Dissolution in Acids

6

GENERAL

ONCE THE TEST PORTION has been selected, we most often must perform a number of operations on it before the analyte content is ready for measurement. Usually the first of these is dissolution. What we mean generally by "dissolution" is the conversion of the total test portion into an aqueous solution of dissociated salts. However, even that definition fails to incorporate a number of important exceptions in metal and ore analysis. Sometimes the medium is nonaqueous, as in halogen-solvent treatment for inclusion isolation, and sometimes only the analyte is leached or distilled from the test portion. Some European workers prefer the term "decomposition" for the general process and subcategorize "dissolution" for low-temperature work like acid treatment and "opening out" for high-temperature techniques like molten salt fusions.

Rather than quibble about terminology, let us arbitrarily choose the term "dissolution" as an umbrella to encompass all processes that lead ultimately to a "solution"—complete or partial, aqueous or not. We *will*, however, pay some homage to the preceding distinction by dividing this rather broad subject into two chapters. In this chapter we will confine our discussion to acid-based dissolution processes, while in the next we will cover all the remaining techniques. There is quite a lot to cover, and while all of it is chemistry, much of it is grounded in lore.

In more than 90% of the situations, the analyst's task will be to completely dissolve the test portion. However, even this seemingly straightforward operation must be understood, like the sampling plan, in terms of the attributes (analyte concentrations) to be measured. Some test portion components will be lost as volatiles, some will precipitate, some may adsorb on the vessel walls. But none of these effects will usually matter if the *analyte* is retained quantitatively in solution.

If the analyte measurement depends upon subsequent chemical reactions, the analyst must proceed in a way in which no interfering species are introduced. For example, if one wishes to determine chromium in a high-carbon steel, one must first be aware that the chromium content of the test portion is likely to be divided between chromium dissolved in the iron matrix and chromium present as precipitated chromium carbide. The former is soluble in a mixture of hydrochloric acid and nitric acid, the latter is not. If one proceeds in this way, when the reaction ceases chromium carbide will remain as part of an undissolved residue on the bottom of the beaker.

Adding perchloric acid and heating the mixture to fumes

of $HClO_4$ will likely dissolve the carbide residue, but it will also evolve volatile chromyl chloride, and the chromium results will be low. In this case, the correct approach is to dilute, filter, and ignite the insoluble residue, fuse it with an appropriate flux such as sodium bisulfate, and leach the cooled melt in the filtrate solution. Similarly, a niobium-bearing stainless steel will yield a clear solution if fumed in a mixture of phosphoric and sulfuric acids, but if phosphorus is the analyte, this approach is closed to the analyst.

Clearly, then, in a manner analogous to sampling, the analyst must prepare and follow a dissolution plan that will dissolve and completely retain the analyte and add no problems to the determination. The search for a universal approach that can be applied to all or most analytical situations is usually a vain effort unless the assortment of sample types is quite limited. Laboratories that have abandoned chemistry in favor of physical measurement soon learn that sample dissolution is not a trivial exercise, but a complex problem requiring the knowledge and experience of an analytical chemist.

Before beginning this two-chapter journey, we must acknowledge the invaluable aid of two excellent references: *A Handbook of Decomposition Methods in Analytical Chemistry* by R. Bock (John Wiley & Sons, New York, 1979) and *Decomposition Techniques in Inorganic Analysis* by J. Dolezal, P. Povondra, and Z. Sulcek (American Elsevier Publishing Co., New York, 1966). These texts have been the source for a significant amount of the detail in this chapter and the next.

ACID DISSOLUTION

All metals, alloys, and ores react with acid to some extent, and an acid attack is most often the method of choice due to simplicity and convenience. Like many solid/liquid reactions, the rate is diffusion limited and would eventually cease due to the buildup of product concentration at the solid/liquid interface without agitation of some kind. Fortunately, most metal-acid reactions generate hydrogen and other gases that provide the requisite agitation. While all acid attacks are exothermic, applying external heat to the solution produces extra convection currents that stir the solution as well as accelerate the reaction. As with all dissolutions, the rate of acid attack is inversely related to particle size and its attendant surface area relationship. A fine powder may dissolve in minutes, while one solid piece of the same weight may take hours or days.

Reaction rate may also be accelerated: (1) by pressure, which prevents the escape of reactive gaseous species; (2) by ultrasonic agitation, which both agitates the sample particles and produces localized heating due to the collapse of microscopic gas bubbles; and (3) by the action of catalysts. The loss of reactive species can also be prevented by the use of a reflux arrangement so that constant boiling azeotropes are continuously returned to the reaction vessel. This same stratagem can prevent the loss of volatile analyte compounds. In recent years, microwave heating has become an important laboratory tool. It can accelerate reaction rates both at atmospheric and elevated pressures. It must also be remembered that acids, like other dissolution media, react with vessels as well as samples. Thus the choice of vessel composition may be critical to a successful analysis.

Nonoxidizing Acids

As discussed in Chapter 3, it is often useful to distinguish oxidizing and nonoxidizing acids. Nowhere is this more apparent than in the selection of an acid attack for dissolution of the test portion. There are times when oxidizing conditions are best avoided, such as in situations where passivation of the alloy surface by oxidizing media (due to the formation of an acid-resistant oxide monolayer) is a problem. Most common nonoxidizing acids are strongly complexing, a characteristic that greatly facilitates dissolution and is often used to great advantage.

Hydrochloric Acid

The most commonly used nonoxidizing acid is hydrochloric acid. Some might suggest that it comes as close as anything to that mythical universal solvent since most metals and alloys and many ores will succumb to it, given enough patience. The dissolving strength of hydrochloric acid depends in part on the stability of chloride complexes that form with the reaction product cations. The ferromagnetic metals (iron, nickel, and cobalt) will all dissolve, as will the alkaline earths, zinc, cadmium, beryllium, gallium, aluminum, indium, and tin. Titanium is slow to dissolve, and aluminum will benefit from the introduction of a drop of mercury as a catalyst. Many ores and minerals will dissolve, including carbonates, sulfides, phosphates, borates, and some oxides and silicates. Iron ore, limestone, and dolomite dissolve relatively easily, while fluorspar requires the addition of borate to complex fluoride.

Attack on oxides depends to a large extent on thermal history, with certain ignited forms showing higher resistance. Thus, the ignited oxides of aluminum, beryllium, chromium, iron (Fe_3O_4), titanium, zirconium, hafnium, and thorium react slowly, if at all. Other impervious oxides include those of niobium, tantalum, tin, and antimony. On the other hand, the rare earth oxides, zinc oxide, gallium oxide, and cobalt oxide dissolve readily. Gypsum ($CaSO_4 \cdot 2H_2O$) dissolves easily, as do calcite and limestone (both $CaCO_3$), orpiment (As_2S_3), magnetite (iron (II, III) oxide), most manganese ores, and ferrotitanium. Somewhat slower reacting are dolomite ($CaMg(CO_3)_2$), magnesite ($MgCO_3$), siderite ($FeCO_3$), hematite (Fe_2O_3), galena (PbS), scheelite ($CaWO_4$), and apatite (a fluoride-bearing phosphate rock). Certain silicate minerals dissolve, leaving gelatinoid residues of silicic acid. Of course,

carbonates dissolve with the evolution of CO_2, while sulfide ores evolve H_2S.

There are a number of ways to facilitate dissolution in hydrochloric acid aside from adding other acids. The addition of copper (II) chloride or mercury (II) chloride or metallic mercury to hydrochloric acid greatly speeds the dissolution of aluminum metal by the creation of a galvanic cell. Platinum (IV) ions will catalyze hydrochloric acid attack on nickel or titanium. Interestingly, platinum metal itself, as well as other members of the platinum group, appear to dissolve to some very minor extent in HCl containing dissolved oxygen in the presence of light. The suggestion has been made that the platinum metals under these conditions catalyze the breakdown of HCl into chlorine gas and some other corrosive, oxidizing chlorine compound. It *is* a fact that hydrochloric acid and a chlorate will dissolve the platinum group metals in a pressure bomb, although it is more than likely that an explosion hazard exists for this approach and it should be avoided.

Other nonacidic oxidizing agents are sometimes added to HCl for use in open vessels: bromine to dissolve lead alloys and antimony alloys; bromate to dissolve tellurium metal; stannous chloride to aid in the dissolution of certain zinc ores; ammonium chloride to aid in the attack on cements (silica, of course, remains undissolved). Carbon tetrachloride and hydrochloric acid under reflux has been recommended to aid the retention of germanium when dissolving soluble minerals. Boric acid or aluminum chloride greatly aid the dissolution of fluorine-bearing materials like fluorspar and phosphate rock. Probably the most useful nonacid additive is hydrogen peroxide, which produces oxidizing conditions in a transient, controlled manner. Excess reagent is easily removed by boiling. HCl and H_2O_2 make an effective medium for dissolving nickel, cobalt, iron, copper, manganese dioxide, bronze, and many other materials. It even attacks platinum and gold to a minor (but not analytically useful) degree. For many metals, the reaction is quite noticeably more vigorous than that from hydrochloric acid alone. The same mixture has been applied to dissolve tungsten, aluminum, Fe_2O_3, and uranium ores. HCl, H_2O_2 and Br_2 has been used to dissolve Sb_2S_5.

