

13 SAMPLE DISSOLUTION

13.1 Introduction

The overall success of any analytical procedure depends upon many factors, including proper sample preparation, appropriate sample dissolution, and adequate separation and isolation of the target analytes. This chapter describes sample dissolution techniques and strategies. Some of the principles of dissolution are common to those of radiochemical separation that are described in Chapter 14 (*Separation Techniques*), but their importance to dissolution is reviewed here.

Sample dissolution can be one of the biggest challenges facing the analytical chemist, because most samples consist mainly of unknown compounds with unknown chemistries. There are many factors for the analyst to consider: What are the measurement quality objectives of the program? What is the nature of the sample; is it refractory or is there only surface contamination? How effective is the dissolution technique? Will any analyte be lost? Will the vessel be attacked? Will any of the reagents interfere in the subsequent analysis or can any excess reagent be removed? What are the safety issues involved? What are the labor and material costs? How much and what type of wastes are generated? The challenge for the analyst is to balance these factors and to choose the method that is most applicable to the material to be analyzed.

The objective of sample dissolution is to mix a solid or nonaqueous liquid sample quantitatively with water or mineral acids to produce a homogeneous aqueous solution, so that subsequent separation and analyses may be performed. Because very few natural or organic materials are water-soluble, these materials routinely require the use of acids or fusion salts to bring them into solution. These reagents typically achieve dissolution through an oxidation-reduction process that leaves the constituent elements in a more soluble form. Moreover, because radiochemists routinely add carriers or use the technique of isotope dilution to determine certain radioisotopes, dissolution helps to ensure exchange between the carrier or isotopic tracer and the element or radioisotope to be determined, although additional chemical treatment might be required to ensure exchange.

There are three main techniques for sample decomposition discussed in this chapter: fusion; wet ashing, acid leaching, or acid dissolution; and microwave digestion.

The choice of technique is determined by the type of sample and knowledge of its physical and chemical characteristics. Fusion and wet ashing techniques may be used singly or in combination to decompose most samples analyzed in radioanalytical laboratories.

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Leaching techniques are used to determine the soluble fraction of the radionuclide of interest under those specific leaching conditions. Different formulas for leaching agents will yield different amounts of leachable analyte. It should be recognized that the information so obtained leaves unknown the total amount of analyte present in the sample. Because recent advances in microwave vessel design (e.g., better pressure control and programmable temperature control) have allowed for the use of larger samples, microwave dissolution is becoming an important tool in the radiochemistry laboratory. Leaching and the newer closed-vessel microwave methods provide assurance that only minimal analyte loss will occur through volatilization.

Because of the potential for injury and explosions during sample treatment, it is essential that proper laboratory safety procedures be in place, the appropriate safety equipment be available, a safe work space be provided, and that the laboratory personnel undergo the necessary training to ensure a safe working environment before any of these methods are used. Review the Material Data Safety Sheets for all chemicals before their use.

Aspects of proper sample preparation, such as moisture removal, oxidation of organic matter, and homogenization, were discussed in Chapter 12, *Laboratory Sample Preparation*. Fundamental separation principles and techniques, such as complexation, solvent extraction, ion exchange, and co-precipitation, are reviewed in Chapter 14, *Separation Techniques*.

There are many excellent references on sample dissolution (e.g., Bock, 1979; Bogen, 1978; Dean, 1995; Sulcek and Povondra, 1989).

13.2 The Chemistry of Dissolution

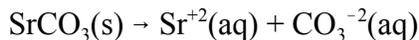
In order to dissolve a sample completely, each insoluble component must be converted into a soluble form. Several different chemical methods may need to be employed to dissolve a sample completely; usually, the tracer is added to the sample at the time of sample dissolution. Initially the sample may be treated with acids yielding an insoluble residue. The residue may need to be dissolved using fusion or hydrofluoric acid (HF) and then combined with the original mixture or analyzed separately. In either case, the tracer/carrier should be added to the sample during the first step of chemical change (e.g., acid dissolution as above) so that the yield for the entire process may be determined accurately. An outline of the principles of these chemical methods is provided in this section, but a complete description is available in Chapter 14, where the principles are applied to a broader range of topics.

13.2.1 Solubility and the Solubility Product Constant, K_{sp}

The solubility data of many compounds, minerals, ores, and elements are available in reference manuals. Solubilities typically are expressed in grams of substance per 100 mL of solvent, although other units are sometimes used. The information is more complete for some substances

than others, and for many substances solubility is expressed only in general terms, such as “soluble,” “slightly soluble,” or “insoluble.” Many environmental samples consist of complex mixtures of elements, compounds, minerals, or ores, most of which are insoluble and must be treated chemically to dissolve completely. In some cases, the sample constituents are known to the analyst, but often they are not. Solubility data might not be available even for known constituents, or the available data might be inadequate. Under these circumstances, sample dissolution is not a simple case of following the solubilities of known substances. For known constituents with solubility data, the solubilities indicate those that must be treated to complete dissolution. This, in turn, provides a guide to the method of treatment of the sample. Given the potential complexity of environmental samples, it is difficult to describe conditions for dissolving all samples. Sometimes one method is used to dissolve one part of the sample while another is used to dissolve the residue.

The solubility of many compounds in water is very low, on the order of small fractions of a grams per 100 mL. The solubility may be expressed by a solubility product constant (K_{sp}), an equilibrium constant for dissolution of the compound in water (see Section 14.8.3.1, “Solubility and Solubility Product Constant”). For example, the solubility product constant for strontium carbonate, a highly insoluble salt (0.0006 g/100 mL), is the equilibrium constant for the process:



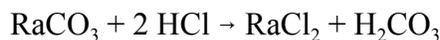
and is represented by:

$$K_{sp} = [\text{Sr}^{+2}][\text{CO}_3^{-2}] = 1.6 \times 10^{-9}$$

The brackets indicate the molar concentration (moles/liter) of the respective ions dissolved in water. The very small value of the constant results from the low concentration of dissolved ions, and the compound is referred to as “insoluble.” Chemical treatment is necessary sometimes to dissolve the components of a compound in water. In this example, strontium carbonate requires the addition of an acid to solubilize Sr^{+2} . The next section describes chemical treatment to dissolve compounds.

13.2.2 Chemical Exchange, Decomposition, and Simple Rearrangement Reactions

Chemical exchange, decomposition, and simple rearrangement reactions refer to one method for solubilizing components of a sample. In this chemical process, the sample is treated to convert insoluble components to a soluble chemical species using chemical exchange (double displacement), decomposition, or simple rearrangement reactions rather than oxidation-reduction processes or complex formations. Some reagents solubilize sample components using chemical exchange. Radium or strontium cations in radium or strontium carbonate (RaCO_3 or SrCO_3) exchange the carbonate anion for the chloride ion on acid treatment with HCl to produce the soluble chlorides; the carbonic acid product decomposes to carbon dioxide and water:

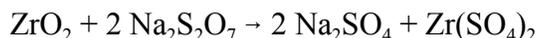




and the net reaction is as follows:



Sodium pyrosulfate fusion, for example, converts zirconia (ZrO_2) into zirconium sulfate [$\text{Zr}(\text{SO}_4)_2$], which is soluble in acid solution by a simple (nonoxidative) rearrangement of oxygen atoms (Hahn, 1961; Steinberg, 1960):



Many environmental samples contain insoluble silicates, such as aluminum silicate [$\text{Al}_2(\text{SiO}_3)_3$ or $\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$], which can be converted into soluble silicates by fusion with sodium carbonate:



Dissolution of radium from some ores depends on the exchange of anions associated with the radium cation (sulfate for example) to generate a soluble compound. Extraction with nitric acid is partly based on this process, generating soluble radium nitrate.

13.2.3 Oxidation-Reduction Processes

Oxidation-reduction (redox) processes are an extremely important aspect of sample dissolution. The analyte may be present in a sample in several different chemical forms or oxidation states. As an example, consider a ground-water sample that contains ^{129}I as the analyte. The iodine may be present in any of the following inorganic forms: I^- , I_2 , IO^- , or IO_3^- . If the ground water has a high reduction potential or certain bacteria are present, the iodine also may be present as CH_3I . It is of paramount importance to ensure that all of these different forms of iodine are brought to the same oxidation state (e.g., to iodate) at the time of first change in redox environment or change in sample composition. Furthermore, accurate assessment of chemical yield only can be determined if the tracer or carrier is added prior to a change in chemical form or oxidation state of the analyte at an initial point in the digestion process. This process is referred to as “equilibration of the tracer/carrier and analyte.” From this point on during the sample analysis, any loss that occurs to the analyte will occur to an equal extent for the tracer/carrier, thus allowing the calculation of a chemical yield for the process.

A redox reaction redistributes electrons among the atoms, molecules, or ions in the reaction. In some redox reactions, electrons actually are transferred from one reacting species to another. In other redox reactions, electrons are not transferred completely from one reacting species to another; the electron density about one atom decreases, while it increases about another atom. A complete discussion of oxidation and reduction is found in Section 14.2, “Oxidation-Reduction Processes.”

