

# 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 the next chapter, but their importance to dissolution is reviewed in this chapter.

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 data quality objective requirements for bias and precision to meet the data 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 to produce an aqueous solution (homogeneous mixture), 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.

Fusion and wet ashing techniques are used singly or in combination to decompose most samples analyzed in radioanalytical laboratories. Generally, fusion techniques are used when a total

33 dissolution of a difficult sample matrix is required. Leaching techniques are used to determine  
34 the soluble fraction of the radionuclide of interest under specific conditions. Because recent  
35 advances in microwave vessel design have allowed for the use of larger samples, microwave  
36 dissolution is becoming an important tool in the radiochemistry laboratory.

37 Because of the potential for injury and explosions, it is essential that proper laboratory safety  
38 procedures be in place, the appropriate safety equipment be available, a safe work space be  
39 provided, and that the laboratory personnel undergo the necessary training to ensure a safe  
40 working environment before any of these methods are used.

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

45 There are many excellent references on the topic of sample dissolution, including *A Handbook of*  
46 *Decomposition Methods in Analytical Chemistry* (Bock, 1979), *Analytical Chemistry Handbook*  
47 (Dean, 1995), *Methods for Decomposition in Inorganic Analysis* (Sulcek and Povondra, 1989),  
48 and “A Decomposition and Dissolution of Samples: Inorganic” (Bogen, 1978).

## 49 **13.2 The Chemistry of Dissolution**

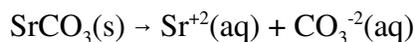
50 In order to dissolve a sample completely, each insoluble component must be converted into a  
51 soluble form. Several basic chemical methods are employed to accomplish complete dissolution  
52 of the sample, but usually the tracer is added to the sample. An outline of the principles of these  
53 chemical methods is provided in this section, but a complete description is available in Chapter  
54 14 (*Chemical Separations*), where the principles are applied to a broader range of topics.

### 55 **13.2.1 Solubility and the Solubility Product Constant, $K_{sp}$**

56 The solubility data of many compounds, minerals, ores, and elements are available in reference  
57 manuals. Solubilities typically are expressed in grams of substance per 100 mL of solvent,  
58 although other units are used sometimes. The information is more complete for some substances  
59 than others, and for many substances solubility is expressed only in general terms, such as  
60 “soluble,” “slightly soluble,” or “insoluble.” Many environmental samples consist of complex  
61 mixtures of elements, compounds, minerals, or ores, most of which are insoluble and must be  
62 treated chemically to dissolve completely. In some cases, the sample constituents are known to  
63 the analyst, but often they are not. Solubility data might not be available even for known

64 constituents, or the available data might be inadequate. Under these circumstances, sample  
65 dissolution is not a simple case of following the solubilities of known substances. For known  
66 constituents with solubility data, the solubilities indicate those that must be treated to complete  
67 dissolution. This, in turn, provides a guide to the method of treatment of the sample. Given the  
68 potential complexity of environmental samples, it is difficult to describe conditions for  
69 dissolving all samples. Sometimes one method is used to dissolve one part of the sample while  
70 another is used to dissolve the residue.

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



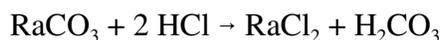
76 and is represented by:

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

77  
78  
79 The brackets indicate the molar concentration (moles/liter) of the respective ions dissolved in  
80 water. The very small value of the constant results from the low concentration of dissolved ions,  
81 and the compound is referred to as “insoluble.” Chemical treatment is necessary sometimes to  
82 dissolve the components of a compound in water. In this example, strontium carbonate requires  
83 the addition of an acid to solubilize  $\text{Sr}^{+2}$ . The next section describes chemical treatment to  
84 dissolve compounds.

### 85 13.2.2 Chemical Exchange, Decomposition, and Simple Rearrangement Reactions

86 Chemical exchange, decomposition, and simple rearrangement reactions refer to one method for  
87 solubilizing components of a sample. In this chemical process, the sample is treated to convert  
88 insoluble components to a soluble chemical species using chemical exchange (double displace-  
89 ment), decomposition, or simple rearrangement reactions rather than oxidation-reduction  
90 processes or complex formations. Some fluxes solubilize sample components using chemical  
91 exchange. Radium or strontium cations in radium or strontium carbonate ( $\text{RaCO}_3$  or  $\text{SrCO}_3$ )  
92 exchange the carbonate anion for the chloride ion on acid treatment with HCl to produce the  
93 soluble chlorides; the carbonic acid product decomposes to carbon dioxide and water:



