

# Laboratory Safety in Metallography

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## Chemicals, Storage, and Handling

Many of the chemicals used in metallography are toxic, corrosive, flammable, or potentially explosive. Therefore, purchase only small quantities that are likely to be used within a reasonably short time. Flammable solvents should be stored in fireproof steel cabinets. Acids and bases should be stored separately, again in fireproof steel cabinets. Strong oxidants must not be stored along with acids, bases, or flammable solvents.

Reagent-grade chemicals or solvents of highest purity are recommended. Although more expensive, the amounts used are small, and the gain in safety and reliability compensates for the cost difference. Chemicals may deteriorate during storage; only reasonably small quantities should be purchased. Exposure to light can accelerate deterioration of some chemicals. Hence, they should be stored in a closed metal cabinet.

Etchants. Most laboratories mix commonly used reagents in quantities of 250 to 1000 mL and then store them as stock reagents. Many reagents can be safely handled in this manner. It is best to store only those reagents that are used regularly. Glass-stoppered bottles are commonly used as stock reagent bottles. If these bottles are opened regularly, the stopper will not become “frozen.” However, if they are used infrequently, a frozen stopper often results. Holding the neck of the bottle under a stream of hot water will usually loosen the stopper. If thermal expansion does not free the stopper, it can be gently tapped with a piece of wood. Glass bottles with plastic screw-on tops can be used so long as the solution does not attack the plastic. These bottles are useful for holding solutions, such as nital, that can build up gas pressure within a tightly stoppered bottle. A small hole can be drilled through the cap top to serve as a pressure relief vent. Tightly stoppered bottles of nital and some other solutions have exploded as the result of pressure buildup. Be certain that the reagent is safe to store, and store only small quantities. All bottles should be clearly labeled. Polyethylene bottles are required for etchants containing hydrofluoric acid, which attacks glass.

Most recipes for etchants or electrolytes list the ingredients by weight if they are solids and by volume if they are liquids. In a few cases, all amounts are given in weight percentages. In most cases, reagent compositions are not extremely critical. An ordinary laboratory balance provides adequate weighing accuracy, while graduated cylinders provide acceptable accuracy for volumetric measurements. These devices should be cleaned after use to prevent accidents to the next user. For weight measurements, a clean piece of filter paper or a cup should be placed on the balance pan to hold the chemical, to protect the pan surface, and to facilitate transfer to the mixing beaker. A large graduated beaker is usually employed for mixing solutions. When using hydrofluoric acid, all containers should be made of polyethylene.

With many etchants, the mixing order is important, especially when dangerous chemicals are used. When water is specified, distilled water should always be used, because most tap water contains minerals or may be chlorinated or fluorinated. Tap water can produce poor results or unexpected problems. Cold water should always be used, never warm or hot water, which can cause a reaction to become violent. In mixing, one should start with the solvents, such as water and alcohol, then dissolve the specified salts. A magnetic stirring device ([Fig. 1](#)) is of great value. Then, the dangerous chemicals, such as acids, should be added carefully and slowly while the solution is being stirred. Whenever sulfuric acid ( $H_2SO_4$ ) is specified, it should be added last. It should be added slowly, while stirring, and it should be cooled, if necessary, to minimize heating. Never just pour one liquid into another ([Fig. 2](#)). If sulfuric acid is added to water without stirring, it can collect at the bottom of the beaker, and enough local heating can occur to throw the contents out of the beaker.



**Fig. 1 Magnetic stirring plate with a magnetic bar for stirring, for use when mixing etchants. Slowly add the liquid ingredients to the solvent by dripping them down a glass stirring rod. If the solution is more dangerous than this one, wear protective gloves and use a face shield. If mixing generates substantial heat, it is a good practice to place a cooling jacket around the beaker.**



**Fig. 2 Illustration of a bad mixing practice. The acid ingredient was poured into an empty acid bottle, and the solvents were added without stirring or cooling. The solution may erupt in the metallographer's face at any moment. It is essential to use gloves on at all times when handling chemicals. Consult the reference guide for the appropriate gloves for a given chemical, for example Nitrile are excellent for HCl and most other acids and solvents. However, if dealing with concentrated HNO<sub>3</sub>, and H<sub>2</sub>SO<sub>4</sub> then nitrile provide little to no resistance and PVC (vinyl) gloves are recommended.**

The literature contains references to a great many formulas for etchants, chemical polishes, and electrolytes that are potentially dangerous or extremely dangerous. Few of these references contain comments regarding safe handling procedures or potential hazards. Fortunately, metallographic applications involve small quantities of these solutions, and accidents do not usually produce catastrophic results. However, even with small solution volumes, considerable damage can be, and has been, done. [Table 3](#) lists examples from the literature ([Ref 2, 3, 4](#)) of chemical polishing solutions, electrolytic polishing solutions, and etchants that have been involved in accidents. [Table 4](#) lists a number of commonly used chemicals and incompatible chemicals.