Many oxidizing agents used in sample dissolution convert metals to a stable oxidation state displacing hydrogen from hydrochloric, nitric, sulfuric, and perchloric acids. (This redox process often is referred to as nonoxidative hydrogen replacement by an active metal, but it is a redox process where the metal is oxidized to a cation, usually in its highest oxidation state, and the hydrogen ion is reduced to its elemental form.) Dissolution of uranium for analysis is an example of hydrogen-ion displacement to produce a soluble substance (Grindler, 1962):



Prediction of the reactivity of a metal with acids is dependent on its position in the electromotive force series (activity series). A discussion of the series appears in Section 13.4.1, “Acids and Oxidants.” In general, metals with a negative standard reduction potential will replace hydrogen and be dissolved. Perchloric acid offers a particular advantage because very soluble metal perchlorate salts are formed.

Other important oxidizing processes depend on either oxidizing a lower, less soluble oxidation state of a metal to a higher, more soluble state or oxidizing the counter anion to generate a more soluble compound. Oxidation to a higher state is common when dissolving uranium samples in acids or during treatment with fusion fluxes. The uranyl ion (UO_2^{+2}) forms soluble salts—such as chloride, nitrate, and perchlorate—with anions of the common acids (Grindler, 1962). (Complexion formation also plays a role in these dissolutions; see the next section). Dissolution of oxides, sulfides, or halides of technetium by alkaline hydrogen peroxide converts all oxidation states to the soluble pertechnetate salts (Cobble, 1964):



13.2.4 Complexation

The formation of complex ions (see also Section 14.3, “Complexation”) is important in some dissolution processes, usually occurs in conjunction with treatment by an acid, and also can occur during fusion. Complexation increases solubility in the dissolution mixture and helps to minimize hydrolysis of the cations. The solubility of radium sulfate in concentrated sulfuric acid is the result of forming a complex-ion, $\text{Ra}(\text{SO}_4)_2^{-2}$. The ability of both hydrochloric and hydrofluoric acids to act as a solubilizing agent is dependent on their abilities to form stable complex ions with cations. Refractory plutonium samples are solubilized in a nitric acid-hydrofluoric acid solution forming cationic fluorocomplexes such as PuF^{+3} (Booman and Rein, 1962). Numerous stable complexes of anions from solubilizing acids (HCl , HF , HNO_3 , H_2SO_4 , HClO_4) contribute to the dissolution of other elements, such as americium, cobalt, technetium, thorium, uranium, and zirconium (see Section 14.10, “Analysis of Specific Radionuclides”). The process of fusion with sodium carbonate to solubilize uranium samples is also based on the formation of $\text{UO}_2(\text{CO}_3)_2^{-4}$ after the metal is oxidized to U^{+6} (Grindler, 1962).

13.2.5 Equilibrium: Carriers and Tracers

Carriers and tracers that are sometimes required for radiochemical separation procedures usually are added to samples before dissolution in order to subject them to the same chemical treatment as the analyte. Addition as soon as practical promotes equilibrium with the analyte. The dissolution process tends to bring the carriers and tracers to the same oxidation state as the analyte and ensures complete mixing of all the components in solution. Acid mixtures also create a large hydrogen-ion concentration that minimizes the tendency of cations to hydrolyze and subsequently form insoluble complexes. Detailed discussions of carriers and tracers as well as radioactive equilibrium are found in Section 14.9, "Carriers and Tracers," Section 14.10, "Analysis of Specific Radionuclides," and Attachment 14A, "Radioactive Decay and Equilibrium." The immediate and final forms of these tracers, carriers, and analytes are crucial information during the analytical process. During each of the steps in a given separation method, the analyst should be aware of the expected oxidation states of the analyte and its tendency to hydrolyze, polymerize, and form complexes and radiocolloids, and other possible interactions. Knowledge of these processes will ensure that the analyst will be able to recognize and address problems if they arise.

13.3 Fusion Techniques

Sample decomposition through fusion is employed most often for samples that are difficult to dissolve in acids such as soils, sludges, silicates, and some metal oxides. Fusion is accomplished by heating a salt (the flux) mixed with an appropriate amount of sample. The mixture is heated to a temperature above the melting point of the salt, and the sample is allowed to react in the molten mixture. When the reaction is completed, the mixture is allowed to cool to room temperature. The fused sample is then dissolved, and the analysis is continued. Any residue remaining may be treated by repeating the fusion with the same salt, performing a fusion with a different salt, acid treatment, or any combination of the three.

Decomposition of the sample matrix depends on the high temperatures required to melt a flux salt and the ratio of the flux salt to the sample. For a fusion to be successful, the sample must contain chemically bound oxygen as in oxides, carbonates, and silicates. Samples that contain no chemically bound oxygen, such as sulfides, metals, and organics, must be oxidized before the fusion process.

Samples to be fused should be oven-dried to remove moisture. Samples with significant amounts of organic material are typically dry ashed or wet ashed before fusion. Solid samples are ground to increase the surface area, allowing the fusion process to proceed more readily. The sample must be mixed thoroughly with the flux in an appropriate ratio. Generally, the crucible should never be more than half-filled at the outset of the fusion process. Fusions may be performed using sand or oil baths on a hot plate, in a muffle furnace, or over a burner. Crucibles are made of platinum, zirconium, nickel, or porcelain (Table 13.1). The choice of heat source and crucible

material generally depends on the salt used for the fusion.

During fusion, samples are heated slowly and evenly to prevent ignition of the sample before the reaction with the molten salt can begin. It is especially important to raise the temperature slowly when using a gas flame because the evolution of water and gases is a common occurrence at the beginning of the fusion, and hence a source of spattering. The crucible can be covered with a lid as an added precaution. Sand and oil baths provide the most even source of heat, but they are difficult to maintain at very high temperatures. Muffle furnaces provide an even source of heat, but when using them it is difficult to monitor the progress of the reaction and impossible to work with the sample during the fusion. Burners are used often as a convenient heat source although they make it difficult to heat the sample evenly.

TABLE 13.1 — Common fusion fluxes

Flux (mp, °C)	Fusion Temperature, °C	Type of Crucible	Types of Sample Decomposed
Na ₂ S ₂ O ₇ (403°) or K ₂ S ₂ O ₇ (419°)	Up to red heat	Pt, quartz, porcelain	For insoluble oxides and oxide-containing samples, particularly those of Al, Be, Ta, Ti, Zr, Pu, and the rare earths.
NaOH (321°) or KOH (404°)	450-600°	Ni, Ag, glassy carbon	For silicates, oxides, phosphates, and fluorides.
Na ₂ CO ₃ (853) or K ₂ CO ₃ (903)	900-1,000°	Ni Pt for short periods (use lid)	For silicates and silica-containing samples (clays, minerals, rocks, glasses), refractory oxides, quartz, and insoluble phosphates and sulfates.
Na ₂ O ₂	600°	Ni; Ag, Au, Zr; Pt (<500 °C)	For sulfides; acid-insoluble alloys of Fe, Ni, Cr, Mo, W, and Li; Pt alloys; Cr, Sn, and Zn minerals.
H ₃ BO ₃	250°	Pt	For analysis of sand, aluminum silicates, titanite, natural aluminum oxide (corundum), and enamels.
Na ₂ B ₄ O ₇ (878°)	1,000-1,200°	Pt	For Al ₂ O ₃ ; ZrO ₂ and zirconium ores, minerals of the rare earths, Ti, Nb, and Ta, aluminum-containing materials; iron ores and slags.
Li ₂ B ₄ O ₇ (920°) or LiBO ₂ (845°)	1,000-1,100°	Pt, graphite	For almost anything except metals and sulfides. The tetraborate salt is especially good for basic oxides and some resistant silicates. The metaborate is better suited for dissolving acidic oxides such as silica and TiO ₂ and nearly all minerals.
NH ₄ HF ₂ (125°) NaF (992°) KF (857°) or KHF ₂ (239°)	900°	Pt	For the removal of silicon, the destruction of silicates and rare earth minerals, and the analysis of oxides of Nb, Ta, Ti, and Zr.

Source: Dean (1995) and Bock (1979).

The maximum temperature employed varies considerably and depends on the sample and the flux. In order to minimize attack of the crucible and decomposition of the flux, excessive temperatures should be avoided. Once the salt has melted, the melt is swirled gently to monitor the reaction. The fusion continues until visible signs of reaction are completed (e.g., formation of

gases, foaming, fumes). It is frequently difficult to decide when heating should be discontinued. In ideal cases, a clear melt serves to indicate the completeness of sample decomposition. In other cases, it is not as obvious, and the analyst must base the heating time on past experience with the sample type.

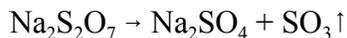
The melt sometimes is swirled during cooling to spread it over the inside of the crucible. Thin layers of salt on the sides of the crucible often will crack and flake into small pieces during cooling. These small fragments are easier to remove and dissolve.

After the sample has returned to room temperature, the fused material is dissolved. The solvent is usually warm water or a dilute acid solution, depending on the salt. For example, dilute acid typically would not be used to dissolve a carbonate fusion because of losses to spray caused by release of CO_2 . The aqueous solution from the dissolution of the fusion melt should be examined carefully for particles of undissolved sample. If undissolved particles are present, they should be separated from solution by centrifugation or filtration, and a second fusion should be performed.