Probably the most universally effective stratagem for extending the dissolving power of hydrochloric acid is the use of pressure dissolution (to be discussed in detail later in this chapter). Many alloys and minerals that are resistant or slow at atmospheric pressure will quickly yield clear or nearly clear solutions by treatment in acid bombs or other sealed vessels, in microwave ovens, or in sealed glass tubes. Remarkably, high-carbon ferrochromium, normally resistant to HCl, will dissolve under pressure in a microwave oven. A small weight of chromium refractory can be dissolved in a small volume of HCl in a sealed glass tube held at about 400°C for almost a day. Rare earth phosphors, such as those used in color television picture tubes, are dissolved in a microwave with HCl. Among the many pressure dissolutions that employ hydrochloric acid alone, many prove unexpectedly successful. They also offer what is frequently a distinct analytical advantage in the avoidance of oxidizing substances and of a large excess of acid.

Pressure vessels offer yet another advantage in helping to retain volatiles, whose loss in open vessels can otherwise curtail the usefulness of hydrochloric acid. Ordinarily, some

sample components will be lost when samples are dissolved in HCl in beakers or flasks. Arsenic (III), antimony (III), germanium (IV), and selenium (IV) are lost completely as chlorides, hydrides, or both. Phosphorus is lost as PH_3 and PCl_3 and sulfur as H_2S. Partial losses of mercury (II), tin (IV), boron (III), and rhenium (VII) also occur. Losses of indium, zinc, and tellurium may be observed if solutions or salt residues are heated vigorously for extended times.

Besides pressure vessel decomposition, another way to control volatiles loss (and limit acid volume) is to dissolve the sample under reflux. Allihn or straight tube condensers mounted vertically above the reaction flask are the most common approach. This technique will only be effective, however, for the high-boiling volatiles such as mercury, tin, indium, zinc, and tellurium. Another scheme could handle low-boiling volatiles by arranging to distill and collect the volatile species as they are being formed during sample dissolution. This approach is little used, however.

The loss of certain volatiles during open vessel HCl dissolution at low temperature is sometimes not as serious as depicted in the literature. With the exception of arsenic, antimony, germanium, selenium, sulfur, and phosphorus, losses are generally minor and may be tolerable, especially in trace analysis work, where they may represent an immeasurably small error. Of course, another answer to volatiles loss is to alter the oxidation state of the problem elements. Some judicious oxidation will thus convert arsenic, antimony, germanium, selenium, sulfur, and phosphorus to nonvolatile forms.

In addition to the loss of volatiles, a few compounds could precipitate in hydrochloric acid dissolutions—notably AgCl, Hg_2Cl_2, BiOCl, $AuCl_3$, CuCl, the partially soluble $PbCl_2$, and TlCl. In practice such precipitation seldom presents an analytical problem unless the metallic element is unexpectedly present in major amounts or if unusual reducing conditions prevail. In such a situation, a different dissolution medium would normally have been chosen. Traces and even minor amounts of elements that precipitate can be generally tolerated in hydrochloric acid dissolution for the determination of other analytes.

Far more serious concerns are inclusions and metallic phases that are not attacked by hydrochloric acid. Generally, concentrated or dilute HCl will leave considerable undissolved residue from most commercial plain carbon and low-alloy steels. This will usually consist of silica and some combination of aluminum oxide, aluminum nitride, graphite, and a mixture assorted metal carbides, oxides, nitrides, and carbonitrides. Often a major portion of the analyte is contained in one or more of these compounds. Certain higher alloy steels are likely to leave undissolved chromium carbides, vanadium carbides, chromium nitrides, and even chromium sulfides. Insoluble residues of titanium, niobium, tantalum, and other metal compounds are also possible. Nonferrous metals also exhibit HCl-resistant compounds and phases.

Several courses of action are open to the analyst: he may (sometimes at his peril) ignore the residue or he may filter it, ignite it, fuse it with molten salt, and leach the cooled melt in the filtrate. A third course is to try a pressure dissolution with HCl, which sometimes will dissolve otherwise resistant compounds. The utility of this approach is illustrated by the fact that mineral forms like spinel ($MgAl_2O_4$), beryl ($Be_3Al_2(SiO_3)_6$), topaz ($Al_2(SiF_6)_3$), bauxite ($Al_2O_3 \cdot 2H_2O$), cassiterite (SnO_2), corundum (Al_2O_3), and others will dissolve in HCl under pressure, leaving only some insoluble silica residue. A fourth alternative is to try a different acid or acid combination.

Hydrochloric acid is sometimes used as a leaching agent when the element of interest is known to be exclusively associated with the soluble portion of the sample. The sample must be finely divided to ensure that all the soluble portion is exposed to the acid. While this approach can prove useful, it can also be a scientifically hazardous practice and should not be widely applied. It has been used for determining the calcium content in finely ground bauxite and sometimes for certain determinations in slag and cement samples.

Perhaps the most chemically significant aspects of hydrochloric acid dissolution are the many anionic and neutral complexes that it forms with dissolved species. These include complexes with iron, nickel, cobalt, titanium, zirconium, and many others, even including the platinum group. The anionic complexes are particularly useful in ion exchange work, and all the complexes are useful in solvent extraction separations.

Hydrofluoric Acid

Hydrofluoric acid is another important complexing, nonoxidizing dissolution agent. It is unique in its aggressive attack on siliceous samples such as glasses, quartz minerals, and refractories, with all or part of the silicon being volatilized upon heating. The volatile species may be silicon tetrafluoride (SiF_4) or fluosilicic acid ($H_2SiF_6 \cdot xH_2 O$), depending upon conditions. Because glass vessels cannot be used, it is necessary to find adequate substitutes that meet the other criteria of the analysis. Typically, polytetrafluoroethylene (Teflon TFE) or platinumware are the materials of choice because of both their resistance to HF and their heat tolerance (see Chapter 2).

With silicate rocks and similar materials, hydrofluoric acid is more effective alone than in mixtures with other acids. In contrast, for most other samples, including metals and alloys, it is a much more efficient solvent in acid mixtures. The acid alone has been used to dissolve quartz, borosilicate glass, bauxite, and titanium dioxide pigments in open vessels and zircon and certain resistant silicate rocks using elevated pressure. Nonoxidizing mixtures with HF include HF/HCl, which has been applied to cement, iron ores, magnesite, niobium and tantalum ores, and titanium and zirconium alloys. HF/H_2SO_4 finds wide application since the high boiling H_2SO_4 allows the complete removal of excess HF, which is a source of potential interference in many analytical procedures. Oxidizing mixtures with HF include HF/HNO_3 and HF/$HClO_4$. All acid mixtures will be discussed later under the appropriate headings.

Hydrofluoric acid, despite its incomplete dissociation at typical dilutions, still contributes a considerable degree of complexing power, forming both negatively charged and neutral soluble fluoride complexes with many elements. Like the chloride complexes formed by hydrochloric acid, these complexes generally show a range of coordination numbers with varying stabilities. Among the elements whose fluoride complexes tend toward great stability are zirconium, beryllium,

and boron. Some other of the more stable anions that have been characterized are FeF_6^{3-}, AlF_6^{3-}, TiF_6^{2-}, $NbOF_5^{2-}$, and TaF_7^{2-}. Volatile compounds include SiF_4, BF_3, GeF_4, SeF_4, AsF_3, and AsF_5, but the losses of specific elements depend on conditions.

Arsenic, boron, germanium, and silicon are likely to be lost to some degree below the boiling point of a hydrofluoric acid solution. Evaporation of the solution to dry salts will result in major to complete losses of those four elements as well as significant losses of antimony. Some selenium, tellurium, and even titanium are likely to be lost as well, but other reported losses, such as zirconium, niobium, and tantalum, are doubtful at hotplate temperatures and are probably apocryphal. Evaporation of a mixture of hydrofluoric and sulfuric acids to strong fumes of SO_3 will volatilize arsenic, boron, germanium, silicon, selenium, antimony, mercury, rhenium, and osmium. If a mixture of hydrofluoric and perchloric acids is taken to fumes of perchloric acid, the same list will also include chromium (lost as $CrOF_4$) and ruthenium (lost as $RuOF_4$). The addition of mannitol or phosphoric acid to a hydrofluoric acid solution will prevent the loss of boron at moderate temperatures.