**Table 3 Chemical and electrolytic polishing solutions and etchants known to be dangerous**

Solution	Use	Problems
5 parts lactic acid 5 parts HNO <sub>3</sub> 2 parts water	Chemical polishing solution for Zr	Lactic and nitric acids react autocatalytically. Explosion will occur if stored.

<b>Solution</b>	<b>Use</b>	<b>Problems</b>
1 part HF		
50 parts lactic acid 30 parts HNO <sub>3</sub> 2 parts HF	Chemical polishing solution for Ta, Nb, and alloys	Same as above
3 parts perchloric acid 1 part acetic anhydride	Electropolishing solution for Al	Mixture is unstable and can, and has, exploded with heating or in the presence of organic compounds, adding to the potential hazard.
60–90 parts perchloric acid 40–10 parts butyl cellosolve	Electropolishing solution	Solution will explode at room temperature. Solutions with ≤30% HClO <sub>4</sub> will be safe if temperature is <20 °C (70 °F).
100 g CrO <sub>3</sub> 200 mL water 700 mL acetic anhydride	Electropolishing solution	CrO <sub>3</sub> was dissolved in water, cooled to approximately 20 °C (70 °F), and the acetic anhydride was added very slowly with stirring. The solution became warm to the touch. Approximately 20 s later, it erupted from the beaker.
1 part HNO <sub>3</sub> 2 parts methanol	Electropolishing solution for Muntz (Cu-40%Zn) metal	Mixture is unstable and cannot be stored.
20 mL HF 10 mL HNO <sub>3</sub> 30 mL glycerol	Etchant for Nb, Ta, Ti, V, Zr	This etchant is unstable. At 20 °C (70 °F), it reacted after 18 h. At 30–35 °C (85–95 °F), it reacted with violence after 8 h. At 100 °C (212 °F), it will react after 1 min.
20–30 mL HCl	Etchant for Ni and stainless steels	Incidents occurred where a violent reaction resulted, producing NO <sub>2</sub> and a spray of acid after the etch was left standing for 2–3 h.

<b>Solution</b>	<b>Use</b>	<b>Problems</b>
10 mL HNO <sub>3</sub> 30 mL glycerol		
40 mL acetic acid 40 mL acetone 40 mL HNO <sub>3</sub>	Etchant for Ni	A closed bottle exploded approximately 4 h after it was mixed. Solutions without the acetic acid also cannot be stored.
10 mL HNO <sub>3</sub> 10 mL acetic acid 20 mL acetone	Etchant	The solution reacted spontaneously approximately 2 min after mixing, with evolution of heat and fumes (nitrous and nitric oxides). The mixed acids were poured into the acetone. The beaker was externally cooled.
50 mL nitric acid 950 mL isopropyl alcohol	Etchant	Mixtures have exploded violently after mixing or approximately 20 min after mixing.

**Table 4 Some incompatible chemicals**

<b>Chemical</b>	<b>Use in metallography</b>	<b>Do not mix with the following</b>
Acetic acid	Chemical polishing, electrolytic polishing	Chromic acid, glycol, hydroxol compounds, nitric acid, peroxides, permanganates
Acetone	Degreasing, cleaning, etchants	Concentrated solutions of nitric and sulfuric acids
Chromic acid	Electropolishing	Acetic acid, flammable liquids, glycerol
Hydrogen peroxide	Chemical polishing, etchants	Flammable liquids, organic materials
Nitric acid (conc.)	Chemical polishing, etchants	Acetic acid, chromic acid, flammable liquids, isopropyl alcohol
Perchloric acid	Electropolishing	Acetic anhydride, alcohol, some organics, oil, grease
Sulfuric acid	Etchants	Methyl alcohol, potassium chlorate, potassium perchlorate, and potassium permanganate

Solvents. Numerous organic solvents are used for cleaning or are ingredients in chemical or electrolytic polishing solutions or etchants, in which they are used to control ionization or the speed and mode of attack. Commonly employed solvents include water, acetone, ethyl ether, ethylene glycol, glycerol (glycerin), kerosene, petroleum ether, trichloroethylene, butyl cellosolve, and alcohols, such as amyl alcohol, ethanol, methanol, and isopropyl alcohol. Most are flammable, and their vapors can form explosive mixtures with air. They should be kept closed when not in use and should be stored in a cool place away from heat and open flames.