Several types of materials are used for crucibles, but platinum, other metals (Ni, Zr, Ag), and graphite are most common. Graphite crucibles are a cost-effective alternative to metal crucibles; they are disposable, which eliminates the need for cleaning and the possibility of cross-sample contamination. Graphite crucibles are chemically inert and heat-resistant, although they do oxidize slowly at temperatures above 430 °C. Graphite is not recommended for extremely lengthy fusions or for reactions where the sample may be reduced. Platinum is probably the most commonly used crucible material. It is virtually unaffected by most of the usual acids, including hydrofluoric, and it is attacked only by concentrated phosphoric acid at very high temperatures, and by sodium carbonate. However, it dissolves readily in mixtures of hydrochloric and nitric acids (aqua regia), nitric acid containing added chlorides, or chlorine water or bromine water. Platinum offers adequate resistance toward molten alkali metal, borates, fluorides, nitrates, and bisulfates. When using a platinum crucible, one should avoid using aqua regia, sodium peroxide, free elements (C, P, S, Ag, Bi, Cu, Pb, Zn, Se, and Te), ammonium, chlorine and volatile chlorides, sulfur dioxide, and gases with carbon content. Platinum crucibles can be cleaned in boiling HNO_3 , by hand cleaning with sea sand or by performing a blank fusion with sodium hydrogen sulfate.

Many kinds of salts are used in fusions. The lowest melting flux capable of reacting completely with the sample is usually the optimum choice. Basic fluxes, such as the carbonates, the hydroxides, and the borates, are used to attack acidic materials. Sodium or potassium nitrate may be added to furnish an oxidizing agent when one is needed, as with the sulfides, certain oxides, ferroalloys, and some silicate materials. The most effective alkaline oxidizing flux is sodium peroxide; it is both a strong base and a powerful oxidizing agent. Because it is such a strong alkali, sodium peroxide is often used even when no oxidant is required. Alternatively, acid fluxes are the pyrosulfates, the acid fluorides, and boric acids. Table 13.1 lists several types of fusions, examples of salts used for each type of fusion, and the melting points of the salts.

SULFATE FUSION is useful for the conversion of ignited oxides to sulfates, but is generally an ineffective approach for silicates. Sulfate fusion is particularly useful for BeO, Fe₂O₃, Cr₂O₃, MoO₃, TeO₂, TiO₂, ZrO₂, Nb₂O₅, Ta₂O₅, PuO₂, and rare earth oxides (Bock, 1979). Pyrosulfate fusions are prepared routinely in the laboratory by heating a mixture of sodium or potassium sulfate with a stoichiometric excess of sulfuric acid:



The rate of heating is increased with time until the sulfuric acid has volatilized and a clear pyrosulfate fusion is obtained. A pyrosulfate melt can be reprocessed if necessary to achieve complete sample dissolution. The analyst must distinguish between insoluble material that has not yet or will not dissolve, and material that has precipitated during the final stages of a prolonged pyrosulfate fusion. In the latter situation the fusion must be cooled, additional sulfuric acid added, and the sample refluxed until the precipitated material redissolves and a clear melt is obtained. Otherwise, the precipitated material will be extremely difficult, if not impossible, to dissolve in subsequent steps. Platinum or quartz crucibles are recommended for this type of fusion, with quartz being preferred for analysis of the platinum group metals. After the melt is cooled and solidified, it should be dissolved in dilute sulfuric or hydrochloric acid rather than in water to avoid hydrolysis and precipitation of Ti, Zr, etc. Niobium and tantalum may precipitate even in the presence of more concentrated acid. In order to avoid precipitation of Nb or Ta, concentrated sulfuric acid, tartaric acid, ammonium oxalate, hydrogen peroxide, or hydrofluoric acid must be used. Mercury and the anions of volatile acids are largely volatilized during these fusion procedures.

13.3.1 Alkali-Metal Hydroxide Fusions

Alkali metal hydroxide fusions are used for silicate analysis of ash and slag; for decomposition of oxides, phosphates, and fluorides (Bock, 1979, pp. 102-108); and for dissolution of soils for actinide analyses (Smith et al., 1995). Sodium hydroxide (NaOH) generally is used because of its lower melting point, but potassium hydroxide (KOH) is just as effective. These fusions generally are rapid, the melts are easy to dissolve in water, and the losses due to volatility are reduced because of the low temperature of the melt. Nickel, silver, or glassy carbon crucibles are recommended for this type of fusion. The maximum suggested temperature for nickel crucibles is 600 °C, but silver crucibles can be used up to 700 °C. Generally, crucibles made of platinum, palladium, and their alloys should not be used with hydroxide fusions because the crucibles are easily attacked in the presence of atmospheric oxygen. The weight ratio of fusion salt to sample is normally 5-10:1. Typically, these fusions are carried out below red heat at 450 to 500 °C for 15 to 20 minutes, or sometimes at higher temperatures between 600 to 700 °C for 5 to 10

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minutes. The solidified melt dissolves readily in water; and therefore, this step may be carried out directly in the crucible, or alternatively in a nickel dish. Under no circumstances should the dissolution be carried out in a glass vessel because the resulting concentrated hydroxide solution attacks glass quite readily.

FUSION WITH SODIUM CARBONATE (Na_2CO_3) is a common procedure for decomposing silicates (clays, rocks, mineral, slags, glasses, etc.), refractory oxides (magnesia, alumina, beryllia, zirconia, quartz, etc.), and insoluble phosphates and sulfates (Bogen, 1978). The fusion may result in the formation of a specific compound such as sodium aluminate, or it may simply convert a refractory oxide into a condition where it is soluble in hydrochloric acid—this is the method of choice when silica in a silicate is to be determined, because the fusion converts an insoluble silicate into a mixture that is easily decomposed by hydrochloric acid (“M” represents a metal in the equations below):



followed by acidification to form a more soluble chloride salt,



Carbonate fusions provide an oxidizing melt for the analysis of chromium, manganese, sulfur, boron, and the platinum group metals. Organic material is destroyed, sometimes violently. Na_2CO_3 generally is used because of its lower melting point. However, despite its higher melting point and hygroscopic nature, K_2CO_3 is preferred for niobium and tantalum analyses because the resulting potassium salts are soluble, whereas the analogous sodium salts are insoluble.

The required temperature and duration of the fusion depend on the nature of the sample as well as particle size. In the typical carbonate fusion, 1 g of the powdered sample is mixed with 4 to 6 g of sodium carbonate and heated at 900 to 1,000 °C for 10 to 30 minutes. Very refractory materials may require heating at 1,200 °C for as long as 1 to 2 hours. Silica will begin to react at 500 °C, while barium sulfate and alumina react at temperatures above 700 °C. Volatility could be a problem at these temperatures. Mercury and thallium are lost completely, while selenium, arsenic, and iodine suffer considerable losses. Nonsilicate samples should be dissolved in water, while silicate samples should be treated with acid (Bock, 1979).

Platinum crucibles are recommended for fusion of solid samples even though there is a 1 to 2 mg loss of platinum per fusion. Attack on the crucible can be reduced significantly by covering the melt with a lid during the fusion process, or virtually eliminated by working in an inert atmosphere. Moreover, nitrate is often added to prevent the reduction of metals and the subsequent alloying with the platinum crucibles. The platinum crucibles may be seriously attacked by samples containing high concentrations of Fe^{2+} , Fe^{3+} , Sn^{4+} , Pb^{2+} , and compounds of Sb and As, because these ions are reduced easily to the metallic state and then form intermetallic alloys with

platinum that are not easily dissolved in mineral acids. This problem is especially prevalent when fusion is carried out in a gas flame. Porcelain crucibles are corroded rapidly and should be discarded after a single use.

13.3.2 Boron Fusions

Fusions with boron compounds are recommended for analysis of sand, slag, aluminum silicates, alumina (Al_2O_3), iron and rare earth ores, zirconium dioxide, titanium, niobium, and tantalum. Relatively large amounts of flux are required for these types of fusions. The melts are quite viscous and require swirling or stirring, so they should not be performed in a furnace. Platinum crucibles should be used for these fusions because other materials are rapidly attacked by the melt, even though some platinum is lost in each fusion.

BORIC ACID (H_3BO_3) can be used to fuse a number of otherwise inert substances such as sand, aluminum silicates, titanite, natural aluminum oxide (corundum), and enamels. Boric acid fusions generally require 4 to 8 times as much reagent as sample. Initially, the mixture should be heated cautiously while water is being driven off, then more strongly until gas evolution is completed, and then more vigorously if the sample has yet to be fully decomposed. Normally, the procedure is complete within 20 to 30 minutes. The cooled and solidified melt usually is dissolved in dilute acid. Additionally, boric acid has one great advantage over all other fluxes in that it can be completely removed by addition of methanol and subsequent volatilization of the methyl ester.