Another way elements are "lost" to the analyst is by precipitation. There are a fair number of insoluble fluorides: the alkaline earths—MgF_2, CaF_2, SrF_2, BaF_2; scandium, yttrium, and the lanthanides (almost all of the form, MF_3); also ThF_4, UF_4; and complex metal fluorides such as $MgAlF_5$ and Fe (II) (AlFe (III))F_5. Reported losses of alkali metal elements, especially potassium, may be traceable to the formation of compounds like $KSiF_6$, K_2AlF_6, and K_2FeF_6. A dry residue of the first of these can be decomposed by warming with calcium hydroxide, whereupon CaF_2 is precipitated and the K^+ is released into solution.

In addition, many common metal fluorides are sparingly soluble, even in dilute acid solution. Thus iron, nickel, and chromium fluorides may be difficult to redissolve once they "salt out" of solution. If the method can tolerate it, warming with boric acid solution will aid in the dissolution of fluoride salts; otherwise, dilution, stirring, warming, and patience are usually rewarded. The precipitation of insoluble fluorides during dissolution can be used to isolate them as analytes. Thorium, uranium, and the rare earths have been separated from mineral matrices in this way by simply diluting and filtering the dissolved sample. For trace quantities, the sample may be spiked with calcium to effect coprecipitation with calcium fluoride. Magnesium is a more useful coprecipitant for X-ray fluorescence micropore membrane work because that element's weaker X-ray response will provide lower background readings.

The use of hydrofluoric acid without its subsequent removal often presents problems later in the analysis. Excess fluoride may prevent an important precipitation from occurring, or it may bleach a color reaction for spectrophotometry or obscure an otherwise sharp visual endpoint in titrimetric work. There are generally three courses to follow when this is the case: (1) complex the excess HF (usually with boric acid, but occasionally with aluminum); (2) precipitate the excess HF (usually with calcium); or (3) drive out the excess HF by heating to fumes with a high boiling mineral acid (H_2SO_4, $HClO_4$, and sometimes one or both of these with H_3PO_4). Ni-

tric acid is also often present, and if organic or other easily oxidizable matter is present, a large excess of nitric acid *must* accompany perchloric acid.

Sulfuric Acid

Sulfuric acid is a good solvent for many metal alloy systems, but is far from a universal one. Iron-base alloys, in general, show vigorous reaction with dilute sulfuric acid and significantly less with the concentrated reagent. The opposite is true for lead- and tin-based alloys. This odd behavior may be explained at least partly by the mild oxidizing effect of the hot concentrated acid and by sulfate complex formation in dilute aqueous solution. Many materials, including second phases and inclusions that may be present in low-alloy and stainless steels and temperature-resistant alloys, are not attacked by sulfuric acid in either concentrated or dilute form. Thus, the analyst must be cautious of residues left after sulfuric acid digestion since they may contain a significant portion of the analyte.

Some other metals that *do* yield to dilute sulfuric acid are beryllium, aluminum, chromium, and titanium metal, as well as ferrotitanium and low-carbon ferrochromium. Certain of these reactions tend to slow down after an energetic interlude, but sometimes a remedy can be found. For aluminum metal, a small amount of mercury (II) salt will produce a mercury amalgam that will accelerate the dissolution. The same device makes dissolution of copper metal in sulfuric acid feasible. Titanium metal requires a drop or two of nitric acid to reach completion (too much and TiO_2 is likely to hydrolyze).

Certain compounds like FeO and ZnO, many carbonates, and titanium and molybdenum borides will dissolve in dilute H_2SO_4 in open vessels. Other materials, like spinel ($MgAl_2O_4$), chromite, and alumina will yield to dilute H_2SO_4 in a pressure bomb. The hot concentrated acid will dissolve thallium metal as well as lead and tin. It is said to attack palladium, rhodium, and platinum to varying degrees and in that approximate order, but is not practical for analytical digestion. It dissolves cryolite (Na_3AlF_6) and fluorspar (CaF_2) by evolving HF.

It is an effective solvent for sulfide ores in general and the ores of tin, antimony, and arsenic in particular. Heating monazite sand (which is largely $CePO_4$) with hot concentrated H_2SO_4 for extended periods will convert it to a water-soluble product. This same technique is sometimes applied to TiO_2 and to certain thorium, niobium, and tantalum ores. Stable cyanide compounds like $KAg(CN)_2$ and $KAu(CN)_2$, which are encountered in precious metal refining, are destroyed by fuming with H_2SO_4 with the evolution of HCN gas. The concentrated acid can be used in a pressure bomb to dissolve orthoclase ($KAlSiO_4$), topaz ($Al_2(SiF_6)_3$), and boron nitride (BN), among other materials. In some cases a very slightly diluted acid is preferable.

The dissolving power of sulfuric acid can be enhanced in certain cases by the addition of solid compounds. The boiling point of the acid is raised and its solvent properties improved by the addition of anhydrous ammonium, potassium, or sodium sulfate. Such digestions are sometimes performed in a fused silica flask fitted with a reflux condenser to help retain volatiles. These mixtures have been used for TiO_2, ZrO_2, WO_3, niobium and tantalum ores, and tungsten carbide (WC), among other materials. In some cases a 0.5-g sample will dis-

solve in a mixture of 20 mL of concentrated H_2SO_4 and 5 g of anhydrous sulfate salt, although several hours may be required.

Ammonium sulfate is the lowest temperature compound of the three salts (it decomposes at 250°C), but is probably the most useful in this application. Mixtures of sulfuric acid and anhydrous ammonium hydrogen sulfate (NH_4HSO_4) have been used for niobium metal, tantalum oxide, and tungsten and tantalum carbides. Mixtures of sulfuric acid and potassium pyrosulfate are a standard approach for lead- and tin-based alloys and for niobium and tantalum metal. Typically for lead and tin alloys, a 1-g sample will dissolve in 20 mL of H_2SO_4 and 5 g of $K_2S_2O_7$. For niobium and tantalum, a 0.2-g sample will dissolve in 5 mL of H_2SO_4 and 10 g of $K_2S_2O_7$. The dissolution is often conducted in a small fused silica or Vycor Erlenmeyer flask, starting at low heat on a hotplate and finishing by heating to strong fumes over a Meker burner. In the case of the low melting lead and tin solders, it is important that the sample remain below its melting point before it dissolves. Clearly, this approach must be regarded as a hybrid of acid dissolution and molten salt fusion. The cooled salts are dissolved in water and generally yield a clear solution.

Another additive that has been used in the sulfuric acid dissolution of metallic mercury or its ore, cinnabar (HgS), is potassium permanganate. A 0.5-g drop of mercury will dissolve in 20 mL of H_2SO_4 and 0.75 g of finely powdered $KMnO_4$ with 10 min of fuming. The cooled sample is diluted and the permanganate is reduced with 3% H_2O_2. Bromine water and very dilute sulfuric acid has been used to dissolve magnesium alloys. And hydrogen peroxide is sometimes added to dilute sulfuric acid to aid in the dissolution of copper metal.

Volatiles losses from sulfuric acid heated to the fuming point include the mercury (II), the selenium (IV), and a significant portion of the rhenium (VII) (lost as Re_2O_7, which boils at 362°C), and the osmium (VIII) (as OsO_4, which boils at 130°C). Some phosphorus is also likely to be lost. Of course, sulfuric acid is most frequently used in the presence of other acids, and, when such solutions are brought to sulfuric acid fumes, quite different mechanisms of volatiles loss may be at work. The insoluble sulfates include barium, strontium, and lead.

Calcium sulfate is considered to be sparingly soluble, but the presence of major amounts of calcium in the sample frequently eliminates sulfuric acid as a dissolution agent. Sparingly, soluble double salts also form in the presence of potassium ion: $KCr(SO_4)_2$, $KAl(SO_4)_2$, and others. Iron (II) sulfate and iron (III) sulfate show limited solubilities that cause "salting out" of steel samples during sulfuric acid fuming. Similar effects occur with nickel sulfate during the fuming of nickel-base alloy samples. These salts cause bumping and spattering during fuming operations, which must be conducted with care to avoid sample loss. The slight oxidizing effect of fuming with sulfuric acid leaves the valence states of most common metals undisturbed; however, it *is* known that tin (II) is oxidized to tin (IV).

