Cyanides

by Gray

CYANIDES

I. Background

Alkali metal cyanides (mostly potassium cyanide, KCN, or sodium cyanide, NaCN) have a history dating back to the 18th century. They are widely used in chemical synthesis, gold mining, electroplating, and a variety of other industrial processes. NaCN and KCN are very similar chemically, although sometimes one form or the other is preferred. They are very toxic to higher forms of life and hence may be difficult to purchase without the backing of a business or educational institute.

Hydrogen cyanide has a characteristic odor that is most often described as that of "bitter almonds." I personally think that the scent, although distinctive, does not resemble any almonds I have ever encountered. Perhaps I haven't yet found the bitter ones. Although the scent of hydrogen cyanide is a handy qualitative test for small amounts, larger quantities or repeated exposure will temporarily dull the nose's capability to distinguish it. Additionally, a fair proportion of the population cannot smell hydrogen cyanide to begin with, so scent alone cannot be counted on to detect cyanides. Alkaline cyanides, especially when damp, have a scent of hydrogen cyanide to them. This is likely due to the slow reaction of carbon dioxide from the air with the cyanide. Since hydrocyanic acid is a very weak acid, the slightly stronger carbonic acid (carbon dioxide dissolved in water) can produce alkali carbonates from alkali cyanides, simultaneously releasing hydrogen cyanide.

SHORTCOMINGS OF EXISTING FRINGE LITERATURE

A variety of fringe literature, both printed and online, has suggested various processes for amateur production of cyanides. Two commonly suggested methods are the decomposition of low-toxicity, unregulated ferrocyanide or ferricyanide compounds by heat (producing alkali cyanides directly) or by strong acids (producing hydrogen cyanide, which must then be led into a solution of metal hydroxide to produce the cyanide salt). These methods are workable, but they still require chemicals that cannot be readily found in consumer products and must be purchased from specialty dealers or tediously synthesized (often, it is suggested, by recreating nineteenth century industrial

production techniques in miniature). Another method that is sometimes suggested is extracting hydrogen cyanide from cyanogenic glycosides found in plants (such as apple seeds or peach pits or leaves). This method would require an unreasonable amount of dedication to produce relatively small quantities of cyanides.

Methods that are much less commonly speculated about but still possible include the distillation of ammonium formate, combustion of alkali carbonate laced carbon in the presence of ammonia or nitrogen, controlled reduction of alkali nitrates by carbon, and Hoffman isonitrile synthesis using ammonia, chloroform, and an alkali hydroxide. All of these methods have drawbacks in terms of requiring the purchase or synthesis of certain chemicals, assembling apparatus, purifying the final product, or obtaining decent yields of cyanides in the first place. Therefore, included in part III of this document is a tested procedure designed for small-scale synthesis of alkali cyanides by an amateur with modest resources, which should crown this document King of the Fringe Cyanide Literature.

A SHORT HISTORY OF CYANIDES

[1]:

"The familiar coloring matter, prussian blue, was discovered about 1710, but the chemical substance cyanogen, the radical common to prussian blue and to a large series of complex substances now known to chemistry, was not isolated until more than a hundred years later. The name cyanogen (generator of blue) was given by Gay Lussac, in 1814, to the new substance which he found to be the characteristic ingredient of this blue and of compounds related to it. The familiar name of "Prussiates," still applied in trade to the double cyanides of iron and potassium as well as the common name 'Prussic Acid,' by which hydrocyanic acid is known, bear evidence of the importance which the blue color originating in Prussia had early acquired as a commercial product.

Some time before the year 1710 a German manufacturer named Diesbach, working with the so-called Dippel's animal oil (commonly obtained by destructive distillation of bones, blood, or other animal waste) happened, in handling a solution of this oil made from blood, to add it to a solution of potash (crude potassium carbonate) and obtained thereby a blue color. The process was soon applied upon a commercial scale. It was first described in a book called Miscellanea Berolinensia, published in 1710. But the discoverer of the color was not known by name until mentioned by Scheele in 1731."