Because MOLTEN SODIUM TETRABORATE ($\text{Na}_2\text{B}_4\text{O}_7$) dissolves so many inorganic compounds, it is an important analytical tool for dissolving very resistant substances. Fusions with sodium tetraborate alone are useful for Al_2O_3 , ZrO_2 and zirconium ores, minerals of the rare earths, titanium, niobium, and tantalum, aluminum-containing materials, and iron ores and slags (Bock, 1979). Relatively large amounts of borax are mixed with the sample, and the fusion is carried out at a relatively high temperature (1,000 to 1,200 °C) until the melt becomes clear. Thallium, mercury, selenium, arsenic, and the halogens are volatilized under these conditions. Boric acid can be removed from the melt as previously described. By dissolving the melt in dilute hydrofluoric acid, calcium, thorium, and the rare earths can be separated from titanium, niobium, and tantalum as insoluble fluorides.

LITHIUM METABORATE ($\text{Li}_2\text{B}_4\text{O}_7$) is well-suited for dissolving basic oxides, such as alumina (Al_2O_3), quicklime (CaO), and silicates. Platinum dishes are normally used for this type of fusion, but occasionally graphite crucibles are advantageous because they can be heated rapidly by induction, and because they are not wetted by $\text{Li}_2\text{B}_4\text{O}_7$ melts. The fusion melt typically is dissolved in dilute acid, usually nitric but sometimes sulfuric. When easily hydrolyzed metal ions are present, dissolution should be carried out in the presence of ethylenediamine tetracetic acid (EDTA) or its di-sodium salt in 0.01 M HCl (Bock, 1979).

LITHIUM METABORATE (LiBO_2), or a mixture of the meta- and tetraborates, is a more basic flux and is better for dissolving highly acidic oxides or very insoluble ones, such as silica (SiO_2) or rutile (TiO_2). The metaborate is, however, suitable for dissolving all metal oxides. After the melt of sample and metaborate are dissolved, hydrogen peroxide should be used to maintain the titanium in solution.

13.3.3 Fluoride Fusions

Fluoride fusions are used for the removal of silicon, the destruction of silicates and rare earth minerals, and the analysis of oxides of niobium, tantalum, titanium, and zirconium. Sill et al. (1974) and Sill and Sill (1995) describe a method using potassium fluoride/potassium pyrosulfate fusion for determining alpha-emitting nuclides in soil (see Section 13.8, “Comparison of Total Dissolution and Acid Leaching”). Sulcek and Povondra (1989) describe the isolation of the rare earth elements and thorium from silicate materials and their minerals, especially monazite, through potassium hydrofluoride fusion. The silicate matrix is first degraded by evaporation with HF, then the residue is fused with tenfold excess flux, and finally the melt is digested with dilute acid. The resulting fluorides (rare earths + Th + Ca + U) are filtered out, dissolved, and further separated.

Platinum crucibles are recommended for fluoride fusions. Silicon, boron, lead, and polonium are volatilized during these fusion procedures, and if the temperature is high enough, some molybdenum, tantalum, and niobium also are lost. Residual fluoride can be a problem for subsequent analysis of many elements such as aluminum, tin, beryllium, and zirconium. This excess fluoride usually is removed by evaporation with sulfuric acid.

13.3.4 Sodium Hydroxide Fusion

Burnett et al. (1997) presented a technique that employs sodium hydroxide as the fusion agent in a 5:1 ratio to the soil. The fusion is performed in an alumina crucible, and deionized water is added to the resultant cake. Sufficient iron exists in most samples to form an $\text{Fe}(\text{OH})_3$ scavenging precipitate for the actinides. The addition of sodium formaldehyde sulfoxylate (“Rongalite”) ensures all actinides are in the +4 or +3 valence state.

13.4 Wet Ashing and Acid Dissolution Techniques

“Wet ashing” and “acid dissolution” are terms used to describe sample decomposition using hot, concentrated acid solutions. Because many inorganic matrices such as oxides, silicates, nitrides, carbides, and borides can be difficult to dissolve completely, geological or ceramic samples can be particularly challenging. Therefore, different acids are used alone or in combination to decompose specific compounds that may be present in the sample. Few techniques will decompose all types of samples completely. Many decomposition procedures use wet ashing to dissolve the

major portion of the sample but leave a minor fraction as residue. Whether or not this residue requires additional treatment (by wet ashing or fusion) depends on the amount of residue and whether it is expected to contain the radionuclides of interest. The residue should not be discarded until all of the results have been reviewed and determined to be acceptable.

13.4.1 Acids and Oxidants

Numerous acids are commonly used in wet ashing procedures. Table 13.2 lists several acids and the types of compounds they generally react with during acid dissolution. The electromotive force series (Table 13.3) is a summary of oxidation-reduction half-reactions arranged in decreasing oxidation strength and is also useful in selecting reagent systems (Dean, 1995).

TABLE 13.2 — Examples of acids used for wet ashing

Acid	Typical Uses
Hydrofluoric Acid, HF	Removal of silicon and destruction of silicates; dissolves oxides of Nb, Ta, Ti, and Zr, and Nb, and Ta ores.
Hydrochloric Acid, HCl	Dissolves many carbonates, oxides, hydroxides, phosphates, borates, and sulfides; dissolves cement.
Hydrobromic Acid, HBr	Distillation of bromides (e.g., As, Sb, Sn, Se).
Hydroiodic Acid, HI	Effective reducing agent; dissolves Sn ⁺⁴ oxide and Hg ⁺² sulfide.
Sulfuric Acid, H ₂ SO ₄	Dissolves oxides, hydroxides, carbonates, and various sulfide ores; hot concentrated acid will oxidize most organic compounds.
Phosphoric Acid, H ₃ PO ₄	Dissolves Al ₂ O ₃ , chrome ores, iron oxide ores, and slag.
Nitric Acid, HNO ₃	Oxidizes many metals and alloys to soluble nitrates; organic material oxidized slowly.
Perchloric Acid, HClO ₄	Extremely strong oxidizer; reacts violently or explosively to oxidize organic compounds; attacks nearly all metals.

The table allows one to predict which metals will dissolve in nonoxidizing acids, such as hydrochloric, hydrobromic, hydrofluoric, phosphoric, dilute sulfuric, and dilute perchloric acid. The dissolution process is simply a replacement of hydrogen by the metal (Dean, 1995). In practice, however, what actually occurs is influenced by a number of factors, and the behavior of the metals cannot be predicted from the potentials alone. Generally, metals below hydrogen in Table 13.3 displace hydrogen and dissolve in nonoxidizing acids with the evolution of hydrogen. Notable exceptions include the very slow dissolution by hydrochloric acid of lead, cobalt, nickel, cadmium, and chromium. Also, lead is insoluble in sulfuric acid because of the formation of a surface film of insoluble lead sulfate.