Other Nonoxidizing Acids

Other nonoxidizing acids are sometimes used alone or in nonoxidizing combinations, but these applications are comparatively rare. *Phosphoric acid* will put certain iron and chromium ores into solution and has also been used for a variety of finely ground refractory materials—chrome-magnesite, blast furnace slag, silica brick, and others. In one approach, 0.5 g of −200 mesh sample is reacted with 15 mL of 12.5M H_3PO_4 in a platinum crucible on a sandbath until the water is expelled. Then a lid is placed on the crucible, and it is heated at 300°C until the sample dissolves. Of course, silica must be filtered from the water-leached melt. Phosphoric acid has also been used to dissolve refractory ferrites in the presence of a weighed excess of solid oxidant (such as cerium (IV) or chromium (VI) salts). Total iron can then be determined by titrating the unreacted excess oxidant. Other materials that have been dissolved in phosphoric acid are alumina and high-alumina slags, uranium nitride, feldspar, mica, and kaolin.

Fluoboric acid (HBF_4) is used in specialized procedures to dissolve tin-based alloys, zeolites, and silicates. Since quartz particles are not attacked, it affords a convenient means of gravimetrically determining the quartz content of silicate minerals. *Hydrobromic acid* is much less stable than hydrochloric acid. It should be stored in dark bottles since it decomposes into bromine under the influence of light. HBr readily dissolves copper alloys, which are extremely slow to react with HCl. The reason for this great difference in reaction rates stems from the very stable bromide complexes that form with copper ion. The presence of traces of bromine in the reagent may also play a role. HBr also dissolves indium, antimony, and tin alloys. In the case of tin-base alloys, the base element matrix can be evolved away by fuming with perchloric acid. Interestingly, lead alloys dissolve to clear solutions in the concentrated acid, but $PbBr_2$ precipitates in 1:1 $HBr:H_2O$. Most commonly, lead and tin-base alloys are dissolved in a 1:9 $Br_2:HBr$ mixture (10 mL will dissolve a 1-g sample).

Hydrobromic acid or Br_2/HBr dissolution of lead alloys will result in the loss of tin, arsenic, antimony, and selenium. If the solution is fumed with a high boiling acid, these losses will be virtually complete and some indium is also likely to be lost. Once the volatiles have been expelled, any visible precipitate of $PbBr_2$ in the cooled solution can be dissolved with a few drops of nitric acid. *Hydroiodic acid* is less stable than HBr, breaking down into I_3^- ion. HI will dissolve SnO_2 and $BaSO_4$, although it is seldom used in inorganic analysis. *Acetic acid* has been used to selectively leach analytes from finely powdered samples, in particular, readily soluble calcium compounds from slag samples.

Nonoxidizing Acid Mixtures

Nonoxidizing acid mixtures are extremely useful for certain alloy and nonmetallic samples. Sometimes two volatile nonoxidizing acids are combined, as with HF/HCl mixtures, which are used for cement and silicon nitride (Si_3N_4) samples and also for certain zirconium and titanium alloys, glass, silicate rocks, magnesite, iron ores, and niobium and tantalum ores. Virtually the entire range of acid ratios have been used, from nearly all HCl (for cement) to equal parts of both acids (Si_3N_4) to 3:1 HF:HCl (for glass). The analyst must be prepared in these instances to potentially lose over a dozen elements as volatile compounds when an open vessel digestion is used. For this reason, pressure techniques are especially useful with this acid mixture. If one includes the rare earths, over two dozen other elements may precipitate, and here there is no facile remedy.

Much more common are mixtures of a volatile acid and a high boiling acid. These combinations, like HF/H_2SO_4 and HCl/H_2SO_4, may be premixed (but not stored) or, more commonly, added at the same time to the sample to take advantage of synergistic effects. Occasionally, it is more advantageous to add the volatile acid and allow it to react alone for a time before adding the high boiling acid. Mixtures of HCl, HF, and H_2SO_4, in particular, might utilize such a sequential addition approach to good effect for certain types of sample.

When the sample has dissolved, heating the solution to strong fumes of the high boiling acid will remove potentially interfering amounts of the volatile acids. Table 6–1 should help the analyst predict just which elements are likely to be lost at fuming temperatures, although it should be borne in mind that complex formation and the formation of uncharacterized intermediates often thwarts predictions.

As with much of inorganic analysis, experience is the best guide. Mixtures of HF and H_2SO_4 are commonly used to dissolve siliceous samples: quartz sand, soda lime glass, borosilicate glass, opal glass, and for zirconium alloys and ferrozirconium. Mixtures of HCl and H_2SO_4 have been used for lithium ores and antimony metal. Mixtures of H_3PO_4 and H_2SO_4 are commonly employed in certain steel dissolutions. This mixture is particularly useful for tool steels bearing tungsten, which is prevented from hydrolyzing to the hydrous oxide. Mixtures of HCl, H_3PO_4, and H_2SO_4 have been used to dissolve ferrotitanium. Such mixtures similarly hold the hydrolyzable titanium (despite an insoluble phosphate, which

does not form under these conditions). Many of these procedures rely upon fuming with sulfuric acid (the highest boiling common mineral acid) to expel the other components of the acid mixture. However, hydrofluoric acid, or rather interfering fluoride, may be difficult to expel completely in the presence of large amounts of elements that form stable fluoride complexes, such as aluminum.

Oxidizing Acids

Some of what has been discussed up to this point are admittedly oxidation reactions, and yet it is useful to distinguish them from reactions that drive the solutes to higher oxidation states. This category has two important members—nitric acid and perchloric acid. The former is a volatile, weakly complexing acid that is oxidizing at all temperatures; the latter is a high-boiling, completely noncomplexing acid that is essentially nonoxidizing at low temperatures but strongly oxidizing at high temperatures. Both find important uses in the dissolution of inorganic materials.

Nitric Acid

Nitric acid, although much more useful in combination with other acids, finds significant use alone. Metals that dissolve readily include nickel, cobalt, copper, mercury, silver, lead, selenium, bismuth, zinc, and cadmium. Many others form an impervious passivation layer, notably aluminum, chromium, titanium, zirconium, hafnium, gallium, indium, niobium, tantalum, thorium, and boron. The alkaline earths will dissolve in the dilute acid, but passivate in the concentrated acid. Iron-base alloys dissolve best in dilute nitric acid, as do thallium and lead oxide. Arsenic and antimony-bearing ores will dissolve, as will galena (PbS_2), MoS_2, certain uranium ores, and selenium and tellurium concentrates. Few elements form stable nitrate complexes—exceptions are $Au(NO_3)_4^-$ and $Th(NO_3)_6^{2-}$. Volatiles loss is limited to OsO_4 and, perhaps, RuO_4. Many elements precipitate as hydrous oxides, notably antimony, tin, niobium, tantalum, titanium, zirconium, hafnium, tungsten, and molybdenum.

Perchloric Acid

Perchloric acid in dilute solution is an excellent solvent for many metals, notably steels of all kinds. Hot, concentrated perchloric acid attacks all metals except gold and certain members of the platinum group. Except in the basic steel industry, where it is used to dissolve steel samples, it is infrequently used alone. For safety reasons, perchloric acid is nearly always used in the presence of a large excess of nitric acid, especially if the solution is heated to fumes of perchloric acid. Explosions have been reported in dissolving bismuth metal, antimony metal, and uranium turnings, and in dissolving steel in the concentrated acid.

After fuming, all metal species are generally in their highest stable oxidation states. Exceptions are lead, manganese, and cobalt, which are in the +II state. Perchloric acid alone or in the presence of nitric acid has been used to dissolve silver, arsenic, lead, manganese, copper, and nickel-copper alloys. Other materials include sulfide ores such as galena, chromite, apatite, and various fluoride-bearing minerals, and chromium carbide (Cr_3C_2) and various other carbides and nitrides extracted from steels.

TABLE 6–1—Boiling points of selected compounds, degrees centigrade.

Acids
HCl (constant boiling:20%) 110
HNO_3 (constant boiling:69%) 121
HBr (constant boiling:48%) 126
$HClO_4$ (constant boiling:72%) 200
H_3PO_4 (ortho) 213
H_2SO_4 330

Fluorides	Chlorides	Bromides
PF_3 −101	BCl_3 12	BBr_3 91
BF_3 −99	PCl_3 76	$SeBr_4$ sublimes at 115
SiF_4 −96	$GeCl_4$ 89	$GeBr_4$ 186
PF_5 −84	$SnCl_4$ 114	$SnBr_4$ 203
AsF_5 −53	$AsCl_3$ 130	$AsBr_3$ 221
GeF_4 sublimes at −37	$SbCl_5$ 140	$SbBr_3$ 280
AsF_3 63	$SeCl_4$ sublimes at 196	
SeF_4 105	$SbCl_3$ 223	
SbF_5 150	$AuCl_3$ 265	

Hydrides	Others
PH_3 −88	CrO_2Cl_2 117
H_2S −61	OsO_4 130
AsH_3 −55	$RuOF_4$ 184
SnH_4 −52	SeO_2 sublimes at 315
H_2Se −42	Re_2O_7 362
SbH_3 −18	
H_2Te −2	
BiH_3 22	

To prevent the loss of silicon during the perchloric acid dissolution of fluoride-bearing samples, boric acid is added before the reaction is initiated. Even without the addition of any HCl or NaCl, some chromium will volatilize as chromyl chloride (CrO_2Cl_2) from a perchloric acid solution heated to strong fumes. Estimates are that from 1 to 3% of the amount of chromium present will be lost. About 30% of the rhenium will be lost as Re_2O_7, and up to 100% of the selenium will be lost as SeO_2. Likewise, all of the osmium and ruthenium will be lost as OsO_4 and RuO_4, respectively. Arsenic, antimony, and mercury will be lost to some degree as well. In addition, some sulfur will be lost as H_2S during low-temperature dissolution.