To make a long story shorter, it was discovered some years later that potassium ferrocyanide could be formed by treating Prussian blue with potassium hydroxide. It was later found that potassium ferrocyanide could be formed directly by heating potassium carbonate, iron scraps, and organic wastes (such as dried blood or scraps of leather, wool, or horn) together in a furnace for several hours, dissolving the fused mass in water, and separating the potassium ferrocyanide by repeated crystallization. The chemistry involved is not straightforward and there were many details involved in the successful commercial application of the process. See [2] for a detailed description of the nineteenth century industrial production of potassium ferrocyanide ("yellow prussiate of potash.")

Much of the nineteenth century's alkali cyanides were produced by the thermal decomposition of ferrocyanides.

[2]:

"CYANIDE OF POTASSIUM -- This useful salt is most advantageously prepared from ferrocyanide of potassium or yellow prussiate of potassa, which is to be carefully dessicated, and reduced to a fine powder, eight parts of which are mixed with three parts of carbonate of potassa and one of charcoal, both in impalpable powder. This mixture is to be exposed to a strong red heat in a closed iron crucible. After cooling, the mass is to be finely powdered, placed in a funnel moistened with a little alcohol, and then washed with cold water. The colorless strong solution of cyanide of potassium which passes through, is then rapidly evaporated to dryness in a porcelain basin and fused at a red heat. This salt, as obtained by ignition of the above ingredients, without the charcoal, usually contains a little cyanate, which, however, does not interfere with its use for forming and dissolving cyanides of gold and silver for the processes of voltaic gilding and plating."

Purer materials required more complicated methods. One such method was passing hydrogen cyanide or hydrocyanic acid into a solution of potassium hydroxide dissolved in alcohol. The potassium cyanide was less soluble than the hydroxide and precipitated.

[2]:

"The preparation of cyanide of potassium in a state of perfect purity, is always attended with difficulty, owing to the action of the carbonic acid of the air upon its solution, and the tendency of the menstrum itself to undergo spontaneous decomposition, even when secluded from the air. It is obtained in a state of great purity by adding absolute hydrocyanic acid, or a strong solution of this acid, to an alcoholic solution of potassa; a portion of the cyanide falls down as a white crystalline precipitate, which should be washed with alcohol and dried."

The strong solution of hydrocyanic acid may be prepared from potassium ferrocyanide.

[2]:

"The last mode of procedure which it will be requisite to describe here is that of Trautwein. Fifteen parts of finely-powdered ferrocyanide of potassium are distilled at a gentle heat with nine parts of sulphuric acid, previously diluted with an equal weight of water; the distillate is collected in a well-cooled receiver, containing five parts of pure chloride of calcium, broken into small pieces. When the hydrocyanic acid has accumulated in sufficient quantity to cover the chloride of calcium, it is poured off into a well-stoppered glass bottle."

The "well-cooled receiver" cannot be emphasized too much. Pure hydrogen cyanide boils at about 25 degrees Celsius (77 degrees Fahrenheit) and concentrated water solutions are also volatile. Attempting to prepare hydrogen cyanide gas or solution without proper glassware and a fume hood is asking for disaster. If it is desired to store the hydrocyanic acid thus procured, it is advisable to keep the bottle cool and away from sunlight, and to add a few drops of sulfuric or hydrochloric acid for stabilization. Unstabilized hydrocyanic acid tends to polymerize with time, forming a complex mixture of organic compounds.

In recent years, most hydrogen cyanide has been obtained by the reaction of methane with ammonia or as a byproduct of acrylonitrile production. These processes are not at all suited to

small-scale production with simple apparatus.

Once you have obtained alkali cyanides, it is very easy to produce hydrocyanic acid from them. Almost all acids are stronger than HCN and will liberate it from its salts. Acetic acid, citric acid, and certainly the mineral acids will all set it free. But I would consider it extremely foolhardy to produce hydrocyanic acid without proper glassware and a fumehood.

