

1.2.3 Sampling

The most important single step in an analysis is collecting the sample of the material to be analyzed. Real materials are usually not homogeneous, so the sample must be chosen carefully to be **representative** of the real material. A representative sample is one that reflects the true value and distribution of the analyte in the original material. If the sample is not taken properly, no matter how excellent the analytical method or how expert the analyst, the result obtained will not provide a reliable characterization of the material. Other scientists, law enforcement officials, and medical professionals often collect samples for analysis, sometimes with no training in how to take a proper sample. The analytical chemist ideally would be part of the team that discusses collection of samples before they are taken, but in reality, samples often "show up" in the lab. It is important that the analyst talks with the sample collector before doing any analyses; if the sample has been contaminated or improperly stored, the analysis will be not only a waste of time but can also lead to erroneous conclusions. In clinical chemistry analysis, this could lead to a misdiagnosis of a disease condition; in forensic analysis, this could lead to a serious miscarriage of justice.

if sample is not taken properly especially in

The amount of sample taken must be sufficient for all analyses to be carried out in duplicate or triplicate, if possible. Of course, if only a small quantity of sample is available, as may be the case for forensic samples from a crime scene or rocks brought back from the moon, the analyst must do the best job possible with what is provided.

A good example of the problems encountered in sampling real materials is collecting a sample of a metal or metal alloy. When a molten metal solidifies, the first portion of solid to form tends to be the most pure (remember freezing point depression from your general chemistry class?). The last portion to solidify is the most impure and is generally located in the center or *core* of the solidified metal. It is important to bear this in mind when sampling solid metals. A sample is often ground from a representative cross section of the solid, or a hole is drilled through a suitable location and the drillings mixed and used as the sample.

Samples have to be collected using some type of collection tool and put into some type of container. These tools and containers can often contaminate the sample. For example, stainless steel needles can add traces of metals to blood or serum samples. Metal spatulas, scissors, drill bits, glass pipettes, filter paper, and plastic and rubber tubing can add unwanted inorganic and organic contaminants to samples. To avoid iron, nickel, and chromium contamination from steel, some implements like tongs and tweezers can be purchased with platinum or gold tips.

The discussion of sampling, which follows, refers to the traditional process of collecting a sample at one location (often called "collection in the field") and transporting the sample to the laboratory at a different location. Today, it is often possible to analyze samples *in situ* or during the production of the material (online or process analysis) with suitable instrumental probes, completely eliminating the need for "collecting" a sample. Examples of *in situ* and online analysis and field portable instruments will be discussed in later chapters.

The process of sampling requires several steps, especially when sampling bulk materials such as coal, metal ore, soil, grain, and tank cars of oil or chemicals. First, a *gross representative sample* is gathered from the *lot*. The lot is the total amount of material available. Portions of the gross sample should be taken from various locations within the lot to ensure that the gross sample is representative. For very large lots of solid material such as coal or ore, the *long pile and alternate shovel* method can be used. The material is formed into a long rectangular pile. It is then separated into two piles by shoveling material first to one side and then to the other, creating two piles. One pile is set aside. The remaining pile may be reduced in size by repeating the process, until a sample of a size to be sent to the laboratory remains. The cone and quarter method is also used to collect a gross sample of solid materials. The sample is made into a circular pile and mixed well. It is then separated into quadrants. A second pile is made up of two opposite quadrants, and the remainder

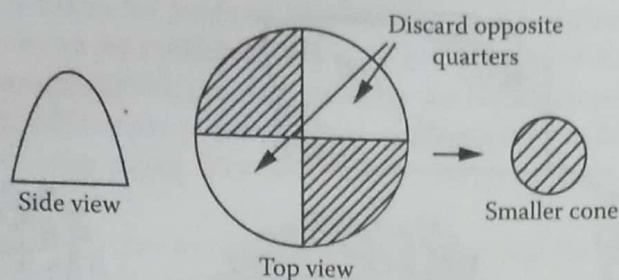


Figure 1.3 The cone and quarter method of sampling bulk materials.

of the first pile discarded. This process is shown in Figure 1.3. This process can be repeated until a sample of a suitable size for analysis is obtained. This sample can still be very large. Ferroalloys, for example, are highly segregated (i.e., inhomogeneous) materials; it is not uncommon for the amount required for a representative sample of alloy in pieces about 2 in. in diameter to be 1 ton (0.9 Mg) of material from the lot of alloy.