Acetone ( $\text{CH}_3\text{COCH}_3$ ) is a colorless liquid with a fragrant, mintlike odor. It is volatile and highly flammable. It is an irritant to the eyes and the mucous membranes. Its vapor is denser than air, can travel along the ground, and can be ignited at a distance. Acetone can form explosive peroxides on contact with strong oxidizers, such as acetic acid, nitric acid, and hydrogen peroxide. It is an irritant to the eyes and respiratory tract and will cause the skin to dry and crack. Butyl cellosolve ( $\text{HOCH}_2\text{CH}_2\text{OC}_4\text{H}_9$ ), or ethylene glycol monobutyl ether, is a colorless liquid with a rancid odor that is used in electropolishing solutions. It is combustible and may form explosive peroxides. It is toxic in contact with the skin, can be absorbed through the skin, and can cause serious damage to the eyes and irritation to the skin and respiratory tract.

Carbitol ( $\text{C}_2\text{H}_5\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$ ), or diethylene glycol monoethyl ether, is a colorless, viscous solvent that is compatible with water and is used in electropolishing solutions. It irritates the skin, eyes, mucous membranes, and upper respiratory tract and is harmful if inhaled or swallowed.

Ethylene glycol ( $\text{HOCH}_2\text{CH}_2\text{OH}$ ) is a colorless, hygroscopic liquid with a sweet taste (but do not swallow, because it is poisonous) that reacts with strong oxidants and strong bases. It is slightly flammable. The substance irritates the eyes, skin, and respiratory tract.

Glycerol (glycerin) ( $\text{CH}_2\text{OHCHOHCH}_2\text{OH}$ ) is a colorless or pale yellow, odorless, hygroscopic, syrupy liquid with a sweet, warm taste. It is relatively nontoxic and nonvolatile but can cause iritis (inflammation of the iris). It is combustible and a moderate fire hazard. Glycerol should never be used in anhydrous solutions containing nitric and sulfuric acids, because nitroglycerin can form. Glycerol should not be used with strong oxidizing agents, such as chromium trioxide and potassium permanganate, because an explosion may occur. Glycerol is often added to aqua regia (glyceregia). This mixture decomposes readily and should be discarded immediately after use. This etchant should not be allowed to stand for more than approximately 15 min after mixing.

Kerosene is occasionally employed in grinding samples and with diamond paste as a lubricant. Only the deodorized form should be used. It is flammable, but the vapors do not readily explode. Contact defatens the skin and can cause dermatitis, irritation, or infections.

Trichloroethylene ( $\text{CHCl:CCl}_2$ ) is a stable, colorless liquid with a chloroform-like odor. Effective laboratory ventilation is necessary. At ambient temperatures, it is nonflammable and nonexplosive but becomes hazardous at higher temperatures. In the presence of strong alkalis, with which it can react, it can form explosive mixtures. In the presence of moisture, the substance can be decomposed by light to corrosive hydrochloric acid. It is probably carcinogenic to humans and is toxic when inhaled or ingested, which may cause acute poisoning.

Amyl alcohol ( $\text{CH}_3(\text{CH}_2)_4\text{OH}$ ), or 1-pentanol, is a colorless liquid with a noxious odor. It is flammable, and the vapors may form explosive mixtures at elevated temperatures. The substance reacts violently with strong oxidants and attacks alkaline metals. The fumes are irritating to the eyes, upper respiratory tract, and skin. The substance is toxic through ingestion, inhalation, or absorption through the skin.