II. Toxicology

[3]:

"Poisoning may arise from any substance which releases the cyanide ion (CN-). Cyanide is a potent and rapidly acting chemical asphyxiant; it deprives tissues of necessary oxygen by inhibiting reversibly such oxidative enzymes as cytochrome oxidase (Stotz et al., 1938). Because oxygen cannot be utilized, venous blood retains the bright red color of oxyhemoglobin. Cyanide does not react to an appreciable extent with the hemoglobin molecule. As with other chemical asphyxiants, the critical organs are those which are most sensitive to oxygen lack, notably the brain. A transient stage of central nervous stimulation is followed by central nervous depression and finally hypoxic convulsions and death due to respiratory arrest (Ward and Wheatley, 1947). Cardiac irregularities are commonly observed, but the heart beat invariably outlasts breathing movements (Wexler et al., 1947).

Few poisons are more rapidly lethal than cyanide. The inhalation of hydrogen cyanide commonly produces reactions within a few seconds and death within minutes. With the ingestion of cyanide salts death may be delayed as much as an hour. The prognosis is fairly good if the patient is still alive 1 hour after swallowing a dose of cyanide, but fatal relapses have been described after periods as long as 4 hours. If the stomach is empty and the free gastric acidity is high, poisoning is especially fast. After large doses some victims have had time only for a warning cry before sudden loss of consciousness. Hydrogen cyanide in aqueous solution (hydrocyanic acid) is readily absorbed from the skin (Potten, 1950; Tovo, 1955) and from all mucous membranes (such as the rectum and vagina), but the alkali salts are usually toxic only when ingested. The average lethal dose of HCN taken by mouth is believed to lie between 60 and 90 mg; this corresponds to about 1 teaspoonful of a 2 per cent solution of hydrocyanic acid and to about 200 mg of potassium cyanide (Gettler and St. George, 1934; Gettler and Baine, 1938). Prompt treatment, however, has saved a person who swallowed 6000 mg of KCN (Miller and Troops, 1951) and 3 to 5 g have been survived without specific therapy (Liebowitz and Schwartz, 1948). The lethality of most derivatives is regarded as proportional to the content of readily available cyanide. The mortality rate is high, but in nonfatal cases recovery is generally complete. Rarely neuropsychiatric sequelae are observed, as in carbon monoxide poisoning.

[much information about detoxification mechanisms and clinical treatment omitted]

Symptomatology:

1. Massive doses may produce, without warning, sudden loss of consciousness and prompt death from respiratory arrest. With smaller but still lethal doses, the illness may be prolonged for 1 or more hours.

2. Upon ingestion a bitter, acrid, burning taste is sometimes noted, followed by a feeling of constriction or numbness in the throat. Salivation and nausea are not unusual, but vomiting rarely occurs except after concentrated solutions of sodium and potassium cyanide, which are corrosive because of their high alkalinity. Other symptoms follow in rapid progression.

3. Anxiety, confusion, vertigo, giddiness, and often a sensation of stiffness in the lower jaw.

4. Hyperpnea and dyspnea. Respirations become very rapid and then slow and irregular. Inspiration is characteristically short while expiration is greatly prolonged.

5. The odor of bitter almonds may be noted on the breath or vomitus. This characteristic odor is sometimes a diagnostic help.

6. In the early phases of poisoning, an increase in vasoconstrictor tone causes a rise in blood pressure and reflux slowing of the heart rate. Thereafter the pulse becomes rapid, weak, and sometimes irregular. The victim notes palpitations and a sensation of constriction in the chest.

7. Unconsciousness, followed promptly by violent convulsions, epileptiform or tonic, sometimes local but usually generalized. Opisthotonos and trismus may develop. Involuntary micturition and defecation occur.

8. Paralysis follows the convulsive stage. The skin is covered with sweat. The eyeballs protrude, and the pupils are dilated and unreactive. The mouth is covered with foam, which is sometimes blood-stained. The skin color may be brick-red. Cyanosis is not prominent in spite of weak and irregular gasping.

9. Death from respiratory arrest. As long as the heart beat continues, prompt and vigorous treatment offers some hope of survival.

Treatment (must be prompt):

1. If the patient is apneic, start artificial respiration immediately. Keep the airway clear.

2. Administer by inhalation amyl nitrite (amyl nitrite perles) for 15 to 30 seconds of every minute, while a sodium nitrite solution is being prepared.