A computer program that generates random numbers can choose the sampling locations and is very useful for environmental and agricultural sampling. If the lot is a field of corn, for example, the field can be divided into a grid, with each grid division given a number. The computer program can pick the random grid divisions to be sampled. Then a smaller, homogeneous *laboratory sample* is prepared from the gross composite sample. If the sample is segregated (i.e., highly inhomogeneous), the representative sample must be a composite sample that reflects each region and its relative amount. This is often not known, resulting in the requirement for very large samples. The smaller laboratory sample may be obtained by several methods but must be representative of the lot and large enough to provide sufficient material for all the necessary analyses. After the laboratory sample is selected, it is usually split into even smaller *test portions*. Multiple small test portions of the laboratory sample are often taken for replicate analyses and for analysis by more than one technique. The term **aliquot** is used to refer to a quantitative amount of a *dissolved* test portion; for example, a 0.100 g test portion of sodium chloride may be dissolved in water in a volumetric flask to form 100.0 mL of test solution. Three 10.0 mL aliquots may be taken with a volumetric pipette for triplicate analysis for chloride using an ion-selective electrode, for example.

As the total amount of the sample is reduced, it should be broken down to successively smaller pieces by grinding, milling, chopping, or cutting. The 1 ton sample of ferroalloy, for example, must be crushed, ground, and sieved many times. During the process, the sample size is reduced using a sample splitter called a **riffle**. After all this and then a final **drying step**, a 1 lb (454 g) sample remains. The sample must be mixed well during this entire process to ensure that it remains representative of the original. The grinding equipment used must not contaminate the sample. For example, boron carbide and tungsten carbide are often used in grinding samples because they are very hard materials, harder than most samples. However, they can contribute boron or tungsten to the ground sample, so would not be used if boron or tungsten must be measured at low concentrations. Zirconium oxide ball mills can contribute Zr and Hf to a sample. Stainless steel grinders are a source of Fe, Cr, and Ni. Some cutting devices use organic fluids as lubricants; these must be removed from the sample before analysis.

It is also possible for the grinding or milling step to cause erroneously low results for some analytes. Malleable metals like gold may adhere to the grinding or milling surface and be removed from the sample in the process, an undesirable effect. An example of sampling a segregated material with a problematic component like gold is illustrated in Figure 1.4. The rectangular piece at the top is a hypothetical piece of gold-bearing quartz. The gold is represented as the dark flecks. You can see that the gold appears in bands within the quartz, separated by bands of pure quartz