Ethyl alcohol ( $\text{CH}_3\text{CH}_2\text{OH}$ ), or ethanol, is a colorless, inoffensive solvent commonly used in metallography. Ethanol is miscible with water and rapidly absorbs up to 5% water from the air. The denatured version is less expensive, contains 5% absolute methanol, and is suitable for any recipe requiring ethyl alcohol. It is a dangerous fire hazard, and its vapors are irritating to the eyes and upper respiratory tract. High concentrations of its vapor can produce intoxication. Because ethanol is completely burned in the body, it is not a cumulative poison like methanol. Methyl alcohol ( $\text{CH}_3\text{OH}$ ) is an excellent, nonhygroscopic solvent, but it is a cumulative poison. Ingestion, inhalation, or absorption through the skin in toxic levels can damage the central nervous system, kidneys, liver, heart, and other organs. Blindness has resulted from severe poisoning. It is particularly dangerous because repeated low-level exposures can also cause acute poisoning as a result of accumulation. Thus, whenever possible, ethanol should be used. When using methanol, always work under a ventilation hood. Mixtures of methanol and sulfuric acid can form dimethyl sulfate, which is extremely toxic. Solutions of methanol and nitric acid are more stable than mixtures of nitric acid and higher alcohols.

Isopropyl alcohol [ $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$ ], also known as 2-propanol, is a clear, colorless liquid that, like ethanol, does not accumulate in the body, although it does have a strong narcotic effect. It is a flammable liquid and a dangerous fire hazard. Metallographers have used it as a substitute for ethanol, but isopropyl alcohol has quite different characteristics and should not be used. Fatal injuries and explosions have been reported due to its use.

Acids. Inorganic and organic acids are common constituents in chemical and electrolytic polishing solutions and in etchants. The inorganic or mineral acids, including the very familiar acids such as hydrochloric, nitric, perchloric, phosphoric, and sulfuric, are highly corrosive and poisonous. They should be stored in a cool, well-ventilated location away from potential fire hazards and, of course, away from open flames. They should not be stored in a location that receives direct sunlight. When the pure acids contact metals, most liberate hydrogen gas—a fire and explosion hazard. The organic acids are naturally occurring substances in sour milk, fruits, and plants and include the following acids: acetic, lactic, citric, oxalic, and tartaric.

Hydrochloric acid ( $\text{HCl}$ ), commonly used in metallography, is a colorless gas or fuming liquid with a sharp, choking odor. It is very dangerous to the eyes and irritating to the nose and throat. It attacks the skin strongly, causing severe burns.

Nitric acid ( $\text{HNO}_3$ ), also commonly used in metallography, is a colorless or yellowish fuming liquid, highly toxic, and dangerous to the eyes. If it contacts organic material or other easily oxidizable materials, it can cause fires and possibly explosions. When it reacts with other materials, toxic oxides of nitrogen are produced. The oxides, which vary with the conditions, include nitrous acid, nitrogen dioxide, nitric oxide, nitrous oxide, and hydroxylamine. A commonly encountered problem involves pouring nitric acid into a graduated cylinder that contains some methanol or ethanol from prior use. The brown fumes given off are quite harmful. Mixtures of nitric acid and alcohols higher than ethanol should not be stored. Mixtures of concentrated nitric and sulfuric acids are extremely dangerous, while strong mixtures of nitric acid and glycerin or glycols can be explosive. Aqua regia, a mixture of one part nitric acid and two to four parts hydrochloric acid, forms several products, including nitrosyl chloride, an exceptionally toxic gas. Aqua regia is a popular etchant but must be used with care under a hood. Ethanol with additions of up to 3% nitric acid (nital) can be safely mixed and stored in small quantities. Higher concentrations result in pressure buildup in tightly stoppered bottles. Explosions of 5% nitric acid in ethanol have occurred as a result of failure to relieve the pressure. If higher concentrations are desired, they can be mixed daily, placed in an open dish, and used

safely. Discard the etchant at the end of the day. Mixtures of methanol with up to 5% nitric acid are safe to use and store in small quantities. Mixtures of methanol with more than 5% nitric acid are subject to violent decomposition if heated. Mixtures of 33% nitric acid in methanol have decomposed suddenly and violently.

Never add nitric acid to isopropyl alcohol. Anderson ([Ref 2](#)) reported that a liter bottle of 5% nitric acid in isopropyl alcohol was mixed and placed in a cabinet. Although this had been done many times in the past without problems, 20 min later, the bottle exploded, destroying the cabinet, other stored bottles, and throwing debris up to 6 m (20 ft) away. Anderson ([Ref 2](#)) also reported that a metallographer was pouring a freshly mixed liter of 5% nitric acid in isopropyl alcohol into another bottle when it exploded. The person died within 3 h without being able to tell anyone what happened. As with the other explosion, this same procedure had been performed many times previously without mishap. Anderson recommends avoiding the use of isopropyl alcohol completely.