3. Discontinue amyl nitrite and immediately inject intravenously 10 mL of a 3 per cent solution of sodium nitrite over a period of 2 to 4 minutes. If necessary, inject a nonsterile solution. Do not remove the needle.

4. Through the same needle infuse intravenously 50 mL of a 25 per cent aqueous solution of sodium thiosulfate. The injection should take about 10 minutes. Other concentrations (5 to 50 per cent) are permissible if the total dose is held at approximately 12 g.

5. Oxygen therapy may be of value in combination with amyl nitrite and sodium thiosulfate therapy, perhaps by speeding detoxification reactions.

6. If symptoms recur, the injections of nitrite and thiosulfate may be repeated at half the above

doses.

7. Because of the speed of absorption and the rapidity with which symptoms appear, gastric lavage is seldom a practical procedure and should be postponed at least until after procedures 1-4. Probably the best lavage fluid is a dilute solution of potassium permanganate (1:5000).

8. Oxygen therapy and a whole blood transfusion may become necessary if nitrite-induced methemoglobinemia become too severe."

III. Production

PROLOGUE

A very dedicated but foolish individual might attempt to produce hydrocyanic acid or hydrogen cyanide by replication of the nineteenth century's methods: heating potassium or sodium carbonate with scrap iron and organic refuse in a small furnace for several hours, extracting and purifying the ferrocyanide by repeated crystalization, and treating the ferrocyanide in one of the ways detailed in part I to yield an alkali cyanide or hydrocyanic acid. This method requires a furnace and a lot of time and labor.

There is a modified method that is slightly more reasonable for amateur production of ferrocyanides. If potassium or sodium hydroxide is substituted for the respective carbonate, a propane torch or small charcoal fire can be substituted for the furnace, since the hydroxides have much lower melting points. Adding copious amounts of dried blood to the molten hydroxide will provide sufficient iron and nitrogen to yield a bountiful crop of ferrocyanide. The ferrocyanide can then either be purified by dissolution, filtration, and recrystalization, or the entire reaction mass (once cool) can be broken up and added to dilute sulfuric acid and heated to distill hydrocyanic acid (again, see part I). There are still problems, though. Molten alkali hydroxides are hazardous to work with. Hydrocyanic acid is very hazardous to work with. The blood meal/hydroxide mixture tends to froth and swell, so that it must be constantly stirred to break up bubbles and fresh blood can be added only slowly. The stench of charring blood will not endear you to friends, family, or neighbors.

A much nicer method for the production of the cyanides is the production of alkali cyanate followed by its reduction to cyanide. This method requires relatively high temperatures but does not need a furnace. All required materials and apparatus can be inexpensively and easily acquired. The writeup that follows produces sodium cyanide, but one would almost surely have equal success starting with potassium compounds to produce potassium cyanide. Parts are estimated by volume in the following writeup. This is generally a terrible method for specifying chemical procedures, since powdered solids can vary considerably in density depending on particle size. However, for this particular procedure we are always going to be using a large excess of certain reactants to force the equilibrium in the direction we desire. Since we are using large excesses of materials to begin with, the imprecision introduced by volume measures should not be a problem, and far more people own measuring spoons than own laboratory balances. I arbitrarily pick "tablespoons" as my standard unit, though any other volume measure, consistently applied, should work equally well.

In chemical terms, cyanic acid (HOCN) or isocyanic acid (HNCO) will be reacted with sodium

carbonate (Na2CO3) to form sodium cyanate (NaOCN), carbon dioxide (CO2), and water (H2O). The water and carbon dioxide escape as gases because the mixture is heated.

heat 2 HOCN + Na2CO3 ----> 2 NaOCN + CO2 + H2O
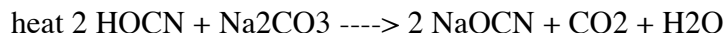
The sodium cyanate will then be reduced with carbon at high temperatures to form sodium cyanide and carbon monoxide. The carbon monoxide gas of course also escapes.

heat NaOCN + C ----> NaCN + CO
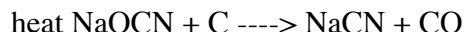
PROCEDURE

Find two medium-sized steel cans (such as used for holding soup, canned vegetables, etc.) They should be sized such that one can be nested inside the other, like thus:

_____ || || || || || || || || || ||_____||

or thus: _____ || || || || | | | | | | | |_____|

The smaller interior can will be used as a disposable crucible for the cyanide production. The larger exterior can will be inverted and set over the top of the smaller can to protect the smaller can's contents from the air during the reduction of the cyanate to cyanide.