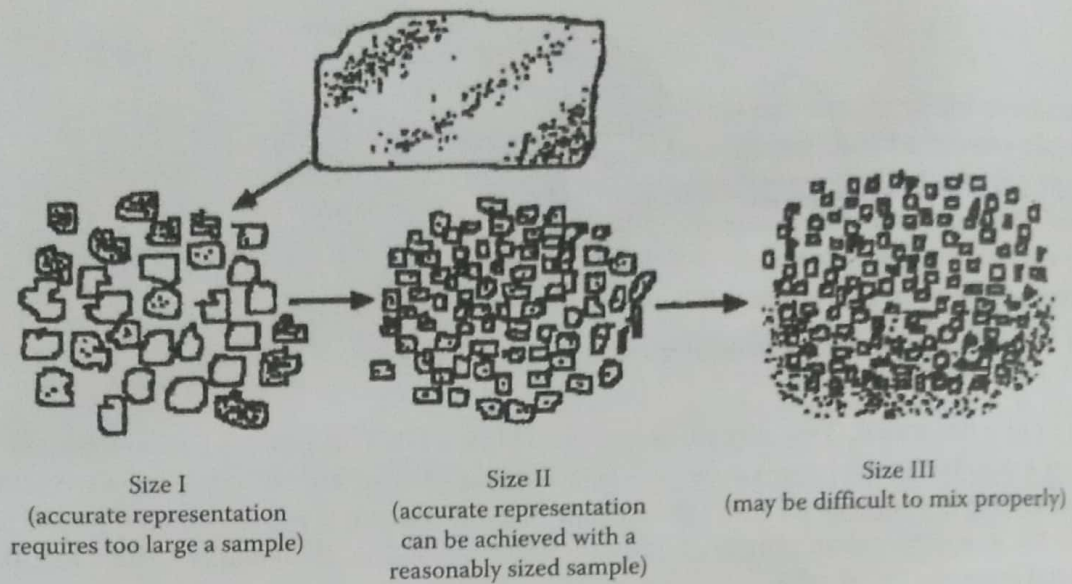


Figure 1.4 Sampling of a segregated material with a problematic component like gold. (Extracted from Dulski, T.R., *A Manual for the Chemical Analysis of Metals*, ASTM International, West Conshohocken, PA, 1996. With permission. Copyright 1996 ASTM International.)

(the white area). If the rock is crushed to Size I, the gold particles have not been liberated from the quartz; some pieces have gold flecks and many large pieces are pure quartz. At this size, it is difficult to remove a sample of the rock pieces and expect it to be representative. If the rock is crushed to a smaller size, Size II, it is evident that a representative small sample can be obtained. If the rock is crushed to Size III, the gold particles are freed from the quartz matrix. If this sample could be mixed perfectly, a smaller sample could be taken to represent the whole than the sample needed at Size II. (Why would this be desirable? The smaller the analytical sample, the less gold is used up by analysis. This is an important consideration with valuable analytes and valuable samples.) But the gold particles and the quartz particles have different densities and shapes and will be difficult to mix well. As mentioned earlier, gold is soft and malleable. If it is broken out of the quartz, it may become embedded in the grinder or smeared onto surfaces in the grinding equipment, so some gold may actually be lost from the sample particles ground to Size III. Size II will give a more representative sample than either of the other sizes.

Sampling procedures for industrial materials, environmental samples, and biological samples are often agreed upon, or *standardized*, by industry, government, and professional societies. Standard sampling procedures help to ensure that the samples analyzed are representative and are not contaminated or changed during the sampling process. Standard sampling procedures for many materials can be found in the *Annual Book of ASTM Standards*, for example. Sampling procedures for soil, water, and air are established by the US EPA in the United States and similar government organizations in other countries. Procedures for sampling of water and wastewater can be found in *Standards Methods for the Analysis of Water and Wastewater*; the AOAC publishes procedures for food products. The bibliography provides some examples of these publications. A good analytical chemist will consult the literature before sampling an unfamiliar material. Some general guidelines for sampling different classes of materials are discussed here.

1.2.3.1 Gas Samples

Gas samples are generally considered homogeneous, but gas mixtures may separate into layers of differing density. Samples that have been collected and allowed to settle will need to be

stirred before a portion is taken for analysis. Gas samples can be taken at a single point in time (called a **grab** sample) or can be collected over a period of time or from different locations to provide an *average* or **composite** sample. Gas samples can be collected using gas-tight syringes, balloons, plastic bags, or containers made of metal or glass that can be evacuated. Sampling of toxic, flammable, or corrosive gases should be done with great care using appropriate safety equipment.

The containers used to collect the samples must not contaminate the sample with analyte. Plastic bags and balloons may leach volatile organic compounds into the gas sample, while glass may adsorb components of the sample onto the surface of the glass.