During fuming with perchloric acid, silicon precipitates as SiO_2, and antimony, tin, tungsten, titanium, niobium, and tantalum precipitate as hydrous oxides. Also, potassium, rubidium, and cesium precipitate as perchlorates. Fuming perchloric acid generates a fine aerosol spray that can result in mechanical loss of some sample solution if proper care is not applied. Typically, a watchglass and careful temperature control are all that are required.

Oxidizing Acid Mixtures

Oxidizing acid mixtures represent the category with the widest range of application. *Mixtures of hydrochloric and nitric acid* are among the most commonly used concoctions. *Aqua regia* (known as *Königswasser* in Germany) is 3:1 HCl:HNO_3. It is said to gain strength as a dissolution medium if allowed to stand for 3 or 4 min after mixing before it is applied to the sample. *Aqua regia* is an unstable mixture of free chlorine, nitrosyl chloride (NOCl), NO_x gases, and free HCl and HNO_3. Undoubtedly, the complexing power of chloride ion combined with the oxidizing power of free chlorine in aqueous solution are two of the keys to its efficacy as a solvent.

While *aqua regia* is a particularly effective mixture, there is nothing magic about the 3:1 HCl:HNO_3 ratio. Many labs routinely employ a 1:1 ratio of these two acids, and so-called LeForte (or inverted) *aqua regia* (1:3 HCl:HNO_3) is sometimes used to oxidize sulfur to sulfate. *Aqua regia* is particularly useful in the dissolution of stainless steels with moderate (about 2%) to low levels of molybdenum. Similarly, it will dissolve iron-, nickel-, and cobalt-based high-temperature alloys so long as the Group IVB, VB, and VIB elements do not exceed a critical level. In particular, as chromium and molybdenum levels climb in unison, *aqua regia* loses effectiveness. Frequently alloys that are slow or tend toward passivation with *aqua regia* will dissolve if they are started in concentrated hydrochloric acid with nitric acid added dropwise while heating over a period of time.

Some superalloys (especially cobalt-base high-temperature alloys like S816, MP35N, and L605) respond better to such treatment if they are *not* heated. *Aqua regia* will dissolve gold as well as platinum and palladium, but the other members of the platinum group are resistant. It is commonly used to dissolve steel of all kinds, silver, zinc alloys, nickel-copper alloys, nickel-chromium alloys, bronze alloys, copper-beryllium and aluminum-beryllium alloys. Ferroboron requires the dropwise addition of HNO_3 into HCl, as do ferromolybdenum and molybdenum metal. Germanium oxide requires large acid volumes and long digestion times.

Iron, manganese, mercury, lead, and zinc ores dissolve, as do molybdenite (MoS_2) and uraninite (UO_2). Tungsten ores dissolve with the hydrolysis of WO_3. *Aqua regia* oxidizes many elements, but not necessarily to their highest aqueous oxidation states. Both selenium and tellurium, however, are elevated to the +VI state, where their volatility is comparatively low. However, the analyst is cautioned to watch for losses of boron and germanium. If any rhenium or osmium has dissolved, it will be evolved from the boiling solution. There are also reported losses of gold if *aqua regia* solutions are rapidly evaporated to dryness. Antimony, tin, tungsten, niobium, tantalum, and major amounts of molybdenum, zirconium, hafnium, and titanium are likely to precipitate.

Mixtures of Hydrofluoric Acid and Nitric Acid—These are extremely effective solvents for a wide range of metals and alloys, including titanium, niobium, tantalum, and other metals that are impervious to *aqua regia*. Platinum does not dissolve, nor do the other five members of the platinum group, nor does gold. Alloys that are high in chromium react slowly. However, many other materials react with such rapidity that it is often best to add hydrofluoric acid to the sample (in a Teflon TFE or platinum vessel) first, then add nitric acid dropwise or in small increments to initiate and sustain the reaction at a controlled rate. Often copious amounts of NO_x gases are evolved. After the reaction subsides, the solution may be warmed if necessary to complete the dissolution.

All of the elements that hydrolyze in *aqua regia* (see above) are held in solution as soluble fluoride complexes in HF/HNO_3 mixtures. As with HCl/HNO_3 mixtures, the volume ratio of HF to HNO_3 varies widely and is not particularly critical. In general, the proportion of hydrofluoric acid should increase with the sample's estimated content of Group IVB, VB, and VIB elements. Sometimes it helps to add a little water to the mixture as well to help prevent the salting out of fluoride compounds.

A combination of 20 mL of HF, 10 mL of H_2O, and 5 mL of HNO_3 will dissolve a 1-g sample of a large number of different alloys, including some of the most acid resistant. HF/HNO_3 mixtures are used to dissolve titanium, tungsten, zirconium, hafnium, niobium, tantalum, and rhenium metals and their alloys, including their ferroalloys. These mixtures are also used for high-purity silicon, silicon-aluminum alloys, silicides, silicates, and ferrosilicon. Tungsten, silver, and lithium ores dissolve, as do apatite, bauxite, niobium and tantalum oxides and carbides, and tungsten carbide. Niobium-tin superconducting alloys dissolve and so do $CdSiAs_2$ semiconductors. More nitric acid than hydrofluoric acid is used in mixtures to dissolve copper-nickel, antimony-tin, lead-tin, and bronze alloys.

Volatiles losses include boron, silicon, and germanium. The alkaline earths and the rare earths are likely to precipitate, especially if present in major amounts. It should also be noted here that mixtures of fluoboric acid (HBF_4) and nitric acid have proved useful in dissolving solders and other alloys of lead, tin, antimony, and copper, and for dissolving uranium-zirconium alloys.

Mixtures of Hydrochloric, Hydrofluoric, and Nitric Acids— These are effective for high-chromium superalloys, which are often resistant to HF/HNO_3. A combination of 15 mL of HF, 5 mL of HNO_3, and 5 mL of HCl will dissolve 1 g of most superalloys. Titanium alloys, ferroniobium, silicate rock, py-

rites, and a great many other samples will succumb to some ratio of these three acids. Volatiles and precipitate losses are about what would be surmised by inference from the previous sections.

Mixtures of HCl + HNO₃, HF + HNO₃, and HCl + HF + HNO₃ with High Boiling Acids—These provide an effective means of removing interfering anionic species (by heating to fumes of the high boiling acid). Sometimes two (or even three) high boiling acids are employed to aid in the dissolution and to prevent hydrolysis of sample component species. One extremely effective and versatile combination makes use of the complexing power of phosphoric acid to circumvent the need for HF. Sample size is limited to about 0.3 g, and the procedure must be followed in the sequence given.

1. Add to the sample in the following order:
   a. 25 mL of HCl.
   b. 5 mL of HNO_3.
   c. 25 mL of H_2O.
   d. 25 mL of a 10:3:12 mixture of H_3PO_4:H_2SO_4:H_2O.
2. Warm, then heat strongly until dissolved.
3. Heat to fumes of H_3PO_4 and fume for 1 min.
4. Remove from heat; cool for 1 min, then add 25 mL of a 7:13 mixture of H_2SO_4:H_2O and swirl to mix.
5. When cool, the sample solution may be diluted up to 100 mL with H_2O.

This procedure will dissolve difficult materials like tungsten metal and hold it in solution for weeks or months. This scheme is effective for: high-speed tool steels; iron-, nickel-, and cobalt-based superalloys; and many other alloys containing significant amounts of elements that ordinarily hydrolyze as hydrous oxides under oxidizing conditions. The dilution mixture is added while the sample is still hot to dissolve the gum-like polymeric metaphosphoric acid, which is otherwise a problem. The diluted sample solution may be conveniently used for inductively coupled plasma spectrometry or for certain spectrophotometric procedures like tungsten, titanium, or niobium determination as hydroquinone complexes. Even though titanium phosphate is insoluble, it does not form under the conditions described. In fact, mixtures of HCl, H_3PO_4, and H_2SO_4 will dissolve ferrotitanium. Similar dissolution procedures are used for nickel and iron ores, while H_3PO_4 and H_2SO_4 alone have been used for aluminum-vanadium alloys.

