, and the solution allowed to stand at room temperature for 8 hours. Excess permanganate is reduced by slow addition o solid sodium hydrogen sulfite until the purple colo disappears. The mixture is then flushed down the drain.

7.D.2.5 Organic Peroxides and Hydroperoxides

(CAUTION: Peroxides are particularly dangerous These procedures should be carried out only b knowledgeable laboratory workers.) Peroxides can b removed from a solvent by passing it through a colum of basic activated alumina, by treating it with indicat ing Molecular Sieves®, or by reduction with ferrou sulfate. Although these procedures remove hydroper oxides, which are the principal hazardous contami nants of peroxide-forming solvents, they do no remove dialkyl peroxides, which may also be presen in low concentrations. Commonly used peroxid reagents, such as acetyl peroxide, benzoyl peroxid *t*-butyl hydroperoxide, and di-*t*-butyl peroxide, are less dangerous than the adventitious peroxides formed in solvents.

Removal of peroxides with alumina:

A 2 × 33 cm column filled with 80 g of 80-mesh basic activated alumina is usually sufficient to remove all peroxides from 100 to 400 mL of solvent, whether water-soluble or water-insoluble. After passage through the column, the solvent should be tested for peroxide content. Peroxides formed by air oxidation are usually decomposed by the alumina, not merely absorbed on it. However, for safety it is best to slurry the wet alumina with a dilute acidic solution of ferrous sulfate before it is discarded.

Removal of peroxides with Molecular Sieves®:

Reflux 100 mL of the solvent with 5 g of 4- to 8-mesh indicating activated 4A Molecular Sieves® for several hours under nitrogen. The sieves are separated from the solvent and require no further treatment because the peroxides are destroyed during their interaction with the sieves.

Removal of peroxides with ferrous sulfate:

$$\mathrm{ROOH} + 2\mathrm{Fe}^{2+} + 2\mathrm{H}^{+} \rightarrow \mathrm{ROH} + 2\mathrm{Fe}^{3+} + \mathrm{H_2O}$$

A solution of 6 g of $FeSO_4 \cdot 7H_2O$, 6 mL of concentrated sulfuric acid, and 11 mL of water is stirred with 1 L of water-insoluble solvent until the solvent no longer gives a positive test for peroxides. Usually only a few minutes are required.

Diacyl peroxides can be destroyed by this reagent as well as by aqueous sodium hydrogen sulfite, sodium hydroxide, or ammonia. However, diacyl peroxides with low solubility in water, such as dibenzoyl peroxide, react very slowly. A better reagent is a solution of sodium iodide or potassium iodide in glacial acetic acid.

Procedure for destruction of diacyl peroxides:

$$(\mathrm{RCO_2})_2 + 2\mathrm{NaI} \rightarrow 2\mathrm{RCO_2Na} + \mathrm{I_2}$$

For 0.01 mol of diacyl peroxide, 0.022 mol (10% excess) of sodium or potassium iodide is dissolved in 70 mL of glacial acetic acid, and the peroxide added gradually with stirring at room temperature. The solution is rapidly darkened by the formation of iodine. After a minimum of 30 minutes, the solution is washed down the drain with a large excess of water.

Most dialkyl peroxides (ROOR) do not react readily at room temperature with ferrous sulfate, iodide, ammonia, or the other reagents mentioned above. However, these peroxides can be destroyed by a modification of the iodide procedure.

Procedure for destruction of dialkyl peroxides:

One milliliter of 36% (w/v) hydrochloric acid is added to the above acetic acid/potassium iodide solution as an accelerator, followed by 0.01 mol of the dialkyl peroxide. The solution is heated to 90 to 100 °C on a steam bath over the course of 30 minutes and held at that temperature for 5 hours.

7.D.3 Inorganic Chemicals

7.D.3.1 Metal Hydrides

Most metal hydrides react violently with water with the evolution of hydrogen, which can form an explosive mixture with air. Some, such as lithium aluminum hydride, potassium hydride, and sodium hydride, are pyrophoric. Most can be decomposed by gradual addition of (in order of *decreasing* reactivity) methyl alcohol, ethyl alcohol, *n*-butyl alcohol, or *t*-butyl alcohol to a stirred, ice-cooled solution or suspension of the hydride in an inert liquid, such as diethyl ether, tetrahydrofuran, or toluene, under nitrogen in a three-necked flask. Although these procedures reduce the hazard and should be a part of any experimental procedure that uses reactive metal hydrides, the products from such deactivation may be hazardous waste that must be treated as such on disposal.