Prepare the steel cans for use by heating them hot enough to burn off the label, glue, and any coating on the inside of the can. Wash out the inside of the can once it has cooled, then heat it enough to dry it.

Prepare 3 tablespoons of finely powdered urea or cyanuric acid. These materials are both often obtained as small pellets or fragments. They must be reduced to powder to ensure good contact with the sodium carbonate so that a high yield of sodium cyanate will be obtained. Repeated use of an electric coffee grinder will quickly convert pellets or pieces to powder. A ceramic mortar and pestle is somewhat more tedious but can still produce good results. Slowest of all, one can use the back of a metal spoon and a hard surface (like a ceramic saucer) to crush the urea or cyanuric acid into a fine powder.

Prepare 2 tablespoons of finely crushed charcoal powder. Charcoal briquettes, such as are used for cooking food, are a terrible source of charcoal powder. They contain clay and binders that will lead to a less pure product, plus they are hard to properly pulverize. Activated charcoal is a source of relatively pure carbon and can be used instead of briquettes. Powder it as you did the urea or cyanuric acid (this may require considerable effort).

Prepare a fire for your crucible. This fire must be capable of heating it to a cherry red glow. If your fire is not hot enough, the cyanate will not be converted to cyanide at a reasonable pace. The simplest source of sufficiently intense heat is a charcoal fire built using barbecue briquettes. You can pile the briquettes in an appropriate barbecue, a large coffee can with airholes punched in the side, or in a small pit dug in dry ground. After you have prepared the fire, you can increase its intensity by blowing air on it (with a fan, hairdryer, etc.) or leave it as-is. You may want to start the fire before you perform the other steps since it can take a while for all the charcoal to ignite and

produce good coals.

Fine, dry sodium carbonate can easily be obtained by heating sodium bicarbonate (which itself is usually found as a fine powder) to convert it to the carbonate.

heat 2 NaHCO3 ----> Na2CO3 + CO2 + H2O

Place two tablespoons of sodium hydrogen carbonate into the smaller can. Heat it upon a gas flame, electric burner, or your charcoal fire. The powder may begin to churn and even appear to "bubble" as it expels carbon dioxide and water vapor, if you are able to apply strong heat. Stir the powder with a long-handled metal spoon or stiff piece of steel wire to ensure even and rapid heating of the whole mass. When it ceases to give off gases, withdraw it from heat (with metal tongs or while wearing leather gloves) and let it cool a bit.

If you must, you can use sodium carbonate to begin with instead of sodium hydrogen carbonate. Sodium carbonate is commonly sold as the hydrate and this water should be driven out before it is used to make cyanate. Unless you are sure that the sodium carbonate is already anhydrous, heat and stir it like you would the sodium hydrogen carbonate. If the sodium carbonate is not already a fine powder, powder it as you have the other materials while it is still warm. The anhydrous carbonate will absorb moisture from the air, so do not take too long to complete the operation.

Combine your powdered urea or cyanuric acid with the still-warm sodium carbonate and thoroughly stir the two powders together with a spoon or wire. The urea or cyanuric acid and sodium carbonate should be powdered as finely as possible and well-mixed to ensure that the cyanic/isocyanic acids react before boiling off to the atmosphere and being wasted. Since a large excess of urea/cyanuric acid is employed in this procedure, most of the sodium carbonate should be converted to cyanate even if the powdering/mixing isn't perfect, but you should still try to prepare the materials as well as you can.

Once the materials are mixed, place the can on the charcoal fire. Heap coals up around the sides. The can will begin expelling vapors and haze of unreacted cyanic/isocyanic acid, water, carbon dioxide, ammonium cyanate, ammonia, etc. It isn't terribly hazardous but neither is it a tonic for the lungs; try to keep upwind from it. If the fire is hot enough, after a few minutes the contents of the can should be reduced in volume and completely melted.