Sulfuric acid's role as a fuming acid after oxidizing dissolution has few challenges. Its high boiling point assures optimum removal of other acids. Mixtures of nitric acid and sulfuric acid are appropriate for most types of copper alloys and copper ores, for cobalt metal, nickel-iron alloys, molybdenum ores, iron pyrites, ferromolybdenum, lead ores and tin ores. Mixtures of nitric, hydrofluoric, and sulfuric acid apply to niobium and niobium alloys, to ferrophosphorus, uranium ores, titanium, zirconium, and tungsten metal, and have been used to dissolve niobium and tantalum carbide. Mixtures of nitric, hydrochloric, hydrofluoric, and sulfuric acid are effective for bauxite, vanadium ores, and a wide array of other industrial materials.

In certain industries, such as the ferrous metals industry, perchloric acid is the principal fuming acid. Its formidable oxidizing power is used to aid in the complete dissolution of carbides, to dehydrate silica, and to oxidize sample compo-

nents. In addition, perchlorate salts, except for the alkali metal and ammonium compounds, are readily soluble, unlike sulfate salts, which can be a problem with sulfuric acid. Mixtures of nitric acid and perchloric acid work well for low- and medium-alloy steels, manganese metal and ferromanganese, as well as nickel-copper alloys. Mixtures of nitric, hydrofluoric, and perchloric acid have been used for silicomanganese and for mullite ($AlSiO_3$). A great many sample types are dissolved in HCl/HNO_3 or HCl/HNO_3/HF mixtures; perchloric acid is then added to the cooled sample, which is then heated to fumes of $HClO_4$. Stainless steels, iron-, nickel-, and cobalt-based high-temperature alloys, iron, manganese, and molybdenum ores, and molybdenum disulfide (MoS_2) are often treated in this way. Hydrous oxides of the "earth acids," of course, will precipitate.

Perchloric acid plus phosphoric acid is known in some quarters as "phosphodent." It is a powerful dissolution mixture by itself for many highly alloyed steels and high-temperature alloys. Resistant alloys will generally yield to the addition of small quantities of HCl, HCl + H_2O_2 or HCl + HNO_3. A disadvantage, however, is that titanium phosphate will precipitate. Mixtures of sulfuric and perchloric acid and sulfuric, phosphoric, and perchloric acid are sometimes used for special applications. Two serious concerns with their use are the precipitation of elemental sulfur and the evolution of explosive anhydrous perchloric acid, both of which occur upon strong fuming.

Additives in Oxidizing Acid Mixtures

Additives in oxidizing acid mixtures are often valuable, and some combinations are common. The oxidizing power of *hydrogen peroxide* appears to be directly proportional to the acid strength of the solution. With hydrochloric acid it has been used to dissolve copper, brass, and bronze, magnesium-copper alloys, steel, aluminum, tungsten, and MnO_2. Many highly alloyed iron-, nickel-, and cobalt-based alloys will eventually succumb. High-chromium/high-molybdenum combinations in many resistant stainless steels dissolve slowly but, unlike attempts with nitric acid mixtures, do not passivate. Dissolution with dilute HCl and dropwise 30% H_2O_2 will keep up to 7 mg of silicon in solution for FAA or ICP determination.

The oxidizing power of hydrogen peroxide is exceptionally high in sulfuric acid (perhaps due to the formation of H_2SO_5). Such a combination (with added water) has been used for iron, nickel, and cobalt alloys. Hydrogen peroxide with concentrated H_2SO_4 has been used for zirconium. Very difficult materials like zirconium and hafnium carbides are also attacked with this approach. In combination with nitric acid, hydrogen peroxide will dissolve lead and lead oxides (including "red lead," Pb_3O_4), calcium tungstate (scheelite), and pyrite minerals, as well as cadmium, zinc, copper, and steels. Hydrofluoric acid and hydrogen peroxide has been used for titanium and titanium alloys, iron and steel, ferrotungsten, silicon metal, and many high-silicon alloys. This combination is especially useful for pickling solid pieces of titanium.

Mixtures of fluoboric acid and hydrogen peroxide have been used for lead alloys. After hydrogen peroxide, the next most useful additive is probably *bromine*. Combinations of hydrobromic acid and bromine are routinely used to dissolve lead- and tin-based solders, antimony and its alloys, and tellurium-bearing steel. High tin content requires a larger pro-

portion of bromine, but the most common ratio is 9:1 $HBr:Br_2$. After dissolution is complete, perchloric acid can be added to the cooled solution; then heating to strong fumes of $HClO_4$ will expel the tin and antimony bromides (as well as the arsenic and selenium). It will also convert any insoluble lead bromide into soluble lead perchlorate. Combinations of hydrochloric acid and bromine have been used in similar applications.

Bromine is often added to a dissolution mixture to help prevent the loss of sulfur as H_2S or phosphorus as PH_3. Thus 0.2 g of an orpiment sample (As_2S_3) can be reacted with 2 mL of ethanol and 3 mL of Br_2, then warmed with 5 mL of HCl to convert the sulfur to stable sulfate. Similarly, 0.5 g of ferrophosphorus can be dissolved in 20 mL of HNO_3 that is saturated with Br_2, 1 mL of H_2SO_4, and 2 mL of HF in order to retain the phosphorus for its determination. Magnesium alloys have been dissolved in water-diluted mixtures of H_2SO_4 and bromine water.

Potassium chlorate ($KClO_3$) has been added to HCl/HNO_3 mixtures to dissolve pyrites. *Potassium bromate* ($KBrO_3$) and HCl will dissolve tellurium. One gram of *potassium dichromate*, 2 mL of H_3PO_4, and 10 mL of HF have been used to dissolve 0.5 g of tantalum metal. *Tartaric, citric, or lactic acid* added to HNO_3 will prevent hydrolysis in the dissolution of antimony and its alloys. There are many other rarely employed, but occasionally invaluable, "tricks" among the notes

TABLE 6–2—Suggested acid dissolutions—pure metals.[a]

Element	Dissolution Procedure
Aluminum	50 mL 1:1 $HCl:H_2O$, plus 1 drop $Hg°$
Antimony	18 mL HBr + 2 mL Br_2
Arsenic	20 mL 1:1 $HNO_3:H_2O$
Beryllium	50 mL 1:1 $HCl:H_2O$
Bismuth	20 mL 1:1 $HNO_3:H_2O$
Cadmium	25 mL 1:1 $HCl:H_2O$
Chromium	30 mL HCl
Cobalt	20 mL 1:1 $HNO_3:H_2O$
Copper	20 mL 1:1 $HNO_3:H_2O$
Gallium	50 mL 1:1 $HCl:H_2O$
Gold	30 mL 3:1 $HCl:HNO_3$
Hafnium	15 mL HF
Indium	25 mL 1:1 $HCl:H_2O$
Iron	20 mL 1:1 $HCl:H_2O$
Lead	15 mL HNO_3
Manganese	20 mL HCl, dropwise HNO_3
Magnesium	30 mL 1:10 $HCl:H_2O$
Mercury	20 mL 1:1 $HNO_3:H_2O$
Molybdenum	20 mL HCl, dropwise HNO_3
Nickel	30 mL 1:1 $HNO_3:H_2O$
Niobium	20 mL HF, then 5 mL HNO_3, dropwise
Palladium	30 mL 3:1 $HCl:HNO_3$
Platinum	50 mL 3:1 $HCl:HNO_3$
Rhenium	15 mL 1:1 $HNO_3:H_2O$ in ice bath; no heat
Selenium	10 mL HNO_3
Silver	20 mL HNO_3
Tantalum	20 mL HF, then 5 mL HNO_3, dropwise
Tellurium	20 mL HCl, dropwise HNO_3
Thallium	20 mL 1:1 $HNO_3:H_2O$
Tin	50 mL 1:1 $HCl:H_2O$
Titanium	20 mL H_2SO_4, 3 to 5 drops of HNO_3
Tungsten	10 mL HF, dropwise HNO_3
Zinc	20 mL HCl
Zirconium	15 mL HF

[a]One gram test portion is implied. Warm to complete reaction unless otherwise indicated. In most cases alternate dissolutions are possible.