Hydrides commonly used in laboratories are lithium aluminum hydride, potassium hydride, sodium hydride, sodium borohydride, and calcium hydride. The following methods for their disposal demonstrate that the reactivity of metal hydrides varies considerably. Most hydrides can be decomposed safely by one of the four methods, but the properties of a given hydride must be well understood in order to select the most appropriate method. **(CAUTION: Most of the methods described below produce hydrogen gas, which can present an explosion hazard. The reaction should be carried out in a hood, behind a shield, and with proper safeguards to avoid exposure of the effluent gas to spark or flame. Any stirring device must be spark-proof.)**

Decomposition of lithium aluminum hydride:

Lithium aluminum hydride ($LiAlH_4$) can be purchased as a solid or as a solution in toluene, diethyl ether, tetrahydrofuran, or other ethers. Although dropwise addition of water to its solutions under nitrogen in a three-necked flask has frequently been used to decompose it, vigorous frothing often occurs. An alternative is to use 95% ethanol, which reacts less vigorously than water. A safer procedure is to decompose the hydride with ethyl acetate, because no hydrogen is formed.

$$2CH_3CO_2C_2H_5 + LiAlH_4 \rightarrow LiOC_2H_5 + Al(OC_2H_5)_3$$

To the hydride solution in a flask equipped with a stirrer, ethyl acetate is added slowly. The mixture sometimes becomes so viscous after the addition that stirring is difficult and additional solvent may be required. When the reaction with ethyl acetate has ceased, a saturated aqueous solution of ammonium chloride is added with stirring. The mixture separates into an organic layer and an aqueous layer containing inert inorganic solids. The upper, organic layer should be separated and disposed of as a flammable liquid. The lower, aqueous layer can often be disposed of in the sanitary sewer.

Decomposition of potassium or sodium hydride:

Potassium and sodium hydride (KH, NaH) in the dry state are pyrophoric, but they can be purchased as a relatively safe dispersion in mineral oil. Either form can be decomposed by adding enough dry hydrocarbon solvent (e.g., heptane) to reduce the hydride concentration below 5% and then adding excess *t*-butyl alcohol dropwise under nitrogen with stirring. Cold water is then added dropwise, and the resulting two layers are separated. The organic layer can be disposed of as a flammable liquid. The aqueous layer can often be neutralized and disposed of in the sanitary sewer.

Decomposition of sodium borohydride:

Sodium borohydride ($NaBH_4$) is so stable in water that a 12% aqueous solution stabilized with sodium hydroxide is sold commercially. In order to effect decomposition, the solid or aqueous solution is added to enough water to make the borohydride concentration less than 3%, and then excess equivalents of dilute aqueous acetic acid are added dropwise with stirring under nitrogen.

Decomposition of calcium hydride:

Calcium hydride (CaH_2), the least reactive of the materials discussed here, is purchased as a powder. It is decomposed by adding 25 mL of methyl alcohol per gram of hydride under nitrogen with stirring. When reaction has ceased, an equal volume of water is gradually added to the stirred slurry of calcium methoxide. The mixture is then neutralized with acid and disposed of in the sanitary sewer.

7.D.3.2 Inorganic Cyanides

Inorganic cyanides can be oxidized to cyanate using aqueous hypochlorite following a procedure similar to the oxidation of thiols. Hydrogen cyanide can be converted to sodium cyanide by neutralization with aqueous sodium hydroxide, and then oxidized.

Procedure for oxidation of cyanide:

$$NaCN + NaOCl \rightarrow NaOCN + NaCl$$

An aqueous solution of the cyanide salt in an ice-cooled, three-necked flask equipped with a stirrer, thermometer, and dropping funnel is cooled to 4 to 10 °C. A 50% excess of commercial hypochlorite laundry bleach containing 5.25% (0.75 M) sodium hypochlorite is added slowly with stirring while maintaining the low temperature. When the addition is complete and heat is no longer being evolved, the solution is allowed to warm to room temperature and stand for several hours. The mixture can then be washed down the drain with excess water. The same procedure can be applied to insoluble cyanides such as cuprous cyanide (though copper salts should not be disposed of in the sanitary sewer). In calculating the quantity of hypochlorite required, the experimenter should remember that additional equivalents may be needed if the metal ion can be oxidized to a higher valence state, as in the reaction,

$$\begin{aligned}&2CuCN + 3OCl^- + H_2O \rightarrow\\&\quad 2Cu^{2+} + 2OCN^- + 2OH^- + 3Cl^-\end{aligned}$$