Most metallographers consider nital to be very safe to use, and indeed it is. However, even with such an apparently safe solution, one can have accidents. One such accident occurred when an employee, not a skilled metallographer, was replenishing a stock of 5% nitric acid in ethanol using a procedure that he had claimed to have performed many times previously (he was not taught the safe way to mix nital, because it was a union chemist's job to mix nital, i.e., not his job). The worker began by adding the desired volume of concentrated nitric acid into the container that contained a small residual amount of stale 5% nital. To his surprise, the contents began boiling and spewing out of the container, along with dense, brown fumes. The acid splashed the worker, resulting in burns on his forehead, face, and eyes. The small amount of aged nitric acid solution (the concentration may have been increased due to evaporation of the alcohol), present in the container when the fresh acid was added, created a dangerous chemical reaction. An experiment also showed that a similar reaction can occur when nitric acid is poured into a graduated cylinder containing only remnants of ethanol or methanol. If the employee had added alcohol to the container first, the accident would have been avoided.

Sulfuric acid ( $H_2SO_4$ ) is a colorless, oily liquid that is highly corrosive, a strong oxidizing agent, and dangerously reactive. It reacts violently with bases and is corrosive to most metals, forming flammable/explosive hydrogen gas. It reacts violently with water and organic materials, with the evolution of heat. Upon heating, toxic sulfur oxides are formed. One should add sulfuric acid very slowly to water, with constant stirring. If added without stirring, it will produce a pocket of steam in the bottom of the vessel, throwing the contents out of the vessel. Concentrated sulfuric acid can cause severe, deep burns on contact with the skin, and permanent vision loss on contact with the eyes. Tissue is destroyed by the dehydrating action of the acid. Lungs may be affected by long-term or chronic exposure to its aerosol. Skin lesions, tooth erosion, and conjunctivitis are other long-term effects.

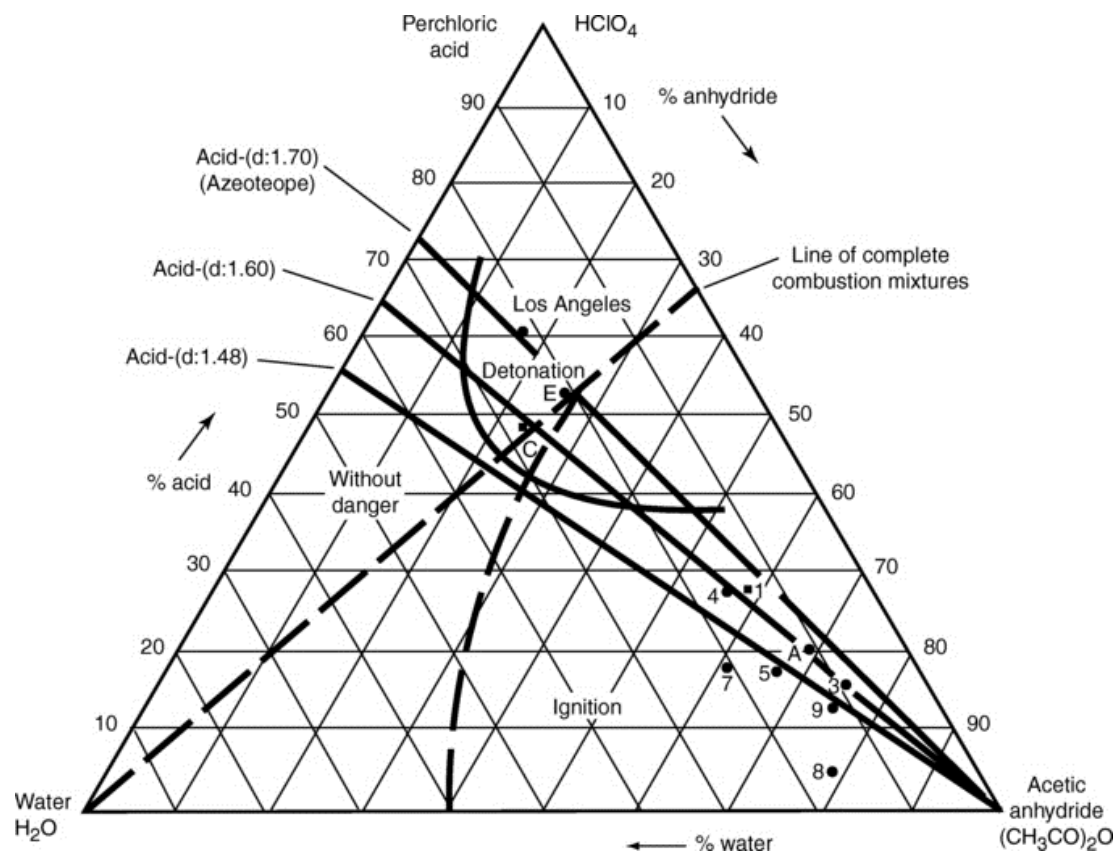
Hydrofluoric acid (HF) is a clear, colorless, fuming liquid or gas with a sharp, penetrating odor. It is very dangerous to the eyes, skin, and upper respiratory tract. The substance can be absorbed into the body by inhalation, through the skin, and by ingestion. A harmful concentration of the gas in air can be reached quickly, making it very dangerous to handle. Exposure by ingestion, inhalation, or contact can be fatal. Undissociated HF poses a unique threat in that it can destroy soft tissues and result in decalcification of the bone. Moreover, the effects may be delayed. Laboratories where HF is used should stock an antidote kit to be used in case of exposure. Although it is a relatively weak mineral acid, HF will attack glass or silicon compounds and should be measured, mixed, and stored in polyethylene vessels (see the section "Safety