Certain components of gas samples, such as organic vapors in air, may be collected by pulling the air through activated charcoal. The organic gases are adsorbed onto the charcoal, while the majority of the air (oxygen, nitrogen, etc.) passes through. This has the advantage of *preconcentrating* the analytes of interest and reducing the physical size of the sample. Many liters of air can be pulled through an activated charcoal bed that is no bigger than a ball-point pen. It is much easier to transport the analytes trapped on the charcoal to the laboratory than to transport hundreds of liters of air. The process of trapping an analyte out of the gas phase is called "scrubbing." Scrubbing a gas sample can also be done by bubbling the gas through a liquid that will absorb the analytes of interest.

Gas samples may contain particles of solid material that need to be removed by filtration. The filter material must be chosen so that it does not adsorb analytes or add contaminants to the gas. Filters are available that will remove particles as small as 0.2 μm in diameter from a gas stream.

1.2.3.2 Liquid Samples

Liquid samples can also be collected as grab samples or as composite samples. Sampling liquids can be quite difficult; it is not always as straightforward as "pouring some" out of a bottle or dipping a bucket into a fluid. Only a few comments with respect to general sampling of liquids can be made here. It is usual to stir liquid samples adequately to obtain a representative sample; however, there may be occasions when stirring is not desired. If the analyst is only interested in identifying an oily layer floating on water, stirring the sample is not needed; the oily layer may be pulled off with a pipette or an eyedropper, for example. Samples must be collected at locations remote from sources of contamination if a representative sample is desired. For example, if a sample of "normal" river water is desired, the sample should be collected away from riverbanks, floating froth, oil, and discharges from industrial and municipal waste treatment sites. Sampling of rivers, lakes, and similar bodies of water may require samples from different depths or different distances from shore. Such samples may be analyzed individually or blended to obtain an average composition.

Liquid samples may contain particles of solid material that need to be removed by filtration or centrifugation. The filter material must be chosen so that it does not adsorb analytes or contaminate the liquid. Some samples that are mostly liquid contain suspended solid material; orange juice and liquid antacids are examples. In these types of samples, the liquid and its associated solids may need to be sampled for analysis without removing the solids. It may be difficult to obtain a representative sample from these suspensions; a standard sampling procedure is needed to ensure that results can be compared from one day to the next. Liquid samples may consist of more than one layer because they contain two or more **immiscible** liquids. Examples include samples of oil and water from an oil spill at sea, oil and vinegar salad dressing, or cream at the top of a bottle of milk. The layers may need to be *emulsified* to provide a representative sample, but it may be more useful to sample each layer separately.

Sampling of hot molten materials such as metals, alloys, and glasses is a form of liquid sampling, but one requiring very specialized equipment and techniques.

1.2.3.3 Solid Samples

Solid samples are often the most difficult to sample because they are usually less homogeneous than gases or liquids. Large amounts of solid sample cannot be conveniently "stirred up." Moreover, unlike the situation with fluids, there are no diffusion or convection currents in solids to ensure mixing. Solids must often be ground or drilled or crushed into smaller particles to homogenize the sample. There are many types of manual and automated grinders and crushers available; the choice depends on the hardness of the material to be ground. Soft materials also pose a challenge in grinding because they often just deform instead of being reduced in size. Polymer pellets may be ground in an electric coffee grinder with a small amount of liquid nitrogen added to the grinder (called cryogrinding). The liquid nitrogen freezes the polymer, making the pellets brittle and capable of being easily powdered. Other soft solids such as foods can be handled the same way. Commercial cryomills that prevent the user from coming into contact with liquid nitrogen are available. Many solid materials must be oven-dried before sampling to remove adsorbed water in order to obtain a representative sample. There are numerous published standard methods for sampling solid materials such as cement, textiles, food, soil, ceramics, and other materials. Examples of the wide variety of analytical pulverizing, grinding, and blending equipment available can be found at the following websites: SpexCertiprep (www.spexcsp.com), Retsch (www.retsch.com), and Netzsch (www.netzsch.com), among others.

1.2.4 Storage of Samples

When samples cannot be analyzed immediately, they must be stored. The composition of a sample may change during storage because of reactions with air, light, or interaction with the container material. The container used for collection and storage of the sample and the storage conditions must be chosen to minimize changes in the sample.