A similar procedure can be used to destroy hydrogen cyanide, but precautions must be taken to avoid exposure to this very toxic gas. Hydrogen cyanide is dissolved in several volumes of ice water. Approximately 1 molar equivalent of aqueous sodium hydroxide is added at 4 to 10 °C to convert the hydrogen cyanide into its sodium salt, and then the procedure described above for sodium cyanide is followed. **(CAUTION: Sodium hydroxide or other bases, including sodium cyanide, must not be allowed to come into contact with liquid hydrogen cyanide because they may initiate a violent polymerization of the hydrogen cyanide.)**

This procedure also destroys soluble ferrocyanides and ferricyanides. Alternatively, these can be precipitated as the ferric or ferrous salt, respectively, for possible landfill disposal.

(See Chapter 6, section 6.D, for details on working with hazardous gases.)

7.D.3.3 Metal Azides

Heavy metal azides are notoriously explosive and should be handled by trained personnel. Silver azide (and also fulminate) can be generated from Tollens reagent, which is often found in undergraduate laboratories. Sodium azide is explosive only when heated to near its decomposition temperature (300 °C), but heating it should be avoided. Sodium azide should never be flushed down the drain. This practice has caused serious accidents because the azide can react with lead or copper in the drain lines to produce an azide that may explode. It can be destroyed by reaction with nitrous acid:

$$2NaN_3 + 2HNO_2 \rightarrow 3N_2 + 2NO + 2NaOH$$

Procedure for destruction of sodium azide:

The operation must be carried out in a hood because of the formation of toxic nitric oxide. An aqueous solution containing no more than 5% sodium azide is put into a three-necked flask equipped with a stirrer and a dropping funnel. Approximately 7 mL of 20% aqueous solution of sodium nitrite (40% excess) per gram of sodium azide is added with stirring. A 20% aqueous solution of sulfuric acid is then added gradually until the reaction mixture is acidic to litmus paper. **(CAUTION: The order of addition is essential. Poisonous, volatile hydrazoic acid (HN_3) will evolve if the acid is added before the nitrite.)** When the evolution of nitrogen oxides ceases, the acidic solution is tested with starch iodide paper. If it turns blue, excess nitrite is present, and the decomposition is complete. The reaction mixture is washed down the drain.

7.D.3.4 Alkali Metals

Alkali metals react violently with water, with common hydroxylic solvents, and with halogenated hydrocarbons. They should always be handled in the absence of these materials. The metals are usually destroyed by controlled reaction with an alcohol. The final aqueous alcoholic material can usually be disposed of in the sanitary sewer.

Procedure for destruction of alkali metals:

Waste sodium is readily destroyed with 95% ethanol. The procedure is carried out in a three-necked, round-bottomed flask equipped with a stirrer, dropping funnel, condenser, and heating mantle. Solid sodium should be cut into small pieces with a sharp knife while wet with a hydrocarbon, preferably mineral oil, so that the unoxidized surface is exposed. A dispersion of sodium in mineral oil can be treated directly. The flask is flushed with nitrogen and the pieces of sodium placed in it. Then 13 mL of 95% ethanol per gram of sodium are added at a rate that causes rapid refluxing. **(CAUTION: Hydrogen gas is evolved and can present an explosion hazard. The reaction should be carried out in a hood, behind a shield, and with proper safeguards (such as in Chapter 5, sections 5.G.4 and 5.G.5) to avoid exposing the effluent gas to spark or flame. Any stirring device must be spark-proof.)** Stirring is commenced as soon as enough ethanol has been added to make this possible. The mixture is stirred and heated under reflux until the sodium is dissolved. The heat source is removed, and an equal volume of water added at a rate that causes no more than mild refluxing. The solution is then cooled, neutralized with 6 M sulfuric or hydrochloric acid, and washed down the drain.

To destroy metallic potassium, the same procedure and precautions as for sodium are used, except that the less reactive *t*-butyl alcohol is used in the proportion of 21 mL/g of metal. **(CAUTION: Potassium metal can form explosive peroxides. Metal that has formed a yellow oxide coating from exposure to air should not be cut with a knife, even when wet with a hydrocarbon, because an explosion can be promoted.)** If the potassium is dissolving too slowly, a few percent of methanol can be added gradually to the refluxing *t*-butyl alcohol. Oxide-coated potassium sticks should be put directly into the flask and decomposed with *t*-butyl alcohol. The decomposition will require considerable time because of the low surface/volume ratio of the metal sticks.