Precautions for Concentrated HF” in this article). Hydrofluoric acid reacts with many compounds, including metals, and will liberate explosive hydrogen gas.

Orthophosphoric acid ( $\text{H}_3\text{PO}_4$ ), a colorless, thick liquid or hygroscopic crystal, is a medium-strong acid. It is corrosive to the skin, eyes, and respiratory tract. Phosphoric acid decomposes on contact with alcohols, aldehydes, cyanides, sulfides, ketones, and can react with halogenated organic compounds, forming organophosphorus nerve-gas-type compounds that are extremely toxic. It reacts violently with bases and will generate hydrogen gas when it reacts with metals. Perchloric acid ( $\text{HClO}_4$ ) is a colorless, fuming, hygroscopic liquid. It is extremely unstable in concentrated form and may explode by shock or concussion when dry or drying, so commercially available perchloric acids come in concentrations of 65 to 72%. In this form, contact with perchloric acid will cause irritation and burns, while its fumes are highly irritating to the mucous membranes. Contact with organic or other easily oxidized material can form highly unstable perchlorates, which can ignite and cause explosions. Regular use of perchloric acid requires that the ventilation system must be specifically designed and maintained for perchloric acid. Special fume hoods with a waterfall-type fume washer will remove the perchlorate fumes before they can enter the exhaust system.

Perchloric acid is very useful in electropolishing solutions. However, never electropolish samples mounted in phenolic (Bakelite, Georgia-Pacific) or other plastics with perchloric acid solutions, because explosions can result. The mixture of perchloric acid and acetic anhydride, which was developed by P.A. Jacquet, is difficult to prepare and highly explosive. Jacquet has reviewed the accidents involving perchloric acid and has described safety procedures ([Ref 5](#)). The worst accident occurred on February 20, 1947, in an electroplating factory in Los Angeles. In this accident, 17 people were killed and 150 were injured ([Ref 4](#)). Médard, Jacquet, and Sartorius have prepared a ternary diagram showing safe compositions of perchloric acid, acetic anhydride, and water ([Fig. 3](#)). Anderson, however, states that accidents have still occurred with solutions in the “safe” region of this diagram ([Ref 2](#)). Thus, electropolishing solutions composed of perchloric acid and acetic anhydride are not recommended. Indeed, many companies forbid the use of such mixtures, and some cities have banned their use. Electropolishing solutions of perchloric acid and alcohol, with or without organic additions, and mixtures of perchloric acid and glacial acetic acid are safe to use. Nevertheless, in using these “safe” mixtures, one should follow the formula instructions carefully, mix only small quantities, keep the temperature under control, and avoid evaporation. These solutions should not be stored.