TABLE 6–3—Suggested acid dissolutions—alloys.[a]

Alloy Type	Dissolution Procedure
Aluminum alloys	20 mL 1:1 $HCl:H_2O$, dropwise H_2O_2
Beryllium alloys	30 mL 1:1 $HCl:H_2O$, dropwise HNO_3
Bismuth alloys	20 mL 1:1 $HNO_3:H_2O$ + 5 g tartaric acid
Cobalt-base high temp.	50 mL HCl, dropwise HNO_3, low heat
Copper alloys	30 mL 1:1 $HNO_3:H_2O$
Die steel	50 mL 1:1 $HCl:H_2O$, dropwise H_2O_2
Ferroboron	50 mL 1:1 $HCl:H_2O$, dropwise HNO_3
Ferrochromium, low C	40 mL 1:1 $H_2SO_4:H_2O$
Ferromanganese	30 mL HNO_3
Ferromolybdenum	30 mL HNO_3 + 5 drops HF
Ferroniobium	40 mL 1:1 $HCl:HF$, dropwise HNO_3
Ferrosilicon	15 mL HF, dropwise HNO_3
Ferrotitanium	30 mL 1:1 $H_2SO_4:H_2O$, 5 mL HF, dropwise HNO_3
Ferrotungsten	15 mL HF, then 5 mL HNO_3 dropwise
Ferrovanadium	30 mL HNO_3 in small portions
Gray iron	25 mL 1:1 $HNO_3:H_2O$; filter
Iron-base high temp.	50 mL HCl, dropwise, HNO_3
Lead alloys	20 mL 9:1 $HBr:Br_2$
Low alloy steels	20 mL 3:1 $HCl:HNO_3$
Manganese alloys	20 mL 3:1 $HCl:HNO_3$
Nickel-base high temp.	50 mL HCl, dropwise HNO_3
Silicon steels	25 mL 3:1 $HCl:HNO_3$ + 5 drops HF
Stainless steels	30 mL 1:1 $HCl:HNO_3$
Tin alloys	30 mL 10:1 $HCl:Br_2$
Titanium alloys	100 mL 1:1 $HCl:H_2O$, 3–5 drops HNO_3
Zinc alloys	30 mL 1:1 $HCl:H_2O$, dropwise HNO_3
Zirconium alloys	40 mL $H_2SO_4:H_2O$; 2 mL HF, dropwise

[a]One gram test portion is implied. Warm to complete reaction. In most cases alternate acid dissolutions are possible and are sometimes necessary.

of experienced metals analysts. Tables 6–2, 6–3, and 6–4 summarize some common acid dissolution schemes for metals, alloys, and related materials.

Special Situations

It sometimes occurs that even the weakest hydrogen donor, like neutral water, is too strong an "acid." This is the case with the alkali metals, which react with increasing violence as they go up in atomic weight (and electropositive potential). With lithium it is a matter of spattering and sample loss, but by the time we get to cesium we are in serious physical danger. Typically, these situations are handled by substituting alcohols for water and excluding atmospheric oxygen. Alcohols and similar polar compounds are more reluctant to release hydrogen ions than water, and in such media there is generally a lower heat of solvation. Cesium can be safely dissolved in butyl alcohol containing a small volume of ethanol. Lithium has been dissolved in a mixture of water and dioxane. Of the alkaline earths (the Group IIA elements, in this case excluding beryllium), calcium, strontium, and barium metal react with water, but magnesium forms a passive oxide. Magnesium metal does, however, react with methanol. Many very reactive metals, like the alkali and alkaline earth elements and the rare earths, are best treated by allowing them to react with atmospheric oxygen in the absence of moisture, weighing them in sealed glass vessels, and then reacting the oxides with dilute acids.

TABLE 6–4—Suggested acid dissolutions—miscellaneous materials.[a]

Material	Dissolution Procedure
Antimony ores	20 mL HNO_3
Bauxite	30 mL 3:1 HCl:HNO_3 + 15 mL 1:1 H_2SO_4:H_2O
Boron nitride (0.25 g)	15 mL HF in acid bomb, 150°C for 4 h
Borosilicate glass	10 mL HF + 2 mL 1:1 H_2SO_4:H_2O
Cobalt ores	30 mL HNO_3 + 20 mL 1:1 H_2SO_4:H_2O (fume)
Copper ores	20 mL HNO_3 + 20 mL 1:1 H_2SO_4:H_2O (fume)
Dolomite	40 mL 1:1 HCl:H_2O
Fluorspar	50 mL 1:1 $HClO_4$:H_2O (fume)
Germanium oxide	50 mL HCl + 5 mL HNO_3 (boil)
Gypsum	50 mL 1:1 HCl:H_2O
Iron ores	40 mL 3:1 HCl:HNO_3
Lead ores	30 mL $HClO_4$ + 10 mL HNO_3
Lead oxide (Pb_3O_4)	20 mL 3:1 HNO_3:H_2O + 3 mL H_2O_2
Limestone	40 mL 1:1 HCl:H_2O
Lithium ores	20 mL 1:1 H_2SO_4:H_2O + 20 mL HF
Manganese ores	40 mL HCl
Mercury ores	30 mL 5:1 HCl:HNO_3
Molybdenum ores	20 mL HNO_3
Molybdenum disulfide	50 mL 1:1 HCl:HNO_3 + 10 mL $HClO_4$ (fume)
Nickel ores	30 mL 1:1 HNO_3:H_2O
Portland cement	20 mL HCl + 3 g NH_4Cl
Selenium ores	20 mL HNO_3 + 1 mL H_2O
Silicate minerals	10 mL HF + 20 mL HNO_3
Silicon nitride	15 mL HF
Steel-making slags	10 mL HCl + 10 mL HNO_3 + 10 mL HF
Tin ores	20 mL 1:1 HNO_3:H_2O + 10 mL H_2SO_4 (fume)
Titanium dioxide	15 mL HF
Uranium ores	30 mL HF + 5 mL HNO_3 + 5 mL H_2SO_4 (fume)
Vanadium ores	40 mL 1:1 HCl:HNO_3 + 10 mL H_2SO_4 (fume)
Zinc oxide	15 mL 1:1 HCl:H_2O

[a]One gram test portion, except as noted. Warm to complete reaction. In most cases alternate acid dissolutions are possible and are sometimes necessary.

The practical inorganic analyst is well aware that the position of metal/ion half-cell potentials below hydrogen in the electromotive series is a poor predictor of how the metal will dissolve in acid. Passivation, complexation, and heat of solvation all play a role, and the nature of the solvent medium is critical. The importance of complex formation and oxidation is illustrated by the fact (incredible to some) that molybdenum, tungsten, and rhenium metal will dissolve in 30% hydrogen peroxide. The reaction is slow and favored by having the sample in a finely divided form, but it works and is even useful. For example, a gram of tungsten powder will dissolve in 50 mL of H_2O_2 overnight with gentle warming. Such an approach finds use where acidity must be restricted, as in the molybdenum blue spectrophotometric method for silicon determination.

Many metals and alloys will dissolve in acetylacetone (2,4-pentanedione), which forms stable complexes with many metal ions. There are also many other unusual low- or moderate-temperature metal dissolution reactions that rely on oxidation, complexation, or both. Some of these will be touched upon in the next chapter.

TREATMENT OF INSOLUBLES

When the analyst has done his best with an acid approach, either in open vessels or under pressure, sometimes insoluble matter still remains. This may be known to be innocuous to his purposes, in which case he can ignore it or filter it off and discard it. In another case, the insoluble residue may be known to contain a significant portion of the analyte, in which case the analyst has no choice but to take some action with it. But much more commonly the analyst has only a suspicion about that black smudge on the bottom of the beaker. The safest course is to treat every insoluble residue as if it was chock full of analyte. But the rigorous treatment of insolubles is very time consuming and may be a wasted effort. Sometimes it is possible to rapidly collect a sample of the insolubles from a trial dissolution and qualitatively or semi-quantitatively survey the composition using X-ray fluorescence (on a Mylar-covered membrane filter), optical emission (in a crater electrode), or even X-ray diffraction (for compound identification).

The treatment of acid insolubles involves first dilution of the solution to an acid concentration that will not destroy the filter. Hardened filter papers and certain membrane filter disks withstand more acid than common grades (see Chapter 2). Sometimes it is necessary to reduce matrix elements that are otherwise difficult to completely wash out of the filter. It is essential that the solution be filtered on a medium that completely retains the insolubles. In low-alloy and plain carbon steels, certain inclusion compounds can occur as extremely fine particles requiring 0.22-μm membrane filters. In other cases a fine porosity filter paper will suffice. The acid dissolution vessel is scrubbed with a rubber policeman and rinsed onto the filter.

The filter is then washed repeatedly, usually alternately with dilute acid and hot water. Rigorous washing of the residue is not a high priority, however, if the soluble and insoluble fractions will ultimately be recombined. The filtrate is retained, and the filter and residue are transferred to a crucible (usually platinum) and ignited in a muffle furnace, then cooled in a desiccator. If silicon is not to be determined, it can be volatilized at this point by heating on a sandbath with H_2SO_4 and HF.