Plastic containers may leach organic components such as plasticizers and monomers into a sample. Plastic containers may also introduce trace metal impurities such as Cu, Mn, or Pt from the catalysts used to make the polymer or elements such as Si, Ti, Sb, Br, and P from inorganic fillers and flame retardants. Glass surfaces both adsorb and release trace levels of ionic species, which can dramatically change the trace element and trace ion concentrations in solutions. It has been observed that trace metals will "plate out" of solution along strain lines in glass. Such strain lines are not reproducible from one container to another; therefore, the loss of trace metals cannot be estimated accurately for one container by measuring the loss in a similar but different container. All containers require appropriate cleaning before use. Containers for organic samples are usually washed in solvent, while containers for samples for trace metal analysis are soaked in acid and then in deionized (DI) water.

Precautions such as freezing biological and environmental samples or displacing the air in a container by an inert gas will often extend the storage life of a sample. Samples should not be stored any longer than is absolutely necessary prior to analysis and should not be stored under conditions of high heat or high humidity. Some samples require storage in the dark to avoid photolytic (light-induced) changes in composition; water samples to be analyzed for silver are a good example. Such samples must be stored in dark plastic bottles to avoid the photolytic formation of colloidal silver, which will precipitate out of the sample. Many samples for environmental analysis require the addition of preservatives or adjustment of pH to prevent the sample from deteriorating. Water samples for trace metals determination must be acidified with high-purity nitric acid to keep the trace metals in solution, for example. Blood samples often require collection in tubes containing an anticoagulant to keep the blood sample fluid, but the anticoagulant must not interfere in the analysis. For example, a sample collected to measure a patient's sodium level cannot be collected in a tube that contains the sodium salt of ethylenediaminetetraacetic acid (EDTA) as the anticoagulant. Other biological samples may need to be collected in sterile containers.

1.4 SAMPLE PREPARATION

Few samples in the real world can be analyzed without some chemical or physical preparation. The aim of all sample preparation is to provide the analyte of interest in the physical form required by the instrument, free of interfering substances, and in the concentration range required by the instrument. For many instruments, a solution of analyte in organic solvent or water is required. We have already discussed some of the sample preparation steps that may be needed. Solid samples may need to be crushed or ground, or they may need to be washed with water, acid, or solvent to remove surface contamination. Liquid samples with more than one phase may need to be extracted or separated. Filtration or centrifugation may be required.

If the physical form of the sample is different from the physical form required by the analytical instrument, more elaborate sample preparation is required. Samples may need to be dissolved to form a solution or pressed into pellets or cast into thin films or cut and polished smooth. The type of sample preparation needed depends on the nature of the sample, the analytical technique chosen, the analyte to be measured, and the problem to be solved. Most samples are not homogeneous. Many samples contain components that interfere with the determination of the analyte. A wide variety of approaches to sample preparation has been developed to deal with these problems in real samples. Only a brief overview of some of the more common sample preparation techniques is presented. More details are found in the chapters on each instrumental method.

Note: None of the sample preparation methods described here should be attempted without approval, written instructions, and close supervision by your professor or laboratory instructor. The methods described present many potential hazards. Many methods use concentrated acids, flammable solvents, and/or high temperatures and high pressures. Reactions can generate harmful gases. The potential for "runaway reactions" and even explosions exists with preparation of real samples. Sample preparation should be performed in a laboratory fume hood for safety. Goggles, lab coats or aprons, and gloves resistant to the chemicals in use should be worn at all times in the laboratory.