TABLE 13.3 — Standard reduction potentials of selected half-reactions at 25 °C

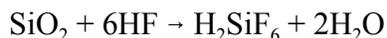
Half-Reaction	E ⁰ (volts)	Half-Reaction	E ⁰ (volts)
Ag ²⁺ + e ⁻ → Ag ⁺	1.980	I ₃ ⁻ + 3e ⁻ → 3I ⁻	0.536
S ₂ O ₈ ²⁻ + 2e ⁻ → 2SO ₄ ²⁻	1.96	I ₂ + 2e ⁻ → 2I ⁻	0.536
Ce ⁴⁺ + e ⁻ → Ce ³⁺	1.72	Cu ⁺ + e ⁻ → Cu	0.53
MnO ₄ ⁻ + 4H ⁺ + 3e ⁻ → MnO ₂ (s) + 2H ₂ O	1.70	4H ₂ SO ₃ + 4H ⁺ + 6e ⁻ → S ₄ O ₆ ²⁻ + 6H ₂ O	0.507
2HClO + 2H ⁺ + 2e ⁻ → Cl ₂ + 2H ₂ O	1.630	Ag ₂ CrO ₄ + 2e ⁻ → 2Ag + CrO ₄ ²⁻	0.449
2HBrO + 2H ⁺ + 2e ⁻ → Br ₂ + 2H ₂ O	1.604	2H ₂ SO ₃ + 2H ⁺ + 4e ⁻ → S ₂ O ₃ ²⁻ + 3H ₂ O	0.400
NiO ₂ + 4H ⁺ + 2e ⁻ → Ni ²⁺ + 2H ₂ O	1.593	UO ₂ ⁺ + 4H ⁺ + e ⁻ → U ⁴⁺ + 2H ₂ O	0.38
Bi ₂ O ₄ (bismuthate) + 4H ⁺ + 2e ⁻ → 2BiO ⁺ + 2H ₂ O	1.59	Cu ²⁺ + 2e ⁻ → Cu	0.340
MnO ₄ ⁻ + 8H ⁺ + 5e ⁻ → Mn ²⁺ + 4H ₂ O	1.51	VO ²⁺ + 2H ⁺ + e ⁻ → V ³⁺ + H ₂ O	0.337
2BrO ₃ ⁻ + 12H ⁺ + 10e ⁻ → Br ₂ + 6H ₂ O	1.478	BiO ⁺ + 2H ⁺ + 3e ⁻ → Bi + H ₂ O	0.32
PbO ₂ + 4H ⁺ + 2e ⁻ → Pb ²⁺ + 2H ₂ O	1.468	UO ₂ ²⁺ + 4H ⁺ + 2e ⁻ → U ⁴⁺ + 2H ₂ O	0.27
Cr ₂ O ₇ ²⁻ + 14H ⁺ + 6e ⁻ → 2Cr ³⁺ + 7H ₂ O	1.36	Hg ₂ Cl ₂ (s) + 2e ⁻ → 2Hg + 2Cl ⁻	0.2676
Cl ₂ + 2e ⁻ → 2Cl ⁻	1.3583	AgCl (s) + e ⁻ → Ag + Cl ⁻	0.2223
2HNO ₂ + 4H ⁺ + 4e ⁻ → N ₂ O + 3H ₂ O	1.297	SbO ⁺ + 2H ⁺ + 3e ⁻ → Sb + H ₂ O	0.212
MnO ₂ + 4H ⁺ + 2e ⁻ → Mn ²⁺ + 2H ₂ O	1.23	CuCl ₂ ²⁻ + e ⁻ → Cu + 3Cl ⁻	0.178
O ₂ + 4H ⁺ + 4e ⁻ → 2H ₂ O	1.229	SO ₄ ²⁻ + 4H ⁺ + 2e ⁻ → H ₂ SO ₃ + H ₂ O	0.158
ClO ₄ ⁻ + 2H ⁺ + 2e ⁻ → ClO ₃ ⁻ + H ₂ O	1.201	Sn ⁴⁺ + 2e ⁻ → Sn ²⁺	0.15
2IO ₃ ⁻ + 12H ⁺ + 10e ⁻ → I ₂ + 3H ₂ O	1.19	CuCl + e ⁻ → Cu + Cl ⁻	0.121
N ₂ O ₄ + 2H ⁺ + 2e ⁻ → 2HNO ₂	1.07	TiO ²⁺ + 2H ⁺ + e ⁻ → Ti ³⁺ + H ₂ O	0.100
2ICl ₂ + 2e ⁻ → 4Cl ⁻ + I ₂	1.07	S ₄ O ₆ ²⁻ + 2e ⁻ → 2S ₂ O ₃ ²⁻	0.08
Br ₂ (aq) + 2e ⁻ → 2Br ⁻	1.065	2H ⁺ + 2e ⁻ → H ₂	0.0000
N ₂ O ₄ + 4H ⁺ + 4e ⁻ → 2NO + 2H ₂ O	1.039	Hg ₂ I ₂ (s) + 2e ⁻ → 2Hg + 2I ⁻	-0.0405
HNO ₂ + H ⁺ + e ⁻ → NO + H ₂ O	0.996	Pb ²⁺ + 2e ⁻ → Pb	-0.125
NO ₃ ⁻ + 4H ⁺ + 3e ⁻ → NO + 2H ₂ O	0.957	Sn ²⁺ + 2e ⁻ → Sn	-0.136
NO ₃ ⁻ + 3H ⁺ + 2e ⁻ → HNO ₂ + H ₂ O	0.94	AgI (s) + e ⁻ → Ag + I ⁻	-0.1522
2Hg ²⁺ + 2e ⁻ → Hg ₂ ²⁺	0.911	V ³⁺ + e ⁻ → V ²⁺	-0.255
Cu ²⁺ + I ⁻ + e ⁻ → CuI (s)	0.861	Ni ²⁺ + 2e ⁻ → Ni	-0.257
OsO ₄ (s) + 8H ⁺ + 8e ⁻ → Os + 4H ₂ O	0.84	Co ²⁺ + 2e ⁻ → Co	-0.277
Ag ⁺ + e ⁻ → Ag	0.7991	PbSO ₄ + 2e ⁻ → Pb + SO ₄ ²⁻	-0.3505
Hg ₂ ²⁺ + 2e ⁻ → 2Hg	0.7960	Cd ²⁺ + 2e ⁻ → Cd	-0.4025
Fe ³⁺ + e ⁻ → Fe ²⁺	0.771	Cr ³⁺ + e ⁻ → Cr ²⁺	-0.424
H ₂ SeO ₃ + 4H ⁺ + 4e ⁻ → Se + 3H ₂ O	0.739	Fe ²⁺ + 2e ⁻ → Fe	-0.44
HN ₃ + 11H ⁺ + 8e ⁻ → 3NH ₄ ⁺	0.695	H ₃ PO ₃ + 2H ⁺ + 2e ⁻ → HPH ₂ O ₂ + H ₂ O	-0.499
O ₂ + 2H ⁺ + 2e ⁻ → H ₂ O ₂	0.695	U ⁴⁺ + e ⁻ → U ³⁺	-0.52
Ag ₂ SO ₄ + 2e ⁻ → 2Ag + SO ₄ ²⁻	0.654	Zn ²⁺ + 2e ⁻ → Zn	-0.7626
Cu ²⁺ + Br ⁻ + e ⁻ → CuBr (s)	0.654	Mn ²⁺ + 2e ⁻ → Mn	-1.18
2HgCl ₂ + 2e ⁻ → Hg ₂ Cl ₂ (s) + 2Cl ⁻	0.63	Al ³⁺ + 3e ⁻ → Al	-1.67
Sb ₂ O ₅ + 6H ⁺ + 4e ⁻ → 2SbO ⁺ + 3H ₂ O	0.605	Mg ²⁺ + 2e ⁻ → Mg	-2.356
H ₃ AsO ₄ + 2H ⁺ + 2e ⁻ → HAsO ₂ + 2 H ₂ O	0.560	Na ⁺ + e ⁻ → Na	-2.714
TeOOH ⁺ + 3H ⁺ + 4e ⁻ → Te + 2H ₂ O	0.559	K ⁺ + e ⁻ → K	-2.925
Cu ²⁺ + Cl ⁻ + e ⁻ → CuCl (s)	0.559	Li ⁺ + e ⁻ → Li	-3.045
		3N ₂ + 2H ⁺ + 2e ⁻ → 2HN ₃	-3.1

Source: Dean, 1995.

Oxidizing acids, such as nitric acid, hot concentrated sulfuric acid, or hot concentrated perchloric acid, are used to dissolve metals whose E^0 values are greater than hydrogen. For nitric acid, the potential of the nitrate ion-nitric oxide couple can be employed as a rough estimate of the solvent power. For aqua regia, the presence of free chlorine ions allows one to make predictions based upon the potential of the chlorine-chloride couple, although NOCl also plays a significant role. Some oxidizing acids exhibit a passivating effect with transition elements such as chromium and pure tungsten, resulting in a very slow attack because of the formation of an insoluble surface film of the oxide in the acid (Bogen, 1978). Moreover, oxides are often resistant to dissolution in oxidizing acids and, in fact, dissolve much more readily in nonoxidizing acids. A common example is ferric oxide, which is readily soluble in hydrochloric acid but is relatively inert in nitric acid.

However, insoluble oxides of the lower oxidation states of an element sometime dissolve in oxidizing acids with concurrent oxidation of the element. For example, UO_2 and U_3O_8 dissolve readily in nitric acid to produce a solution of uranyl ion (UO_2^{+2}).

HYDROFLUORIC ACID. The most important property of HF is its ability to dissolve silica and other silicates. For example:



whereby the fluorosilicic acid formed dissociates into gaseous silicon tetrafluoride and hydrogen fluoride upon heating:



HF also exhibits pronounced complexing properties that are widely used in analytical chemistry. Hydrofluoric acid prevents the formation of sparingly soluble hydrolytic products in solution, especially of compounds of elements from the IV to VI groups of the periodic table (Sulcek and Povondra, 1989). In the presence of fluoride, soluble hydrolytic products that are often polymeric depolymerize to form reactive monomeric species suitable for further analytical operations. Formation of colloidal solutions is avoided and the stability of solutions is increased even with compounds of elements that are hydrolyzed easily in aqueous solution (e.g., Si, Sn, Ti, Zr, Hf, Nb, Ta, and Pa).

HF should never be used or stored in glass, or porcelain containers. Digestion in platinum containers is preferred, and Teflon™ is acceptable as long as the temperature does not exceed 250 °C. This would occur only with HF if the mix were taken to dryness, because the constant boiling azeotrope is 112 °C. HF works most effectively when used alone, as all other acids or oxidizing agents used are less volatile than HF and would cause the HF concentration to be decreased at elevated temperatures. HF is most effective when used on a solid residue. Samples should be ground to a fine powder to increase the surface area and moistened with a minimal

amount of water to prevent losses as dust and spray when the acid is added to the sample. After the addition of HF, the sample may be allowed to react overnight to dissolve the silicates. However, heating the solution to 80 °C will allow reaction to occur within 1-2 hours. Because it is such a strong complexing agent, excess fluoride ion can cause problems with many separation methods. Residual fluoride is usually removed by evaporation to fumes in a low-volatility acid (e.g., H₂SO₄, HNO₃, HClO₄) or, in extreme cases, excess fluoride ion can be removed by fusing the residue with boric acid or sodium tetraborate. The fluorides are converted to BF₃ that is then removed by evaporation.