Lithium metal can be treated by the same procedure, but using 30 mL of 95% ethanol per gram of lithium. The rate of dissolution is slower than that of sodium.

7.D.3.5 Metal Catalysts

Metal catalysts such as Raney nickel and other fine metal powders can be slurried into water; dilute hydrochloric acid is then added carefully until the solid dissolves. Depending on the metal and on local regulations, the solution can be discarded in the sanitary sewer or with other hazardous or nonhazardous solid waste. Precious metals should be recovered from this process.

7.D.3.6 Water-Reactive Metal Halides

Liquid halides, such as $TiCl_4$ and $SnCl_4$, can be added to well-stirred water in a round-bottomed flask cooled by an ice bath as necessary to keep the exothermic reaction under control. It is usually more convenient to add solid halides, such as $AlCl_3$ and $ZrCl_4$, to stirring water and crushed ice in a flask or beaker. The acidic solution can be neutralized and, depending on the metal and local regulations, discarded in the sanitary sewer or with other hazardous or nonhazardous solid waste.

7.D.3.7 Halides and Acid Halides of Nonmetals

Halides and acid halides such as PCl_3, PCl_5, $SiCl_4$, $SOCl_2$, SO_2Cl_2, and $POCl_3$ are water-reactive. The liquids can be hydrolyzed conveniently using 2.5 M sodium hydroxide by the procedure described earlier for acyl halides and anhydrides. These compounds are irritating to the skin and respiratory passages and, even more than most chemicals, require a good hood and skin protection when handling them. Moreover, PCl_3 may give off small amounts of highly toxic phosphine (PH_3) during hydrolysis.

Sulfur monochloride (S_2Cl_2) is a special case. It is hydrolyzed to a mixture of sodium sulfide and sodium sulfite, so that the hydrolyzate must be treated with hypochlorite as described earlier for sulfides before it can be flushed down the drain.

The solids of this class (e.g., PCl_5) tend to cake and fume in moist air and therefore are not conveniently hydrolyzed in a three-necked flask. It is preferable to add them to a 50% excess of 2.5 M sodium hydroxide solution in a beaker or wide-mouth flask equipped with a stirrer and half-filled with crushed ice. If the solid has not all dissolved by the time the ice has melted and the stirred mixture has reached room temperature, the reaction can be completed by heating on a steam bath, and then the acidic solution neutralized and disposed of in the sanitary sewer.

7.D.3.8 Inorganic Ions

Many inorganic wastes consist of a cation (metal or metalloid atom) and an anion (which may or may not contain a metalloid component). It is often helpful to examine the cationic and anionic parts of the substance separately to determine whether either possesses a hazard.

If a substance contains a "heavy metal," it is often assumed that it is highly toxic. While salts of some heavy metals, such as lead, thallium, and mercury, are highly toxic, those of others, such as gold and tantalum, are not. On the other hand, compounds of beryllium, a "light metal," are highly toxic. In Table 7.1, cations of metals and metalloids are listed alphabetically in two groups: those whose toxic properties as described in the toxicological literature present a significant hazard, and those whose properties do not. The basis for separation is relative, and the separation does not imply that those in the second list are "nontoxic." Similarly, Table 7.2 lists anions according to their level of toxicity and other dangerous properties, such as strong oxidizing power (e.g., perchlorate), flammability (e.g., amide), water reactivity (e.g., hydride), and explosivity (e.g., azide).

Materials that pose a hazard because of significant radioactivity are outside the scope of this volume, although they may be chemically treated in a manner similar to the nonradioactive materials discussed in this chapter. Their handling and disposal are highly regulated in most countries. Low-level radioactive mixed waste is discussed in section 7.C above.

7.D.3.8.1 Chemicals in Which Neither the Cation Nor the Anion Presents a Significant Hazard

Chemicals in which neither the cation nor the anion presents a significant hazard consist of those chemicals composed of ions from the right-hand columns of Tables 7.1 and 7.2. Those that are soluble in water to the extent of a few percent can usually be disposed of in the sanitary sewer. Only laboratory quantities should be disposed of in this manner, and at least 100 parts of water per part of chemical should be used. Local regulations should be checked for possible restrictions. Dilute slurries of insoluble materials, such as calcium sulfate or aluminum oxide, also can be handled in this way, provided the material is finely divided and not contaminated with tar, which might clog the piping. Some incinerators can handle these chemicals. If time and space permit, dilute aqueous solutions can be boiled down or allowed to evaporate to leave only a sludge of the inorganic solid for landfill disposal. However, appropriate precautions, including the use of traps, must be considered to ensure that toxic or other prohibited materials are not released to the atmosphere.