**Fig. 3** Diagram developed by Médard, Jacquet, and Sartorius showing safe (A and 1 to 9) nonexplosive electropolishing solutions and explosive (C, E, and Los Angeles) compositions of perchloric acid, acetic anhydride, and water (brought in by the perchloric acid but not corrected for the effect of acetic anhydride). The Los Angeles accident occurred in an electroplating factory on February 20, 1947 (Ref 4).

Mixtures of acetic acid and 5 to 10% perchloric acid have been commonly used to electropolish iron-base alloys and are reasonably safe. Do not use these solutions to electropolish bismuth, arsenic, or tin, because explosions have occurred. Anderson suggests that arsenic, antimony, and tin may also be incompatible with perchloric electrolytes (Ref 2). Do not store these electrolytes for more than a few days. Discard them when they become colored by dissolved metallic ions (from electropolishing). Always keep these solutions cool; increasing the temperature increases the oxidizing power of perchloric acid.

Comas et al. have studied the hazards associated with mixtures consisting of butyl cellosolve and from 10 to 95% of 70% perchloric acid (Ref 6). Mixtures with 60 to 90% acid were explosive at room temperature. Acid concentrations of 30% or less were inflammable but were judged to be safe to use as long as the operating temperature does not exceed 20 °C (70 °F).

Acetic acid (CH<sub>3</sub>COOH) is a clear, colorless liquid with a pungent odor. It is a weak acid that reacts with strong oxidizers, bases, and metals. It is flammable and not easily ignited, although when heated, it releases vapors that can be ignited and can travel some distance to an ignition source. Contact with the skin results in serious burns. Inhalation of the fumes irritates the mucous membranes. Anderson states that acetic acid is a good solvent for nitric acid, and that a

50% solution can be prepared, but not stored, without danger ([Ref 2](#)). Lewis and Sax, however, state that mixtures of nitric and acetic acids are dangerous ([Ref 7](#)).

Acetic anhydride  $[(\text{CH}_3\text{CO})_2\text{O}]$ , or acetic oxide, is a colorless liquid with a very strong acetic odor. It can cause irritation and severe burns to the skin and eyes. Acetic anhydride decomposes on heating, producing toxic fumes. It reacts violently with boiling water, steam, strong oxidants (specifically, sulfuric acid), alcohols, amines, strong bases, and others. It attacks metals and is very corrosive, especially in the presence of water or moisture. It is extremely flammable and should be avoided. The electrolytic polishing mixtures of acetic anhydride and perchloric acid (4:1 to 2:1 mixtures) developed by Jacquet, as mentioned previously, are exceptionally dangerous and should never be used. Dawkins ([Ref 8](#)) reported an accident involving a mixture of chromium trioxide and acetic anhydride that had been used for electropolishing ([Table 3](#)).

Citric acid  $[\text{C}_3\text{H}_4(\text{OH})(\text{COOH})_3 \cdot \text{H}_2\text{O}]$  comes as colorless, odorless crystals that are water soluble. It is an irritant to the skin, eyes, and respiratory tract, and no unusual problems are encountered except for occasional allergic reactions.

Lactic acid  $(\text{CH}_3\text{CHOHCOOH})$  is a yellow or colorless, thick liquid. It is damaging to the eyes. Oxalic acid  $(\text{COOHCOOH} \cdot 2\text{H}_2\text{O})$  comes as transparent, colorless crystals. It is poisonous if ingested and is irritating to the upper respiratory tract and digestive system if inhaled. Skin contact produces caustic action and will discolor and embrittle the fingernails. It is not compatible with nitric acid, because it reacts violently with strong oxidants. It can also form explosive compounds due to reactions with silver.

Picric acid  $[(\text{NO}_2)_3\text{C}_6\text{H}_2\text{OH}]$ , or 2,4,6-trinitrophenol, comes as yellow crystals that are wet with 10 to 350% water. When picric acid is dry, it is a dangerous explosive. It is toxic and stains the skin. It is incompatible with all oxidizable substances. Picrates, which are metal salts of picric acid, are explosive. When picrates are dry, they can detonate readily, possibly spontaneously. Purchase in small quantities, keep it moist, and store it in a safe, cool place. If it starts to dry out, add a small amount of water to keep it moist. The maximum solubilities of picric acid in water and in ethanol are approximately 1.3 and 8 g/100 mL, respectively. Picral can be stored safely. During use, the solution should not be allowed to dry out. The etching residue should be discarded at the end of the day to avoid potential explosions.