HYDROCHLORIC ACID (HCl) is one of the most widely used acids for sample dissolution because of the wide range of compounds it reacts with and the low boiling point of the azeotrope (110 °C); after a period of heating in an open container, a constant boiling 6M solution remains. HCl forms strong complexes with Au⁺³, Ti⁺³, and Hg⁺². The concentrated acid will also complex Fe⁺³, Ga⁺³, In⁺³, and Sn⁺⁴. Most chloride compounds are readily soluble in water except for silver chloride, mercury chloride, titanium chloride, and lead chloride. HCl can be oxidized to form chlorine gas by manganese dioxide, permanganate, and persulfate. While HCl dissolves many carbonates, oxides, hydroxides, phosphates, borates, sulfides, and cement, it does not dissolve the following:

- Most silicates or ignited oxides of Al, Be, Cr, Fe, Ti, Zr, or Th;
- Oxides of Sn, Sb, Nb, or Ta;
- Zr phosphate;
- Sulfates of Sr, Ba, Ra, or Pb;
- Alkaline earth fluorides;
- Sulfides of Hg; or
- Ores of Nb, Ta, U, or Th.

The dissolution behavior of specific actinides by hydrochloric acid is discussed by Sulcek and Povondra (1989):

“The rate of decomposition of oxidic uranium ores depends on the U(VI)/U(+4) ratio. The so-called uranium blacks with minimal contents of U(+4) are even dissolved in dilute hydrochloric acid. Uraninite (UO₂) requires an oxidizing mixture of hydrochloric acid with hydrogen peroxide, chlorate, or nitric acid for dissolution. Uranium and thorium compounds cannot be completely leached from granites by hydrochloric acid. Natural and synthetic thorium dioxides are highly resistant toward hydrochloric acid and must be decomposed in a pressure vessel. Binary phosphates of uranyl and divalent cations, e.g., autunite and tobernite, are dissolved without difficulties. On the other hand, phosphates of thorium, tetravalent uranium, and the rare earths (monazite and xenotime) are only negligibly attacked, even with the concentrated acid.”

As⁺³, Sb⁺³, Ge⁺³, and Se⁺⁴ are volatilized easily in HCl solutions, while Hg⁺², Sn⁺⁴, and Rh(VII)

are volatilized in the latter stages of evaporation. Glass is the preferred container for HCl solutions.

HYDROBROMIC ACID (HBr) has no important advantages over HCl for sample dissolution. HBr forms an azeotrope with water containing 47.6 percent by weight of HBr, boiling at 124.3 °C. HBr is used to distill off volatile bromides of arsenic, antimony, tin, and selenium. HBr can also be used as a complexing agent for liquid-liquid extractions of gold, titanium, and indium.

HYDROIODIC ACID (HI) is readily oxidized. Solutions often appear yellowish-brown because of the formation of the triiodide complex (I_3^-). HI is most often used as a reducing agent during dissolutions. HI also dissolves Sn^{+4} oxide, and complexes and dissolves Hg^{+2} sulfide. HI forms an azeotrope with water containing 56.9 percent by weight of HI, boiling at 127 °C.

SULFURIC ACID (H_2SO_4) is another widely used acid for sample decomposition. Part of its effectiveness is due to its high boiling point (about 340 °C). Oxides, hydroxides, carbonates, and sulfide ores can be dissolved in H_2SO_4 . The boiling point can be raised by the addition of sodium or potassium sulfate to improve the attack on ignited oxides, although silicates will still not dissolve. H_2SO_4 is not appropriate when calcium is a major constituent because of the low solubility of $CaSO_4$. Other inorganic sulfates are typically soluble in water, with the notable exceptions of strontium, barium, radium, and lead.

Non-fuming H_2SO_4 does not exhibit oxidizing properties, but the concentrated acid will dissolve many elements and react with almost all organic compounds. Concentrated sulfuric acid is a powerful dehydrating agent. Its action on organic materials is a result of removing OH and H groups (to form water) from adjacent carbon atoms. This forms a black char (residue) that is not easily dissolved using wet-ashing techniques. Moreover, because of the high boiling point of H_2SO_4 , there is an increased risk of losses because of volatilization. Iodine can be distilled quantitatively, and boron, mercury, selenium, osmium, ruthenium, and rhenium may be lost to some extent. The method of choice is to oxidize the organic substances with HNO_3 , volatilize the nitric acid, add H_2SO_4 until charred, followed by HNO_3 again, repeating the process until the sample will not char with either HNO_3 or H_2SO_4 . Dissolution is then continued with $HClO_4$. Glass, quartz, platinum, and porcelain are resistant to H_2SO_4 up to the boiling point. Teflon™ should not be used above 250 °C, and, therefore, it is not recommended for applications involving concentrated H_2SO_4 that require elevated temperature.

Glass, quartz, platinum, and porcelain are resistant to H_2SO_4 up to the boiling point. Teflon decomposes at 300 °C, below the boiling point, and, therefore, is not recommended for applications involving H_2SO_4 that require elevated temperature.

PHOSPHORIC ACID (H_3PO_4) seldom is used for wet ashing because the residual phosphates interfere with many separation procedures. H_3PO_4 attacks glass, although glass containers are usually acceptable at temperatures below 300 °C. Alumina, chromium ores, iron oxide ores, and

Sample Dissolution

slags can be dissolved in H_3PO_4 . The acid also has been used to dissolve silicates selectively without attacking quartz.

NITRIC ACID (HNO_3) is one of the most widely used oxidizing acids for sample decomposition. Most metals and alloys are oxidized to nitrates, which are usually very soluble in water, although many metals exhibit a pronounced tendency to hydrolyze in nitric acid solution. Nitric acid does not attack gold, hafnium, tantalum, zirconium, and the metals of the platinum group (except palladium). Aluminum, boron, chromium, gallium, indium, niobium, thorium, titanium, calcium, magnesium, and iron form an adherent layer of insoluble oxide when treated with HNO_3 , thereby passivating the metal surface. However, calcium, magnesium, and iron will dissolve in more dilute acid.

Complexing agents (e.g., Cl^- , F^- , citrate, tartrate) can assist HNO_3 in dissolving most metals. For example, Sulcek and Povondra (1989) describe the decomposition of thorium and uranium dioxides in nitric acid, which is catalytically accelerated by the addition of 0.05 to 0.1 M HF. They also report that a solid solution of the mixed oxides (Pu, U) O_2 or PuO_2 ignited at temperatures below 800 °C behaves analogously.

Although nitric acid is a good oxidizing agent, it usually boils away before sample oxidation is complete. Oxidation of organic materials proceeds slowly and is usually accomplished by repeatedly heating the solution to HNO_3 fumes. Refluxing in the concentrated acid can help facilitate the treatment, but HNO_3 is seldom used alone to decompose organic materials.

PERCHLORIC ACID (HClO_4). Hot concentrated solutions of HClO_4 act as a powerful oxidizer, but dilute aqueous solutions are not oxidizing. Hot concentrated HClO_4 will attack nearly all metals (except gold and platinum group metals) and oxidize them to the highest oxidation state, except for lead and manganese, which are oxidized only to the +2 oxidation state. Perchloric acid is an excellent solvent for stainless steel, oxidizing the chromium and vanadium to the hexavalent and pentavalent acids, respectively. Many nonmetals also will react with HClO_4 . Because of the violence of the oxidation reactions, HClO_4 is rarely used alone for the destruction of organic materials. H_2SO_4 or HNO_3 are used to dilute the solution and break down easily oxidized material before HClO_4 becomes an oxidizer above 160 °C.

The concentrated acid is a dangerous oxidant that can explode violently. The following are examples of some reactions with HClO_4 that *should never be attempted*:

- Heating bismuth metal and alloys with concentrated acid.
- Dissolving metals (e.g., steel) in concentrated acid when gaseous hydrogen is heated.
- Heating uranium turnings or powder in concentrated acid.
- Heating finely divided aluminum and silicon in concentrated acid.
- Heating antimony or Sb^{+3} compounds in HClO_4 .
- Mixing HClO_4 with hydrazine or hydroxylamine.

- Mixing HClO₄ with hypophosphates.
- Mixing HClO₄ with fats, oils, greases, or waxes.
- Evaporating solutions of metal salts to dryness in HClO₄.
- Evaporating alcoholic filtrates after collection of KClO₄ precipitates.
- Heating HClO₄ with cellulose, sugar, and polyhydroxy alcohols.
- Heating HClO₄ with N-heterocyclic compounds.
- Mixing HClO₄ with any dehydrating agent.

Perchloric acid vapor should never be allowed to contact organic materials such as rubber stoppers. The acid should be stored only in glass bottles. Splashed or spilled acid should be diluted with water immediately and mopped up with a woolen cloth, never cotton. HClO₄ should only be used only in specially designed fume hoods incorporating a washdown system.

Acid dissolutions involving HClO₄ should only be performed by analysts experienced in working with this acid. When any procedure is designed, the experimental details should be recorded exactly. These records are used to develop a detailed standard operating procedure that must be followed exactly to ensure the safety of the analyst (Schilt, 1979).

AQUA REGIA. One part concentrated HNO₃ and three parts concentrated HCl (by volume) are combined to form aqua regia:



However, the interaction of these two acids is much more complex than indicated by this simple equation. Both the elemental chlorine and the trivalent nitrogen of the nitrosyl chloride exhibit oxidizing effects, as do other unstable products formed during the reaction of these two acids. Coupled with the catalytic effect of Cl₂ and NOCl, this mixture combines the acidity and complexing power of the chloride ions. The solution is more effective if allowed to stand for 10 to 20 minutes after it is prepared.