An alternative procedure is to precipitate the metal ion by the agent recommended in Table 7.1. The precipitate can often be disposed of in a secure landfill. The most generally applicable procedure is to precipitate the cation as the hydroxide by adjusting the pH to the range shown in Table 7.3.

7.D.3.8.2 Precipitation of Cations as Their Hydroxides

Because the pH range for precipitation varies greatly among metal ions, it is important to control it carefully. The aqueous solution of the metal ion is adjusted to the recommended pH (Table 7.3) by addition of a solu-

TABLE 7.1 High- and Low-Toxicity Cations and Preferred Precipitants

High Toxic Hazard		Low Toxic Hazard	
Cation	Precipitant[a]	Cation	Precipitant[a]
Antimony	OH^-, S^{2-}	Aluminium	OH^-
Arsenic	S^{2-}	Bismuth	OH^-, S^{2-}
Barium	SO_4^{2-}, CO_3^{2-}	Calcium	SO_4^{2-}, CO_3^{2-}
Beryllium	OH^-	Cerium	OH^-
Cadmium	OH^-, S^{2-}	Cesium	
Chromium(III)[b]	OH^-	Copper[c]	OH^-, S^{2-}
Cobalt(II)[b]	OH^-, S^{2-}	Gold	OH^-, S^{2-}
Gallium	OH^-	Iron[c]	OH^-, S^{2-}
Germanium	OH^-, S^{2-}	Lanthanides	OH^-
Hafnium	OH^-	Lithium	
Indium	OH^-, S^{2-}	Magnesium	OH^-
Iridium[d]	OH^-, S^{2-}	Molybdenum(VI)[b,e]	
Lead	OH^-, S^{2-}	Niobium(V)	OH^-
Manganese(II)[b]	OH^-, S^{2-}	Palladium	OH^-, S^{2-}
Mercury	OH^-, S^{2-}	Potassium	
Nickel	OH^-, S^{2-}	Rubidium	
Osmium(IV)[b,f]	OH^-, S^{2-}	Scandium	OH^-
Platinum(II)[b]	OH^-, S^{2-}	Sodium	
Rhenium(VII)[b]	S^{2-}	Strontium	SO_4^{2-}, CO_3^{2-}
Rhodium(III)[b]	OH^-, S^{2-}	Tantalum	OH^-
Ruthenium(III)[b]	OH^-, S^{2-}	Tin	OH^-, S^{2-}
Selenium	S^{2-}	Titanium	OH^-
Silver[d]	Cl^-, OH^-, S^{2-}	Yttrium	OH^-
Tellurium	S^{2-}	Zinc[c]	OH^-, S^{2-}
Thallium	OH^-, S^{2-}	Zirconium	OH^-
Tungsten(VI)[b,e]			
Vanadium	OH^-, S^{2-}		

[a] Precipitants are listed in order of preference: OH^-, CO_3^{2-} = base (sodium hydroxide or sodium carbonate), S^{2-} = sulfide, SO_4^{2-} = sulfate, and Cl^- = chloride.

[b] The precipitant is for the indicated valence state.

[c] Very low maximum tolerance levels have been set for these low-toxicity ions in some countries, and large amounts should not be put into public sewer systems. The small amounts typically used in laboratories will not normally affect water supplies, although they may be prohibited by the local pubicly owned treatment works (POTW).

[d] Recovery of these rare and expensive metals may be economically favorable.

[e] These ions are best precipitated as calcium molybdate(VI) or calcium tungstate(VI).

[f] CAUTION: Osmium tetroxide, OsO_4, a volatile, extremely poisonous substance, is formed from almost any osmium compound under acid conditions in the presence of air. Reaction with corn oil or powdered milk will destroy it.

tion of 1 M sulfuric acid, or 1 M sodium hydroxide or carbonate. The pH can be determined over the range 1 through 10 by use of pH test paper.

The precipitate is separated by filtration, or as a heavy sludge by decantation, and packed for disposal. Some gelatinous hydroxides are difficult to filter. In such cases, heating the mixture close to 100 °C or stirring with diatomaceous earth, approximately 1 to 2 times the weight of the precipitate, often facilitates filtration.

As shown in Table 7.1, precipitants other than a base may be superior for some metal ions, such as sulfuric acid for calcium ion. For some ions, the hydroxide precipitate will redissolve at a high pH (Table 7.3). For a number of metal ions the use of sodium carbonate will result in precipitation of the metal carbonate or a mixture of hydroxide and carbonate.