Add the powdered charcoal to this melt and stir it in with your spoon/wire. The charcoal may ignite on the surface and take a while to be wetted by the molten cyanate; don't worry. When the charcoal seems to be well-mixed with the melt, invert your larger can over the crucible to form a lid (as illustrated before). Now you will have to wait some time. Depending on the intensity of your fire, somewhere from 30 minutes to 2 hours should suffice to convert the cyanate to cyanide. The lower portion of the can should visibly be glowing after a few minutes. If it isn't, the fire is probably not hot enough. You can check the progress once in a while by removing the covering can with tongs or leather gloves. A burst of flame when the lid is removed indicates that the reaction is still in progress; carbon monoxide produced by the reduction of the cyanate ignites when it is exposed to a fresh source of oxygen. If there is no burst of flame when the cover is removed after a period of cooking, the reduction is complete or almost complete (or your fire is not hot enough!) and the can may be removed from the fire immediately or after just a few more minutes.

Do not remove the covering too often. Its job is to keep carbon dioxide from the fire away from the cyanide being formed inside the can. Excessive exposure to carbon dioxide may convert a considerable portion of the cyanide to carbonate, rendering your hard work useless.

After the reaction appears to be complete, remove the can from the fire and wait for it to cool enough to be touched with bare hands. Then remove the covering. You want to extract the hard mass of leftover charcoal powder and cyanide from the bottom of the can. You may be able to smash it free with a hammer or rock. It is easier to cut and tear the can open with a pair of pliers and heavy scissors or tin snips. Perform all of this over a sheet of newspaper to catch the fragments that fall as you work. The can's metal may be very hard and brittle from oxidation and exposure to hot cyanide. When you have finally extracted the black lumpy mass out of the bottom of the can, smash or crush it enough that you can fit it all in an empty glass or plastic jar with a lid. Be sure to wash your hands after you've finished handling the cyanide-containing mass. You may also want to decontaminate the pieces of your crucible before you dispose of them in the regular trash (see section V).

Add enough warm water to completely cover the cyanide/charcoal mixture now sitting in the jar. If everything went well and you are one of those people who is able to smell cyanide, you should be able to catch a peculiar odor from the jar at this point. If you smell an odor like rotten eggs, a sulfur impurity was introduced into your mix at some point and has produced some sodium sulfide. Put the lid on the jar to protect the cyanide solution from carbon dioxide in the air. Periodically swirl or shake the water in the jar over the next few hours. The longer you wait and the finer the charcoal was, the better the cyanide will leach into the water. If the charcoal was not powdered very finely, much of the cyanide will remain trapped inside of it. 2-3 hours of standing combined with periodic swirling/shaking should do, although you may wait longer.

Take a plastic kitchen or automotive funnel and fold a paper towel or coffee filter into a cone inside of it. Sprinkle a little water on the filter so that it sticks to the inside of the funnel. This will be used to filter the unreacted charcoal powder out of your sodium cyanide solution. The finer charcoal particles will not be trapped by paper towels or coffee filters. If you want to remove all traces of charcoal, place a layer of diatomaceous earth about as thick as your thumb in the filter; this will catch even the finest bits. Place the funnel/filter in the mouth of a second glass or plastic jar, then slowly pour the water/cyanide/charcoal mixture into it. You want all the liquid to pass through the filter, not to overflow the funnel or to slip down the sides past the filtration materials. It may take several minutes for the liquid to pass through depending on how badly the charcoal clogs the filter.

When all of the liquid has been filtered, pour the clear sodium cyanide solution into a shallow glass baking dish. Set it on a hotplate or electric stove burner and evaporate it at low heat. Too much heat may hydrolyze the solution, forming sodium formate and ammonia. Too little heat will give the solution too much time to be exposed to the air, which contains carbon dioxide and will slowly convert it back to sodium carbonate while liberating hydrogen cyanide. If the hot solution smells mildly of ammonia, don't worry. If it smells strongly of ammonia, the conversion of cyanate to cyanide probably wasn't complete. It needed more time or more heat in the fire.