Aqua regia dissolves sulfides, phosphates, and many metals and alloys including gold, platinum, and palladium. Ammonium salts are decomposed in this acid mixture. Aqua regia volatilizes osmium as the tetroxide; has little effect on rhodium, iridium, and ruthenium; and has no effect on titanium. Oxidic uranium ores with uraninite and synthetic mixed oxides (U₃O₈) are dissolved in aqua regia, with oxidation of the U⁺⁴ to UO₂⁺² ions (Sulcek and Povondra, 1989). However, this dissolution procedure is insufficient for poor ores; the resistant, insoluble fraction must be further attacked (e.g., by sodium peroxide or borate fusion) or by mixed-acid digestion with HF, HNO₃, and HClO₄.

Oxysalts, such as KMnO₄ (potassium permanganate) and K₂Cr₂O₇ (potassium dichromate), are commonly not used to solubilize or wet ash environmental samples for radiochemical analysis because of their limited ability to oxidize metals and the residue that they leave in the sample

mixture. These oxysalts are more commonly used to oxidize organic compounds.

POTASSIUM PERMANGANATE (KMnO_4) is a strong oxidizer whose use is limited primarily to the decomposition of organic substances and mixtures, although it oxidizes metals such as mercury to the ionic form. Oxidation can be performed in an acid, neutral, or basic medium; near-neutral or basic solutions produce an insoluble residue of manganese dioxide (MnO_2) that can be removed by filtration. Oxidation in acid media leaves the Mn^{+2} ion in solution, which might interfere with additional chemical procedures or analyses. Extreme caution must be taken when using this reagent because KMnO_4 reacts violently with some organic substances such as acetic acid and glycerol, with some metals such as antimony and arsenic, and with common laboratory reagents such as hydrochloric acid and hydrogen peroxide.

POTASSIUM DICHROMATE ($\text{K}_2\text{Cr}_2\text{O}_7$) is a strong oxidizing agent for organic compounds but is not as strong as KMnO_4 . $\text{K}_2\text{Cr}_2\text{O}_7$ has been used to determine carbon and halogen in organic materials, but the procedure is not used extensively. $\text{K}_2\text{Cr}_2\text{O}_7$ is commonly mixed with sulfuric acid and heated as a strong oxidizing agent to dissolve carbonaceous compounds. The Cr^{+3} ion remains after sample oxidation and this might interfere with other chemical procedures or analyses. $\text{K}_2\text{Cr}_2\text{O}_7$ can react violently with certain organic substances such as ethanol and might ignite in the presence of boron. Caution also must be observed in handling this oxidizing agent because of human safety concerns, particularly with the hexavalent form of chromium.

SODIUM BROMATE (NaBrO_3) is an oxidizing agent for organic compounds but is not used for metals. Unlike KMnO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$, the bromate ion can be removed from solution after sample oxidation by boiling with excess HCl to produce water and Br_2 . Caution must be observed when using this oxidizing agent because it can react violently with some organic and inorganic substances.

13.4.2 Acid Digestion Bombs

Some materials that would not be totally dissolved by acid digestion in an open vessel on a hotplate, can be completely dissolved in an acid digestion bomb. These pressure vessels hold strong mineral acids or alkalis at temperatures well above normal boiling points, thereby allowing one to obtain complete digestion or dissolution of samples that would react slowly or incompletely at atmospheric pressure. Sample dissolution is obtained without losing volatile elements and without adding contaminants from the digestion vessel. Ores, rock samples, glass and other inorganic samples can be dissolved quickly using strong mineral acids such as HF , HCl , H_2SO_4 , HNO_3 , or aqua regia.

These sealed pressure vessels are lined with Teflon™, which offers resistance to cross-contamination between samples and to attack by HF . In all reactions, the bomb must never be completely filled; there must be adequate vapor space above the contents. When working with inorganic materials, the total volume of sample plus reagents must never exceed two-thirds of the capacity

of the bomb. Moreover, many organic materials can be treated satisfactorily in these bombs, but critical attention must be given to the nature of the sample as well to possible explosive reactions with the digestion media.

13.5 Microwave Digestion

Microwave energy as a heat source for sample digestion was first described more than 20 years ago (Abu-Samra et al., 1975). Its popularity is derived from the fact that it is faster, cleaner, more reproducible, and more accurate than traditional hot-plate digestion. However, until recently, this technology has had limited application in the radiochemical laboratory because of constraints on sample size resulting from vessel pressure limitations. Because of this drawback, microwave dissolution was not practical for many radiochemical procedures where larger sample sizes are dictated to achieve required detection limits. However, recent advances in vessel design and improved detection methods, such as ICP-MS (inductively coupled plasma-mass spectrometry) and ion chromatography have eliminated this disadvantage, and microwave dissolution is an important radiochemical tool (Smith and Yaeger, 1996; Alvarado et al., 1996). A series of articles in *Spectroscopy* describes recent advances in microwave dissolution technology (Kammin and Brandt, 1989; Grillo, 1989 and 1990; Gilman and Engelhardt, 1989; Lautenschlager, 1989; Noltner et al., 1990), and Dean (1995) presents a synopsis of current microwave theory and technology. Kingston and Jassie (1988) and Kingston and Haswell (1997) are other excellent resources for this topic.

The American Society for Testing and Materials (ASTM) has issued several protocols for various media. ASTM D5258 describes the decomposition of soil and sediment samples for subsequent analyte extraction; ASTM D4309 addresses the decomposition of surface, saline, domestic, and industrial waste water samples; and ASTM D5513 covers the multistage decomposition of samples of cement raw feed materials, waste-derived fuels, and other industrial feedstreams for subsequent trace metal analysis. A method for acid digestion of siliceous and organically based matrices is given in EPA (1996).

There are various microwave instruments that may be satisfactory depending on sample preparation considerations. The three main approaches to microwave dissolution are: focused open-vessel, low-pressure closed-vessel, and high-pressure closed-vessel. Each has certain advantages and disadvantages and the choice of system depends upon the application.

13.5.1 Focused Open-Vessel Systems

A focused open-vessel system has no oven but consists of a magnetron to generate microwaves, a waveguide to direct and focus the microwaves and a cavity to contain the sample (Grillo, 1989). Because of the open-vessel design, there is no pressure buildup during processing, and reagents may be added during the digestion program. These systems are quite universal in that any reagent

and any type of vessel (glass, Perfluoroalcoholoxil™ [PFA], or quartz) can be used.

The waveguide ensures that energy is directed only at the portion of the vessel in the path of the focused microwaves thereby allowing the neck of the vessel and refluxer to remain cool and ensuring refluxing action. Because of this refluxing action, the system maintains all elements, even selenium and mercury. The focused microwaves cause solutions to reach higher temperatures faster than with conventional hotplates or block-type digesters and do so with superior reproducibility. An aspirator removes excess acid vapors and decomposition gases. Depending on the system, up to 20 g of solids or 50 to 100 mL of liquids can be digested within 10 to 30 minutes on average.

13.5.2 Low-Pressure, Closed-Vessel Systems

These systems consist of a microwave oven equipped with a turntable, a rotor to hold the sample vessels, and a pressure-control module (Grillo, 1990). The PFA vessels used with these systems are limited to approximately 225 °C, and, therefore, low-boiling reagents or mixtures of reagents should be used. Waste is minimized in these systems because smaller quantities of acid are required. Moreover, because little or no acid is lost during the digestion, additional portions of acid may not be required and blank values are minimized. Additionally, these sealed vessels are limited to 100 to 300 psi (689 to 2,068 kPa), depending on the model thereby limiting the size of organic samples utilized. However, inorganic materials such as metals, water and waste waters, minerals, and most soils and sediments are easily digested without generating large amounts of gaseous by-products. Typical sample sizes are on the order of 0.5 g for solids and 45 mL for aqueous samples.

The pressure control module regulates the digestion cycle by monitoring, controlling, and dwelling at several preferred pressure levels for specified time periods in order to obtain complete dissolution and precise recoveries in the minimum amount of time. As the samples are irradiated, temperatures in the vessels rise thereby increasing the pressure. The pressure transducer will cycle the magnetron to maintain sufficient heat to hold the samples at the programmed pressure level for a preset dwell time. The vessels are designed to vent safely in case of excessive internal pressure.

13.5.3 High-Pressure, Closed-Vessel Systems

Recent advances in vessel design have produced microwave vessels capable of withstanding pressures on the order of 1,500 psi (10 mPa; Lautenschlager, 1989), allowing for larger sample sizes on the order of 1 to 2 g for soil (Smith and Yaeger, 1996) or 0.5 to 3 g for vegetation (Alvarado et al., 1996) and, consequently, better detection limits. These high-pressure vessels are used to digest organic and inorganic substances, such as coals, heavy oils, refractories, and ceramic oxides, which cannot easily be digested with other techniques. Additionally, vessel composition continues to improve. Noltner et al. (1990) have demonstrated that

Tetrafluorometoxil™ (TFM) vessels exhibit significantly lower blank background values from residual contamination and reuse than vessels produced with the more traditional PFA. This lower “memory” results in lower detection limits, a clear advantage for environmental laboratories.