7.D.3.8.3 Chemicals in Which the Cation Presents a Relatively High Hazard from Toxicity

In general, waste chemicals containing any of the cations listed as highly hazardous in Table 7.1 can be precipitated as their hydroxides or oxides. Alternatively, many can be precipitated as insoluble sulfides by treatment with sodium sulfide in neutral solution (Table 7.4). Several sulfides will redissolve in excess sulfide ion, and so it is important that the sulfide ion concentration be controlled by adjustment of the pH.

Precipitation as the hydroxide is achieved as described above. Precipitation as the sulfide is accomplished by adding a 1 M solution of sodium sulfide to the metal ion solution, and then adjusting the pH to

TABLE 7.2 High- and Low-Hazard Anions and Preferred Precipitants

High-Hazard Anions			
Ion	Hazard Type[a]	Precipitant	Low-Hazard Anions
Aluminium hydride, AlH_4^-	F, W	—	Bisulfite, HSO^{3-}
Amide, NH_2^-	F, E[b]	—	Borate, BO_3^{3-}, $B_4O_7^{2-}$
Arsenate, AsO_3^-,AsO_4^{3-}	T	Cu^{2+}, Fe^{2+}	Bromide, Br^-
Arsenite, AsO_2^-, AsO_3^{3-}	T	Pb^{2+}	Carbonate, CO_3^{2-}
Azide, N_3^-	E, T	—	Chloride, Cl^-
Borohydride, BH_4^-	F	—	Cyanate, OCN^-
Bromate, BrO_3^-	O, F, E	—	Hydroxide, OH^-
Chlorate, ClO_3^-	O, E	—	Iodide, I^-
Chromate, CrO_4^{2-}, $Cr_2O_7^{2-}$	T, O	[c]	Oxide, O^-
Cyanide, CN^-	T	—	Phosphate, PO_4^{3-}
Ferricyanide, $[Fe(CN)_6]^{3-}$	T	Fe^{2+}	Sulfate, SO_4^{2-}
Ferrocyanide, $[FE(CN)_6]^{4-}$	T	Fe^{3+}	Sulfite, SO_3^{2-}
Fluoride, F^-	T	Ca^{2+}	Thiocyanate, SCN^-
Hydride, H^-	F, W	—	
Hydroperoxide, O_2H^-	O, E	—	
Hydrosulfide, SH^-	T	—	
Hypochlorite, OCl^-	O	—	
Iodate, IO_3^-	O, E	—	
Nitrate, NO_3^-	O	—	
Nitrite, NO_2^-	T, O	—	
Perchlorate, ClO_4^-	O, E	—	
Permanganate, MnO_4^-	T, O	—	
Peroxide, O_2^{2-}	O, E	[d]	
Persulfate, $S_2O_8^{2-}$	O	—	
Selenate, SeO_4^{2-}	T	Pb^{2+}	
Selenide, Se^{2-}	T	Cu^{2+}	
Sulfide, S^{2-}	T	[e]	

[a] T = toxic; O = oxidant; F = flammable; E = explosive; and W = water reactive.

[b] Metal amides readily form explosive peroxides on exposure to air.

[c] Reduce and precipitate as Cr(III).

[d] Reduce and precipitate as Mn(II); see Table 7.1.

[e] See Table 7.4.

neutral with 1 M sulfuric acid. **(CAUTION: Avoid acidifying the mixture because hydrogen sulfide could be formed.)** The precipitate is separated by filtration or decantation and packed for disposal. Excess sulfide ion can be destroyed by the addition of hypochlorite to the clear aqueous solution.

The following ions are most commonly found as oxyanions and are not precipitated by base: As^{3+}, As^{5+}, Re^{7+}, Se^{4+}, Se^{6+}, Te^{4+}, and Te^{6+}. These elements can be precipitated from their oxyanions as the sulfides by the above procedure. Oxyanions of Mo^{6+} and W^{6+} can be precipitated as their calcium salts by the addition of calcium chloride. Some ions can be absorbed by passing their solutions over ion-exchange resins. The resins can be landfilled, and the effluent solutions poured down the drain.