When the residue has evaporated to dryness, the crucible is again cooled in a desiccator. A weighed amount of flux is added, and the residue is fused over a burner or in a muffle furnace and again cooled. The crucible's exterior is wiped clean and then it is immersed in the appropriate filtrate solution, which is then heated to leach the melt. The crucible is removed with Teflon-coated forceps and rinsed into the solution. Alternatively, the melt can be leached in a small amount of dilute acid that is then combined with the appropriate filtrate. Another choice is to analyze the acid soluble and acid insoluble portions separately. This approach is twice the work, but provides information that cannot be otherwise obtained. The two values can, of course, be combined mathematically to obtain the total analyte content. Details about molten salt fusions and high-temperature sinters will be presented in the following chapter.

PRESSURE DISSOLUTIONS

There is no doubt that dissolution in acid proceeds more rapidly and more completely if the reaction is conducted in a confined vessel above atmospheric pressure. This has been known for a long time, and much early work was performed in sealed glass tubes. More recently, armored acid dissolution bombs have been commercially available, increasing the safety and convenience of the approach. These devices consist of a Teflon TFE vessel and lid that contain the sample and the acid. This vessel and lid fit snugly in a heavy stainless steel or nickel alloy cannister that screws together to form a sealed reaction bomb that can be conveniently heated in a drying oven.

Typically, a small sample (0.5 g or less) and a small volume of acid (15 mL or less) are reacted for 1 to 4 h at a temperature of 150°C or less, then cooled to room temperature before the vessel is opened. It is possible with such devices to dissolve substances in a type and quantity of acid that would be impossible at atmospheric pressure. Moreover, volatiles that are normally lost in open vessels will be retained. The disadvantages are the danger and inconvenience. Although such bombs are used routinely, the analyst must always be aware that he is dealing with hundreds of atmospheres of pressure, and the manufacturer's instructions must be carefully followed. Also, the heating and cooling processes are time consuming, and it is a rare laboratory that can afford these devices in great quantity. Like microwave dissolution, the acid dissolution bomb offers its best advantage for well-characterized samples that are slow to dissolve in open vessels and for those cases where the dissolution medium is restricted by the requirements of the determination.

Certain sample/solvent combinations are too dangerous for any pressure dissolution approach. Perchloric acid with any sample is one example, and sulfuric and nitric acids with any organic material are another. Too much acid of any kind is another danger. Hydrofluoric and hydrochloric acids, however, are particularly effective under pressure, and sometimes amazing dissolutions occur with a minimum of acid. Method development, however, is often a lengthy process because of the time required for the vessels to heat and cool.

MICROWAVE DISSOLUTIONS

Even more recently, microwave techniques have entered the analytical laboratory, promising a revolution in dissolution procedures. Some facilities have benefitted greatly, while others have been left wondering what all the fuss was about. There are two approaches to microwave dissolution—open vessel and closed vessel techniques. Open vessel techniques offer only a little advantage over hotplate dissolution since the shorter heating times are offset by the time required to load and unload the microwave oven. Closed vessel techniques are essentially a more convenient way to perform pressure dissolutions. But that advantage is partly offset by the pressure limit of the plastic vessels, which is always significantly less than the pressure limit of metal acid dissolution bombs. Clearly, some surprising dissolutions can be routinely performed with a closed vessel microwave oven approach—for example, a high carbon ferrochromium sample will dis-

solve in a small volume of hydrochloric acid. And many daylong dissolutions can be reduced to an hour.

But it is always necessary to consider the loading and unloading times involved, as well as the development time required to establish a procedure. Labs that analyze only a few grades of alloy or ore may find that the microwave approach is a godsend, since they can usually develop one or two short compromise programs applicable to all or most of their workload. However, labs with more complicated requirements may become bogged down in a confusion of complex protocols or find themselves running every sample for 90 min or so, whether such a lengthy program is necessary or not.

Microwave usage usually involves considerable capital investment, whether the lab has opted for the expensive laboratory models that control power by pressure and/or temperature probes, or inexpensive home consumer ovens that corrode from fumes and must be regularly replaced. It is evident that the investment is justified in some cases. However, labs that expect a tremendous increase in sample throughput as a result of introducing microwave oven dissolution may be disappointed. Laboratory managers that view these devices as a supplement and expansion of their current capabilities are much more likely to ultimately feel satisfied.

REFLUX DISSOLUTIONS

One useful alternative to open vessel acid dissolutions is the use of a reflux condenser. In a sense, a beaker watchglass or the Tuttle covers designed for Erlenmeyer flasks are reflux condensers, albeit of limited efficiency. Water-cooled condensers, especially those with sizable internal cooling surface areas like the Allihn and Graham designs, can restrict or eliminate the loss of volatile acids. Many otherwise volatile sample components will also be retained. Thus, with such an apparatus it is frequently possible to dissolve a test portion in a very small amount of acid and to prevent the loss of analytes like boron, arsenic, and antimony, which are easily lost in open beakers.

In a typical arrangement, an Allihn condenser with a ground glass joint is fitted to the ground glass neck of an Erlenmeyer or round-bottomed flask. Sometimes a Teflon sleeve and plastic clip are used to seal and secure the connection. Erlenmeyer flasks are typically heated on small electric hotplates, while round-bottomed flasks are heated with electric heating mantles. The condenser is held in position above the flask with a three-fingered clamp attached to a ringstand or a "monkey-bar" arrangement. When the sample has dissolved, the condenser is rinsed down from the top into the cooled flask. A modified version of this basic arrangement is sometimes used for a different purpose. If the flask mouth is fitted with a side-arm joint, inert gas can be introduced to prevent the oxidation of analyte. Such setups are typically used for the dissolution of samples for ferrous iron and tin determinations.

OTHER STRATEGIES

There are certain other dissolution strategies that are used with acids. Ultrasonic agitation will accelerate reaction rates

and sometimes help to expose undissolved sample particles to the acid if a compound has precipitated. Leaching techniques in which the analyte is dissolved but a major portion of the test portion remains untouched have been applied to calcium compounds in slags and cement (as discussed under HCl earlier in this chapter), among other analytes and sample types. Such approaches, in general, must be applied only to finely divided samples and always with cautious analytical judgement. The use of acids to "wet ash" organic materials for inorganic analysis will be discussed in the next chapter since the general topic of the decomposition of organics arguably constitutes a separate subject. Acids are also employed in some inclusion isolations, and, again, discussion is deferred to where that field is treated in the next chapter.

REFERENCES

Annual Book of ASTM Standards, Vol. 03.05, American Society for Testing and Materials, Philadelphia, 1992, Standards E 46 and E 50.

Beamish, F. E., *The Analytical Chemistry of the Noble Metals*, Pergamon Press, Oxford, 1966, pp. 1–4.

Bock, R., *A Handbook of Decomposition Methods in Analytical Chemistry*, John Wiley & Sons, New York, 1979.

Churchill, H. V. and Bridges, R. W., *Chemical Analysis of Aluminum*, Aluminum Company of America, New Kensington, PA, 1935, pp. 6–7.

Dolezal, J., Povondra, P., and Sulcek, Z., *Decomposition Techniques in Inorganic Analysis*, American Elsevier Publishing Co., New York, 1966.

Elwell, W. T. and Wood, D. F., *Analysis of the New Metals, Titanium, Zirconium, Hafnium, Niobium, Tantalum, Tungsten and their Alloys*, Pergamon Press, Oxford, 1966.

Hobart, E. W. and Kallmann, S., "Dissolution of Metals for Analysis," *Some Fundamentals of Analytical Chemistry, ASTM STP 564*, American Society for Testing and Materials, Philadelphia, 1974, pp. 68–72.

Hofton, M. E. and Baines, S., British Steel Corp. Open Report GS/EX/42/72/C, British Steel Corp., Sheffield, U.K., 1975.

Lange's Handbook of Chemistry, 11th ed., J. Dean, Ed., McGraw-Hill, New York, 1973.

Lundell, G. E. F. and Hoffman, J. I., *Outlines of Methods of Chemical Analysis*, John Wiley & Sons, New York, 1938.

Murau, P. C., *Analytical Chemistry*, Vol. 33, No. 8, 1961, pp. 1125–1126.

Povondra, P. and Sulcek, Z., *Methods of Decomposition in Inorganic Analysis*, CRC Press, Boca Raton, FL, 1989.

Van Nostrand's Scientific Encyclopedia, 4th ed., D. Van Nostrand, Princeton, NJ, 1968.

Zehr, B., *American Laboratory*, December 1992, pp. 24–29.