13.6 Verification of Total Dissolution

Following aggressive acid digestion or fusion, the analyst often must determine if the sample has indeed been dissolved. This determination is made first through visual inspection for particulate matter in the acid leachate, post-digestion solution, or dissolved fusion melt. (The analyst should allow the solution to cool prior to making an assessment of total dissolution.) A hot digestate may appear to be free from particulate matter. However, upon cooling, finely divided particulate or colloidal matter may agglomerate, forming a residue. If a residue is observed, this residue must be physically separated, or the sample digestate must be retreated to ensure a single final aqueous phase. Sometimes these residues are inconsequential and contain no analyte of interest. Project-specific requirements will dictate how these residues are handled.

If no particles are readily observed, small undissolved particles that are invisible to the unaided eye may be present. A method to assess this may be to filter a duplicate cooled solution (see Section 10.3.2, “Liquid Sample Preparation: Filtration”) and count it using a gamma spectrometer, alpha spectrometer, or proportional counter. The analyst should focus on the analytes of interest to assess whether any activity is lost in this residue. Finally, for those cases where the laboratory has decided to perform an acid leaching, rather than a total dissolution or fusion, it is advisable to perform total dissolution on a subset of the samples and compare the results to those obtained from the acid digestion. This check will help to substantiate that the acid leaching approach is adequate for the particular sample matrix.

13.7 Special Matrix Considerations

13.7.1 Liquid Samples

Aqueous samples usually are considered to be in solution. This may not always be true, and, based on the objectives of the project, additional decomposition of aqueous samples may be requested.

Most radiochemical analyses are performed in aqueous solutions. Because nonaqueous liquids are incompatible with this requirement, these samples must be converted into an aqueous form. In most cases, the nonaqueous liquid is simply a solvent that does not contain the radionuclide of interest, and the nonaqueous solvent simply can be removed and the residue dissolved as described in Sections 13.3 (“Fusion Techniques”) and 13.4 (“Wet Ashing and Acid Dissolution Techniques”).

Occasionally, the nonaqueous phase must be analyzed. A procedure for the decomposition of petroleum products is described by Coomber (1975). There are restrictions on how many nonaqueous liquids can be disposed of, even as laboratory samples. Evaporation of volatile solvents may initially be an attractive alternative, but the legal restrictions on evaporating solvents into the air should be investigated before this method is implemented. Burning flammable liquids such as oil may also initially appear attractive, but legal restrictions on incineration of organic liquids need to be considered. A liquid-liquid extraction or separation using ion exchange resin may be the only alternative for transferring the radionuclide of interest into an aqueous solution. Unfortunately, these methods require extensive knowledge of the sample matrix and chemical form of the contaminant, which is seldom available. Often, gross radioactivity measurements using liquid scintillation counting techniques or broad spectrum direct measurements such as gamma spectroscopy are the only measurements that can be practically performed on nonaqueous liquids.

13.7.2 Solid Samples

Decomposition of solid samples is accomplished by applying fusion, wet ashing, leaching, or combustion techniques singly or in some combination. A discussion of each of these techniques is included in this chapter.

13.7.3 Filters

Air filter samples generally have a small amount of fine particulate material on a relatively small amount of filter media. In many cases, filters of liquid samples also have limited amounts of sample associated with the filter material. This situation may initially appear to make the sample decomposition process much easier, the small amount of sample appears to dissolve readily in a simple acid dissolution. The ease with which many filters dissolve in concentrated acid does not always mean that the sample has dissolved, and the fine particles are often impossible to observe in an acid solution. If the radionuclides of concern are known to be in the oxide form, or if the chemical form of the contaminants is unknown, a simple acid dissolution will not completely dissolve the sample. In these cases, the sample may be dry ashed to destroy the filter and the residue subjected to fusion or other decomposition of oxides in the sample.

13.7.4 Wipe Samples

If oxides and silicates are not present in wipe samples, acid dissolutions are generally acceptable for sample decomposition. In many cases, it is not the sample but the material from which the wipe is constructed that causes problems with acid dissolution. Paper wipes are decomposed easily in sulfuric-nitric solutions or in perchloric nitric solutions or by combustion, and it may be necessary to dry ash the sample before dissolution. If volatile isotopes are expected, precautions must be taken to prevent loss when heating (see Section 14.5, "Volatilization and Distillation). "Sticky" smears can be more difficult to dissolve—the glue can be especially troublesome and

should be watched closely if perchloric acid is used. Other materials used for wipe samples should be evaluated on an individual basis to determine the best method for sample decomposition. In some cases, the sample will be a problem to decompose as well. Oil and grease are often collected on wipe samples from machinery, and these samples are usually dry ashed before acid dissolution to remove the organic material. If large amounts of solid material (i.e., soil, dust, etc.) are collected with the wipe, it is recommended that the sample be treated as a solid (the analytical protocol specification or the project manager should be consulted before removing the wipe and simply analyzing the solid sample).

13.8 Comparison of Total Dissolution and Acid Leaching

Sample dissolution can be one of the biggest challenges facing the analyst because the adequacy of the dissolution has direct and profound effects on the resultant data. The analyst must balance numerous factors such as the nature of the sample and the analyte (e.g., is it refractory or volatile?), the effects of excess reagents during subsequent analyses, the accuracy and precision requirements for the data, and the costs associated with effort, materials, and waste generation. Consequently, the question of total dissolution through fusion or digestion, or through acid leaching, is under constant debate, and it is important for the analyst to be aware of the limitations of both methods.

The MARLAP process enables one to make a decision concerning the dissolution required through its process of establishing data quality objectives, analytical protocol specification, and measurement quality objectives. During this process, all pertinent information is available to the radioanalytical specialist who then evaluates the alternatives and assists with the decision. The following discussion on acid leaching focuses on its use for the complete dissolution of the analyte of interest and not for such procedures as the Environmental Protection Agency's "Toxicity Characteristic Leaching Procedure" (TCLP; 40 CFR 261, Appendix II, Method 1311), which are intended to determine the leachability of a nonradioactive analyte.

"Acid leaching" has no accepted definition, but will be defined here as the use of nitric or hydrochloric acid to put the radionuclide into solution. The acid concentration may vary up to and include concentrated acid. Normally, the use of hydrofluoric acid and aqua regia are not included in this definition. Sample size is usually relatively much larger than that used for fusion. Although mineral acids might not totally break down all matrices, they have been shown to be effective leaching solvents for metals, oxides, and salts in some samples. In some cases, leaching requires fewer chemicals and less time to accomplish than complete sample dissolution. For matrices amenable to leaching, multiple samples are easily processed simultaneously using a hotplate or microwave system, and excess reagents can be removed through evaporation. Complete dissolution of a sample is not necessary if it can be demonstrated confidently that the radionuclide of interest is completely leached from the sample medium. However, as indicated by Sill and Sill (1995), this may not always be possible:

“In many cases, the mono-, di-, and small trivalent elements can be leached fairly completely from simple solids by boiling with concentrated hydrochloric or nitric acids. However, even these elements cannot necessarily be guaranteed to be dissolved completely by selective leaching. If they are included in a refractory matrix, they will not be removed completely without dissolution of the matrix. If the samples have been exposed to water over long periods of time, such as with sediments in a radioactive waste pond, small ions such as divalent cobalt will have diffused deeply into the rock lattice from which they cannot be removed without complete dissolution of the host matrix. In contrast, because of its large size, ionic cesium has a marked tendency to undergo isomorphous replacement in the lattice of complex silicates from which it too cannot be removed completely.”

Thus, the results of acid leaching processes should be used with caution.

There are those within the radiochemistry community who contend that total sample dissolution provides the most analytically accurate and reproducible analyte concentration in the sample. Sill and Sill (1995), longtime proponents of total dissolution, state:

“Any procedure that fails to obtain complete sample dissolution . . . will inevitably give low and erratic results. The large ter-, quadri-, and pentavalent elements are extremely hydrolytic and form hydroxides, phosphates, silicates, carbides, etc., that are very insoluble and difficult to dissolve in common acids, particularly if they have been heated strongly and converted to refractory forms.”

However, there are also disadvantages and challenges associated with the fusion approach. Fusions are frequently more labor intensive than the leaching approach. More often than not, single-sample processing requires a dedicated analyst. Large quantities of the flux are generally required to decompose most substances, often 5 to 10 times the sample weight. Therefore, contamination of the sample by impurities in the reagent is quite possible. Furthermore, the aqueous solutions resulting from the fusions will have a very high salt content, which may lead to difficulties in subsequent steps of the analysis, i.e., difficulties of entrainment, partial replacements, etc. The high temperatures associated with some fusion processes increase the danger of loss of certain analytes by volatilization. Finally, the crucible itself may be attacked by the flux, once again leading to possible contamination of the sample. The typical sample size for fusions ranges from typically one to ten grams. The analyst must consider whether this sample is representative.

13.9 References

13.9.1 Cited References

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