Another class of compounds whose cations may not be precipitated by the addition of hydroxide ions are the most stable complexes of metal cations with Lewis bases, such as ammonia, amines, and tertiary phosphines. Because of the large number of these compounds and their wide range of properties, it is not possible to give a general procedure for separating the cations. In many cases, metal sulfides can be precipitated directly from aqueous solutions of the complexes by the addition of aqueous sodium sulfide. If a test-tube experiment shows that other measures are needed, the addition of hydrochloric acid to produce a slightly acidic solution will often decompose the complex by protonation of the basic ligand. Metal ions that form insoluble sulfides under acid conditions can then be precipitated by dropwise addition of aqueous sodium sulfide.

A third option for this waste is incineration, provided that the incinerator ash is to be sent to a secure landfill. Incineration to ash reduces the volume of

TABLE 7.3 pH Ranges for Precipitation of Metal Hydroxides and Oxides

pH:	1	2	3	4	5	6	7	8	9	10
Ag^{1+}									|	→ 1N
Al^{3+}							|	|		
As^{3+}	Not precipitated (precipitate as sulfide)									
As^{5+}	Not precipitated (precipitate as sulfide)									
Au^{3+}							|	|		
Be^{2+}							|	|		
Bi^{3+}							|	—	—	→ 1N
Cd^{2+}							|	—	—	→ 1N
Co^{2+}								|	—	→ 1N
Cr^{3+}							|	—	—	→ 1N
Cu^{1+}									|	→ 1N
Cu^{2+}							|	—	—	→ 1N
Fe^{2+}							|	—	—	→ 1N
Fe^{3+}							|	—	—	→ 1N
Ga^{3+}							|	|		
Ge^{4+}						|	—	|		
Hf^{4+}						|	|			
Hg^{1+}								|	—	→ 1N
Hg^{2+}								|	—	→ 1N
In^{3+}						|	—	—	—	→ pH13
Ir^{4+}						|	—	|		
Mg^{2+}									|	→ 1N
Mn^{2+}								|	—	→ 1N
Mn^{4+}							|	—	—	→ 1N
Mo^{6+}	Not precipitated (precipitate as Ca salt)									
Nb^{5+}	|	—	—	—	—	—	—	—	—	|
Ni^{2+}								|	—	→ 1N
Os^{4+}							|	|		
Pb^{2+}							|	|		
Pd^{2+}							|	|		
Pd^{4+}							|	|		
Pt^{2+}							|	|		
Re^{3+}						|	—	—	—	→ 1N
Re^{7+}	Not precipitated (precipitate as sulfide)									
Rh^{3+}							|	|		
Ru^{3+}							|	—	—	→ 1N
Sb^{3+}							|	|		
Sb^{5+}							|	|		
Sc^{3+}								|	—	→ 1N
Se^{4+}	Not precipitated (precipitate as sulfide)									
Se^{6+}	Not precipitated (precipitate as sulfide)									
Sn^{2+}							|	|		
Sn^{4+}							|	|		
Ta^{5+}	|	—	—	—	—	—	—	—	—	|
Te^{4+}	Not precipitated (precipitate as sulfide)									
Te^{6+}	Not precipitated (precipitate as sulfide)									
Th^{4+}						|	—	—	—	→ 1N
Ti^{3+}								|	—	→ 1N
Ti^{4+}								|	—	→ 1N
Tl^{3+}									|	→ 1N
V^{4+}							|	|		
V^{5+}							|	|		
W^{6+}	Not precipitated (precipitate as Ca salt)									
Zn^{2+}							|	|		
Zr^{4+}						|	|			

NOTE: Most metal ions are precipitated as hydroxides or oxides at high pH. However, many precipitates will redissolve in excess base. For this reason, it is necessary to control pH closely in a number of cases. This table shows the recommended pH range for precipitating many cations in their most common oxidation state. The notation "1 N" in the right-hand column indicates that the precipitate will not dissolve in 1 N sodium hydroxide (pH 14).

SOURCES: Erdey (1965) and Burns et al. (1981).

TABLE 7.4 Precipitation of Sulfides

Precipitated at pH 7	Not Precipitated at Low pH	Soluble Complex at High pH
Ag^{+}		
As^{3+a}		x
Au^{+a}		x
Bi^{3+}		
Cd^{2+}		
Co^{2+}	x	
Cr^{3+a}		
Cu^{2+}		
Fe^{2+a}	x	
Ge^{2+}		x
Hg^{2+}		x
In^{3+}	x	
Ir^{4+}		x
Mn^{2+a}	x	
Mo^{3+}		x
Ni^{2+}	x	
Os^{4+}		
Pb^{2+}		
Pd^{2+a}		
Pt^{2+a}		x
Re^{4+}		
Rh^{2+a}		
Ru^{4+}		
Sb^{3+a}		x
Se^{2+}		x
Sn^{2+}		x
Te^{4+}		x
Tl^{+a}	x	
V^{4+a}		
Zn^{2+}	x	

NOTE: Precipitation of ions listed without an x is usually not pH-dependent.