1.4.1 Acid Dissolution and Digestion

Metals, alloys, ores, geological samples, ceramics, and glass react with concentrated acids, and this approach is commonly used for dissolving such samples. Organic materials can be decomposed (digested or "wet ashed") using concentrated acids to remove the carbonaceous material and solubilize the trace elements in samples such as biological tissues, foods, and plastics. A sample is generally weighed into an open beaker, concentrated acid is added, and the beaker heated on a hot plate until the solid material dissolves. Dissolution often is much faster if the sample can be heated at pressures greater than atmospheric pressure. The boiling point of the solvent is raised at elevated pressure, allowing the sample and solvent to be heated to higher temperatures than can be attained at atmospheric pressure. This can be done in a sealed vessel, which also has the advantage of not allowing volatile elements to escape from the sample. Special stainless steel high-pressure vessels, called "bombs," are available for acid dissolution and for the combustion of organic samples under oxygen. While these vessels do speed up the dissolution, they operate at pressures of hundreds of atmospheres and can be very dangerous if not operated properly. Another sealed vessel digestion technique uses **microwave digestion**. This technique uses sealed sample vessels made of polymer, which are heated in a specially designed laboratory microwave oven. (*Never* use a kitchen-type microwave oven for sample preparations. The electronics in kitchen-type units are not protected from corrosive fumes, arcing can occur, and the microwave source, the magnetron, can easily overheat and burn out.) The sealed vessel microwave digestion approach keeps volatile elements in solution, prevents external contaminants from falling into the sample, and is much faster than digestion on a hot plate in an open beaker. Microwave energy efficiently heats solutions of polar molecules (such as water) and ions (aqueous mineral acids) and samples that contain polar molecules and/or ions. In addition, the sealed vessel results in increased pressure and increased boiling point. Commercial analytical microwave digestion systems for sealed vessel digestions are shown in Figure 1.6.

The acids commonly used to dissolve or digest samples are hydrochloric acid (HCl), nitric acid (HNO₃), and sulfuric acid (H₂SO₄). These acids may be used alone or in combination. The choice of acid or acid mix depends on the sample to be dissolved and the analytes to be measured. The purity of the acid must be chosen to match the level of analyte to be determined. Very-high-purity acids



(a)



(b)

Figure 1.6 (a, b) Commercial analytical microwave digestion systems for sealed vessel digestions. (Courtesy of CEM Corporation, Matthews, NC. www.cem.com.)

for work at ppb or lower levels of elements are commercially available but are much more expensive than standard reagent grade acid. For special applications, perchloric acid (HClO_4) or hydrofluoric acid (HF) may be required. A student should never use HClO_4 or HF without specific training from an experienced analytical chemist and only then under close supervision. While a mixture of HNO_3 and HClO_4 is extremely efficient for wet ashing organic materials, HClO_4 presents a very serious explosion hazard. Specially designed fume hoods are required to prevent HClO_4 vapors from forming explosive metal perchlorate salts in the hood ducts, and reactions of hot HClO_4 with organic compounds can result in violent explosive decompositions. A blast shield should be used, and the organic sample must first be heated with HNO_3 alone to destroy easily oxidized material before the HClO_4 is added. Concentrated HF is used for dissolving silica-based glass and many refractory metals such as tungsten, but it is extremely dangerous to work with. It causes severe and extremely painful deep tissue burns that do not hurt immediately upon exposure. However, delay in treatment for HF burns can result in serious medical problems and even death from contact with relatively small amounts of acid.

HCl is the most commonly used nonoxidizing acid for dissolving metals, alloys, and many inorganic materials. HCl dissolves many materials by forming stable chloride complexes with the dissolving cations. There are two major limitations to the universal use of HCl for dissolution. Some elements may be lost as volatile chlorides; examples of volatile chlorides include arsenic, antimony, selenium, and germanium. Some chlorides are not soluble in water; the most common insoluble chloride is silver chloride, but mercurous chloride, cuprous chloride, BiOCl , and AuCl_3 are not soluble, while PbCl_2 and TlCl are only partially soluble. A 3:1 mixture of HCl and HNO_3 is called *aqua regia* and has the ability to dissolve gold, platinum, and palladium. The mixture is also very useful for stainless steels and many specialty alloys.