Bases, such as ammonium hydroxide  $(\text{NH}_4\text{OH})$ , potassium hydroxide  $(\text{KOH})$ , and sodium hydroxide  $(\text{NaOH})$ , are commonly used in metallography, chiefly in etchants.

Ammonium hydroxide is a colorless liquid with a strong, obnoxious odor. Solutions are extremely corrosive and irritating to the skin, eyes, and mucous membranes. It reacts exothermically with sulfuric acid and other strong mineral acids, producing boiling solutions. Sodium and potassium hydroxides are strong bases, available as white deliquescent pellets that are soluble in water. They can rapidly absorb carbon dioxide and water from the air. Solutions stored in flasks with ground stoppers may leak air and freeze the stoppers, making reopening difficult. Dissolving NaOH or KOH in water will generate considerable heat. Do not dissolve either in hot water. Never pour water onto these hydroxides; always add the pellets slowly to the water. Alkali metal hydroxides react violently with acid and are corrosive in moist air to metals such as zinc, aluminum, tin, and lead, forming flammable/explosive hydrogen gas. They are very corrosive to the skin, eyes, and respiratory tract. Long-term exposure may lead to dermatitis. Potassium hydroxide is somewhat more corrosive than sodium hydroxide.

Other Chemicals. Hydrogen peroxide  $(\text{H}_2\text{O}_2)$  is available as a liquid in concentrations of either 3 or 30%. The 3% solution is reasonably safe to use, while the 30% solution is a very powerful oxidant whose effect on the skin is approximately as harmful as that produced by contact with

sulfuric acid. Hydrogen peroxide by itself is not combustible, but if brought in contact with combustible materials, it can produce violent combustion. Hydrogen peroxide is very damaging to the eyes. Because the release of oxygen can cause high pressures to develop within the container, the container caps are vented.

Bromine ( $\text{Br}_2$ ), a fuming, reddish-brown liquid with a pungent, suffocating odor, is commonly used in deep-etching solutions. It is very corrosive, reacting violently with easily oxidized substances, including some metals. Bromine is a dangerous liquid that should only be handled by well-qualified personnel. Its vapors are extremely irritating to the eyes, skin, and mucous membranes. Skin contact produces deep, penetrating burns that are slow to heal. Contact with organic matter can cause fires.

Chromic acid ( $\text{H}_2\text{CrO}_4$ ) is formed when chromium trioxide ( $\text{CrO}_3$ ) is dissolved in water.

Chromium trioxide is used in electropolishing solutions (see the previous comment and [Table 3](#) about the explosive nature of mixtures with acetic anhydride). Dilute aqueous solutions are widely used for attack polishing. It is a powerful oxidant; always wear gloves when using it for attack polishing, or use automatic devices and avoid contact potential. Chronic or long-term inhalation exposure may produce asthmalike reactions.

Potassium permanganate ( $\text{KMnO}_4$ ), a black crystalline powder, is a powerful oxidant used in etchants. It is a dangerous fire and explosion hazard, especially when in contact with organic materials. Ingestion produces serious damage. Potassium permanganate and sulfuric acid should never be mixed together, because a violent explosion can result.

Potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ), a bright-orange crystalline powder, is another powerful oxidant that is also used in etchants. Contact can cause ulceration of the hands, severe damage to nasal tissue, or asthma and allergies with long-term exposure.

Cyanide compounds are occasionally used in metallographic applications. Potassium cyanide (KCN) and sodium cyanide (NaCN) are extremely dangerous and highly toxic. Exposure by eye or skin contact or by ingestion is fatal. The vapors of NaCN and KCN are intensely poisonous. They are particularly hazardous when brought in contact with acids or acid fumes because of liberation of hydrogen cyanide, which is extremely toxic and highly flammable. Potassium ferricyanide ( $\text{K}_3\text{Fe}(\text{CN})_6$ ), a ruby-red crystalline powder and an ingredient in Murakami-type reagents, is poisonous but stable and reasonably safe to use.

A number of nitrates, such as ferric nitrate [ $\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ], lead nitrate [ $\text{Pb}(\text{NO}_3)_2$ ], and silver nitrate ( $\text{AgNO}_3$ ), are employed by metallographers. Because they are powerful oxidizers, they pose a dangerous fire hazard, especially when in contact with organic materials. They may evolve toxic fumes, such as oxides of nitrogen and lead, and are poisonous and corrosive to the eyes, skin, and respiratory tract.

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