[a] Higher oxidation states of this ion are reduced by sulfide ion and precipitated as this sulfide.

SOURCE: Swift and Schaefer (1961).

waste going to a landfill. Waste that contains mercury, thallium, gallium, osmium, selenium, or arsenic should not be incinerated because volatile, toxic combustion products may be emitted.

7.D.3.8.4 Chemicals in Which an Anion Presents a Relatively High Hazard

The more common dangerous anions are listed in Table 7.2. Many of the comments made above about the disposal of dangerous cations apply to these anions. The hazard associated with some of these anions is their reactivity or potential to explode, which makes them unsuitable for landfill disposal. Most chemicals containing these anions can be incinerated, but strong oxidizing agents and hydrides should be introduced into the incinerator only in containers of not more than a few hundred grams. Incinerator ash from anions of chromium or manganese should be transferred to a secure landfill.

Some of these anions can be precipitated as insoluble salts for landfill disposal, as indicated in Table 7.2. Small amounts of strong oxidizing agents, hydrides, cyanides, azides, metal amides, and soluble sulfides or fluorides can be converted into less hazardous substances in the laboratory before being disposed of. Suggested procedures are presented in the following paragraphs.

7.D.3.8.5 Procedure for Reduction of Oxidizing Salts

Hypochlorites, chlorates, bromates, iodates, periodates, inorganic peroxides and hydroperoxides, persulfates, chromates, molybdates, and permanganates can be reduced by sodium hydrogen sulfite. A dilute solution or suspension of a salt containing one of these anions has its pH reduced to less than 3 with sulfuric acid, and a 50% excess of aqueous sodium hydrogen sulfite is added gradually with stirring at room temperature. An increase in temperature indicates that the reaction is taking place. If the reaction does not start on addition of about 10% of the sodium hydrogen sulfite, a further reduction in pH may initiate it. Colored anions (e.g., permanganate and chromate) serve as their own indicators of completion of the reduction. The reduced mixtures can often be washed down the drain. However, if large amounts of permanganate have been reduced, it may be necessary to transfer the manganese dioxide to a secure landfill, possibly after a reduction in volume by concentration or precipitation. *Do not dispose of chromium salts in the sanitary sewer.*

Hydrogen peroxide can be reduced by the sodium hydrogen sulfite procedure or by ferrous sulfate as described earlier for organic hydroperoxides. However, it is usually acceptable to dilute it to a concentration of less than 3% and dispose of it in the sanitary sewer. Solutions with a hydrogen peroxide concentration greater than 30% should be handled with great care to avoid contact with reducing agents, including all organic materials, or with transition metal compounds, which can catalyze a violent reaction.

Concentrated perchloric acid (particularly when stronger than 60%) must be kept away from reducing agents, including weak ones such as ammonia, wood, paper, plastics, and all other organic substances, because it can react violently with them. Dilute perchloric acid is not reduced by common laboratory reducing agents such as sodium hydrogen sulfite, hydrogen sulfide, hydriodic acid, iron, or zinc. Perchloric acid is most easily disposed of by stirring it gradually into enough cold water to make its concentration less than 5%, neutralizing it with aqueous sodium hydroxide, and washing the solution down the drain with a large excess of water.

Nitrate is most dangerous in the form of concentrated nitric acid (70% or higher), which is a potent oxidizing agent for organic materials and all other reducing agents. It can also cause serious skin burns. Dilute aqueous nitric acid is not a dangerous oxidizing agent and is not easily reduced by common laboratory reducing agents. Dilute nitric acid should be neutralized with aqueous sodium hydroxide before disposal down the drain; concentrated nitric acid should be diluted carefully by adding it to about 10 volumes of water before neutralization. Metal nitrates are generally quite soluble in water. Those of the metals listed in Table 7.1 as having a low toxic hazard, as well as ammonium nitrate, should be kept separate from oil or other organic materials because on heating such a combination, fire or explosion can occur. Otherwise, these can be treated as chemicals that present no significant hazard.

Nitrites in aqueous solution can be destroyed by adding about 50% excess aqueous ammonia and acidifying with hydrochloric acid to pH 1:

$$HNO_2 + NH_3 \rightarrow N_2 + 2H_2O$$