HNO_3 is an oxidizing acid; it has the ability to convert the solutes to higher oxidation states. It can be used alone for dissolving a number of elements, including nickel, copper, silver, and zinc. The problem with the use of HNO_3 by itself is that it often forms an insoluble oxide layer on the surface of the sample that prevents continued dissolution. For this reason, it is often used in combination with HCl, H_2SO_4 , or HF. A mixture of HNO_3 and H_2SO_4 or HNO_3 and HClO_4 can be used to destroy the organic material in an organic sample, by converting the carbon and hydrogen to CO_2 and H_2O when the sample is heated in the acid mixture. The trace metals in the sample are left in solution. This use of acids to destroy organic matter is called wet ashing or digestion, as has been noted. H_2SO_4 is a strong oxidizing acid and is very useful in the digestion of organic samples. Its main drawback is that it forms a number of insoluble or sparingly soluble sulfate salts.

HF is a nonoxidizing, complexing acid like HCl. Its most important attribute is that it dissolves silica-based substances like glass and many minerals. All or most of the silicon is volatilized on heating with sufficient HF. Glass beakers and flasks cannot be used to hold or store even dilute HF. Teflon or other polymer labware and bottles are required. Commercial "heatable" Teflon beakers with graphite bottoms are available for use on hot plates. HF is used in acid mixtures to dissolve many refractory elements and minerals by forming fluoride complexes; such elements include tungsten, titanium, niobium, and tantalum. Some elements can be lost as volatile fluorides (e.g., Si, B, As, Ge, and Se). There are a number of insoluble fluoride compounds, including most of the alkaline-earth elements (Ca, Mg, Ba, and Sr) and the rare-earth elements (lanthanides). Table 1.11 gives examples of some typical acid digestions.

Some bases, such as sodium hydroxide and tetramethylammonium hydroxide, are used for sample dissolution, as are some reagents that are not acids or bases, like hydrogen peroxide. The chemical literature contains sample dissolution procedures for virtually every type of material known and should be consulted. For elements and inorganic compounds, the *CRC Handbook of Chemistry and Physics* gives guidelines for dissolution in the tables of physical properties of inorganic compounds.

Table 1.11 Common Acid Dissolutions of Metals, Alloys, and Materials for Inorganic Compositional Analysis

Material ^a	Total Volume of Reagent (mL)	Reagent (vol:vol)
<i>Elements</i>		
Copper metal	20	1:1 HNO ₃ /H ₂ O
Gold metal	30	3:1 HCl/HNO ₃
Iron metal	20	1:1 HCl/H ₂ O
Titanium metal	20	H ₂ SO ₄ , 3–5 drops HNO ₃
Zinc metal	20	HCl
Zirconium metal	15	HF
<i>Alloys</i>		
Copper alloys	30	1:1 HNO ₃ /H ₂ O
Low alloy steels	20	3:1 HCl/HNO ₃
Stainless steels	30	1:1 HNO ₃ /HCl
Titanium alloys	100	1:1 HCl/H ₂ O, 3–5 drops HNO ₃
Zinc alloys	30	1:1 HCl/H ₂ O, dropwise HNO ₃
Zirconium alloys	40	1:1 H ₂ SO ₄ /H ₂ O, 2 mL HF dropwise
<i>Other materials</i>		
Borosilicate glass	12	10 mL HF + 2 mL 1:1 H ₂ SO ₄ /H ₂ O
Dolomite	40	1:1 HCl/H ₂ O
Gypsum	50	1:1 HCl/H ₂ O
Portland cement	20	HCl + 3 g NH ₄ Cl
Silicate minerals	30	10 mL HF + 20 mL HNO ₃
Titanium dioxide	15	HF
Zinc oxide	15	1:1 HCl/H ₂ O

Source: Extracted from Dulski, T.R., *A Manual for the Chemical Analysis of Metals*, ASTM International, West Conshohocken, PA, 1996. With permission. Copyright 1996 ASTM International.

Note: "Dropwise" means add drop by drop until dissolution is complete.

^a 1 g test portion is used; warm to complete reaction.