When the sodium cyanide is nearing dryness it will form a sort of damp slush that can be scraped up with the edge of a credit card or similar implement. Do so, otherwise it may be hard to remove from the pan when completely dry. Periodically stir and crush the slush as it dries until it appears to

be mostly or completely free of water. You now have solid sodium cyanide of an unknown degree of purity. Store it in a sealed glass or plastic bottle, sealed away from the air.

IV. Analysis

PROLOGUE

There are probably hundreds of qualitative and quantitative tests for cyanides. One of the oldest, simplest, and best qualitative tests is the Prussian blue test. This test combines the unknown with a mixture of iron (II) and iron (III) salts in acidic media. The formation of a blue solution or precipitate indicates the presence of cyanide. Consult an older book of analytical chemistry if you are interested in quantitative determination of cyanide by amateur-accessible methods.

PROCEDURE

First prepare a solution of iron (II) sulfate. This can be conveniently accomplished by adding an excess of fine steel wool to dilute sulfuric acid or copper sulfate solution. The reaction with copper sulfate completes faster and it is usually easier to obtain copper sulfate than sulfuric acid.

Dissolve a tablespoon of copper sulfate crystals in a cup of hot water inside a glass or plastic jar. Shake/swirl the jar until the crystals dissolve. Add fine steel wool to the solution. It may take a while for the reaction to start, since steel wool is often lightly coated with oil to retard rusting. Prodding and swirling the wool with a glass, plastic, or wooden rod may help to start the reaction. The wool will turn copper-red as iron (II) sulfate is formed in the solution and metallic copper deposits in place of the iron in the steel wool. When fresh steel wool added to the jar no longer obtains a copper coating, the reaction is complete. You can use dilute sulfuric acid in place of copper sulfate solution. The reaction is complete when steel wool added to the liquid no longer forms bubbles of hydrogen. Heating the liquid will cause the reaction to complete faster, but be careful to keep the hydrogen-producing reaction away from ignition sources.

Filter the pale dirty-green liquid through a paper towel or coffee filter and store the clarified fluid in an airtight jar. Iron (II) sulfate is easily oxidized to iron (III) sulfate by atmospheric oxygen, which is why it can be used in the Prussian blue test and why it needs to be protected from air when not in use. As the liquid oxidizes it will form an orange scum and the liquid will darken. Eventually it may become too dirty to use and will need to be replaced by a fresh batch.

To perform the test, place a small amount of your iron (II) sulfate solution in a small jar. Add a few drops of sulfuric or hydrochloric acid (you may try a small amount of vinegar if you cannot get sulfuric or hydrochloric acid). Add a few drops or small pieces of the liquid or solid that you wish to test for cyanide. Do not use a large sample; dangerous amounts of hydrogen cyanide could be released. There may not be an immediate reaction even if cyanide is present. Swirl and shake the jar to expose the liquid to the air. If cyanide is present, the liquid should take on a beautiful blue tinge after a while and may even precipitate deep-blue material. This is the Prussian blue, the dye that started the ball rolling with artificial cyanides in 1704. As some of the iron (II) sulfate is oxidized by air to the iron (III) state, the acidified mixture of iron (II) and (III) ions interacts with cyanide to form this characteristic coloration. If the test for cyanide is positive, you may wish to dispose of the test liquid as described in section V.

V. Disposal

It is not a good idea to just flush cyanides down the sink or toilet, or to throw them in the trash. They should first be converted to non-poisonous compounds. Sodium hypochlorite solution (household chlorine bleach) does an admirable job. The hypochlorite oxidizes cyanide to harmless cyanate, which can then be disposed of like other household waste.

Hydrocyanic acid solutions should be converted to cyanide salts before they are oxidized, so that the heat of oxidation does not cause free hydrogen cyanide to volatilize. Add the hydrocyanic acid to an excess of sodium or potassium hydroxide solution before oxidizing it. The solid or dissolved cyanide should be poured into an excess of household bleach. The reaction may be fairly vigorous and generate considerable heat. The liquid that remains is no more dangerous than ordinary bleach. You may decontaminate jars, funnels, and leftover filtered materials the same way. If the charcoal used for the cyanate reduction had large coarse pieces in it, they may retain cyanide on the interior even after being treated with bleach.