1.4.2 Fusions

Heating a finely powdered solid sample with a finely powdered salt at high temperatures until the mixture melts is called a fusion or molten salt fusion. The reacted and cooled melt is leached with water or dilute acid to dissolve the analytes for determination of elements by atomic spectroscopy or ICP-MS. Often, the molten fusion mixture is poured into a flat-bottomed mold and allowed to cool. The resulting glassy disk is used for quantitative XRF measurements. Molten salt fusions are useful for the dissolution of silica-containing minerals, glass, ceramics, ores, human bone, and many difficultly soluble materials like carbides and borides. The salts used (called "fluxes") include sodium carbonate, borax (sodium tetraborate), lithium metaborate, and sodium peroxide. The fusions are carried out over a burner or in a muffle furnace in crucibles of the appropriate material. Depending on the flux used and the analytes to be measured, crucibles may be made of platinum, nickel, zirconium, porcelain, quartz, or glassy carbon. Automated "fluxers" are available that will fuse up to six samples at once and pour the melts into XRF molds or into beakers, for laboratories that perform large numbers of fusions. The drawback of fusion is that the salts used as fluxes can introduce many trace element contaminants into the sample, the crucible material itself may contaminate the sample, and the elements present in the flux itself cannot be analytes in the sample. Fusion cannot

Table 1.12 Molten Salt Fusions of Materials

Material ^a	Dissolution Procedure
Bauxite	2 g Na ₂ CO ₃ ; Pt c&l
Corundum	3 g Na ₂ CO ₃ + 1 g H ₃ BO ₃ ; Pt c&l
Iron ores	5 g Na ₂ O ₂ + 5 g Na ₂ CO ₃ ; Zr c&l
Niobium alloys	10 g K ₂ S ₂ O ₇ ; fused silica crucible
Silicate minerals	10 g 1:1 Na ₂ CO ₃ :Na ₂ B ₄ O ₇ ; Pt c&l
Tin ores	10 g Na ₂ O ₂ + 5 g NaOH; Zr c&l
Titanium ores	7 g NaOH + 3 g Na ₂ O ₂ ; Zr c&l
Tungsten ores	8 g 1:1 Na ₂ CO ₃ /K ₂ CO ₃ ; Pt c&l

Source: Extracted from Dulski, T.R., *A Manual for the Chemical Analysis of Metals*, ASTM International, West Conshohocken, PA, 1996. With permission. Copyright 1996 ASTM International.

Note: c&l, crucible and lid.

^a 1 g test portion is used.

be used for boron determinations if the flux is borax or lithium metaborate, for example. Platinum crucibles cannot be used if trace levels of platinum catalyst are to be determined. Table 1.12 gives examples of typical fusions employed for materials.

1.4.3 Dry Ashing and Combustion

To analyze organic compounds or substances for the inorganic elements present, it is often necessary to remove the organic material. Wet ashing with concentrated acids has been mentioned as one way of doing this. The other approach is "dry ashing," that is, ignition of the organic material in air or oxygen. The organic components react to form gaseous carbon dioxide and water vapor, leaving the inorganic components behind as solid oxides. Ashing is often done in a crucible or evaporating dish of platinum or fused silica in a muffle furnace. Volatile elements will be lost even at relatively low temperatures; dry ashing cannot be used for the determination of mercury, arsenic, cadmium, and a number of other metals of environmental and biological interest for this reason. Oxygen bomb combustions can be performed in a high-pressure steel vessel very similar to a bomb calorimeter. One gram or less of organic material is ignited electrically in a pure oxygen atmosphere with a small amount of absorbing solution such as water or dilute acid. The organic components form carbon dioxide and water and the elements of interest dissolve in the absorbing solution. Combustion in oxygen at atmospheric pressure can be done in a glass apparatus called a *Schöniger flask*. The limitation to this technique is sample size; no more than 10 mg sample can be burned. However, the technique is used to obtain aqueous solutions of sulfur, phosphorus, and the halogens from organic compounds containing these heteroatoms. These elements can then be determined by ion-selective potentiometry, IC, or other methods.