VI. Materials

Most of the materials that I have referenced can be obtained in ordinary retail establishments, at least in the United States.

ACETIC ACID: Ordinary distilled white vinegar is a dilute solution of acetic acid. More concentrated acetic acid is used to make up "stop bath" in photography; photo suppliers should carry or be able to order it.

ACTIVATED CHARCOAL: Often used to filter water in fish tanks. It can be purchased from pet stores.

CITRIC ACID: This acid is found in citrus fruits and juices (like lemon juice). It can also be purchased in pure form from some health food stores, grocery stores, and pharmacies.

COPPER SULFATE: Often sold as "root killer," sometimes as a fungicide. Found in hardware or agricultural stores. Also found in some pharmacies.

CYANURIC ACID: Used to protect swimming pool chlorine from photodegradation. Look for "pool chlorine stabilizer" in hardware and pool/spa supply stores.

DIATOMACEOUS EARTH: Sometimes used in gardening, also used to filter swimming pool water. Look at hardware stores, pool/spa suppliers, and gardening centers.

DRIED BLOOD: "Blood meal" is dried blood collected from slaughterhouse animals. It is often sold in gardening centers as an organic fertilizer.

HYDROCHLORIC ACID: Also called "muriatic acid" or sometimes "spirits of salt." It is often found in pool, hardware, and paint stores. It is used to clean brickwork and adjust swimming pool acidity among other things.

POTASSIUM CARBONATE: Can be purchased from ceramics/pottery suppliers. Also can be obtained by heating potassium hydrogen tartrate until it is completely charred, then crushing the

mass of charcoal, extracting with water, and filtering to produce potassium carbonate solution and dried to obtain the solid.

POTASSIUM FERRICYANIDE: This material is sometimes used in photography and for making blueprints. A few online photo supply outfits sell it. I *believe* that it behaves very similarly to potassium ferrocyanide, but I have not personally investigated its properties.

POTASSIUM FERROCYANIDE: This has little use outside of the laboratory. However, it is fairly harmless and can be purchased without difficulty from chemical suppliers who deal with individuals.

POTASSIUM HYDROGEN TARTRATE: Sold in grocery stores as "cream of tartar."

POTASSIUM HYDROXIDE: Used in soapmaking; sometimes found in craft stores or can be ordered online from outlets specializing in soap/candle manufacturers. Also sometimes found in hardware stores.

SODIUM CARBONATE: Sold as "washing soda" in some grocery stores (look near the cleaning products). Also can be purchased from ceramics/pottery suppliers.

SODIUM HYDROGEN CARBONATE: Also called baking soda, sold in grocery stores.

SODIUM HYDROXIDE: Sold as "lye," used for opening drains and making soap. Often found in hardware stores and in grocery stores among the cleaning products.

STEEL WOOL: Fine fibers of steel used for polishing and cleaning. Found in hardware and paint stores.

SULFURIC ACID: Sometimes found in dilute form for adjusting swimming pool acidity. Also found in more concentrated (but still dilute) form as replacement electrolyte for lead/acid storage batteries. Found in concentrated form in professional drain opener liquids from hardware/plumbing stores.

UREA: Found at agricultural suppliers as fertilizer. It is easy to find a 50 pound sack at a dedicated farm-oriented outfit but harder to find in small quantities or in ordinary urban/suburban gardening centers. Some instant chemical cold packs (such as you might use on a sprained ankle) contain urea. Consult the package and/or manufacturer website to find out if a particular brand uses urea or ammonium nitrate. When you find one that uses urea, you can cut the cover open to retrieve the urea pellets without bursting the water pouch.

VII. References

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[2] Muspratt, James Sheridan. Chemistry: Theoretical, Practical, and Analytical as Applied and Relating to the Arts and Manufactures - Volume 2. London, 1860.

[3] Gleason MN, Gosselin RE, Hodge HC, Smith RP [1969]. Clinical Toxicology of Commercial Products. 3rd ed. Baltimore, MD: Williams & Wilkins Company.