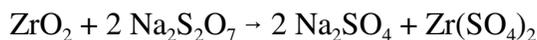
94



96 and the net reaction is as follows:



98 Sodium pyrosulfate fusion, for example, converts zirconia ( $\text{ZrO}_2$ ) into zirconium sulfate  
99 [ $\text{Zr}(\text{SO}_4)_2$ ], which is soluble in acid solution by a simple (nonoxidative) rearrangement of oxygen  
100 atoms (Hahn, 1961, p. 81; Steinberg, 1960, p. 4):



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



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

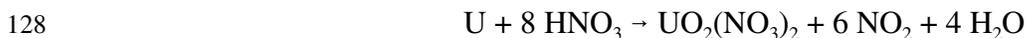
### 108 **13.2.3 Oxidation-Reduction Processes**

109 Oxidation-reduction (redox) processes play an important role in sample dissolution because  
110 solubility is highly dependent not only on the chemical form of the element, but also on oxidation  
111 state. Moreover, many radiochemical procedures require the addition of a carrier and isotope  
112 tracer, and to achieve quantitative yields, there must be complete equilibration (isotopic  
113 exchange) between the added isotopes and all chemical species present. Dissolution of the  
114 sample in the presence of the appropriate carrier and/or tracer is one way to promote  
115 equilibration by exposing all components of the analytical mixture to the same redox conditions.

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

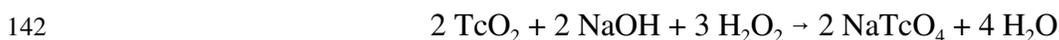
122 Many oxidizing agents used in sample dissolution convert metals to a stable oxidation state  
123 displacing hydrogen from hydrochloric, nitric, sulfuric, and perchloric acids. (This redox process

124 often is referred to in the literature as nonoxidative hydrogen replacement by an active metal, but  
125 it is a redox process where the metal is oxidized to a cation, usually in its highest oxidation state,  
126 and the hydrogen ion is reduced to its elemental form.) Dissolution of uranium for analysis is an  
127 example of hydrogen-ion displacement to produce a soluble substance (Grindler, 1962, p. 252):



129 Prediction of the reactivity of a metal with acids is dependent on its position in the electromotive  
130 force series (activity series). A discussion of the series appears in Section 13.4.1, “Acids and  
131 Oxidants.” In general, metals below hydrogen in the reduction series will displace hydrogen from  
132 acid solution and be dissolved, while acids above the series will not. Perchloric acid offers a  
133 particular advantage because very soluble perchlorate salts are formed.

134 Other important oxidizing processes depend on either oxidizing a lower, less soluble oxidation  
135 state of a metal to a higher, more soluble state or oxidizing the counter anion to generate a more  
136 soluble compound. Oxidation to a higher oxidation state is common when dissolving uranium  
137 samples in acids or during treatment with fluxes. The uranyl ion ( $\text{UO}_2^{+2}$ ) forms soluble salts—  
138 such as chloride, nitrate, and perchlorate—with anions of the common acids (Grindler, 1962, p.  
139 255 and pp. 9-14). (Complex-ion formation also plays a role in these dissolutions; see the next  
140 section). Dissolution of oxides, sulfides, or halides of technetium by alkaline hydrogen peroxide  
141 converts all oxidation states to the soluble technate salts (Cobble, 1964, p. 418):



#### 143 **13.2.4 Complexation**

144 The formation of complex ions (see also Section 14.3, “Complexation”) is important in some  
145 dissolution processes and usually occurs in conjunction with treatment by an acid, but can also  
146 occur during fusion. Complexation increases solubility in the dissolution mixture and helps to  
147 minimize hydrolysis of the cation. The solubility of radium sulfate in concentrated sulfuric acid  
148 is the result of forming a complex-ion,  $\text{Ra}(\text{SO}_4)_2^{-2}$ . The ability of both hydrochloric and  
149 hydrofluoric acids to act as a solubilizing agent is dependent on their abilities to form stable  
150 complex ions with cations. Refractory plutonium samples are solubilized in a nitric acid-  
151 hydrofluoric acid solution forming cationic fluorocomplexes such as  $\text{PuF}^{+3}$  (Booman and Rein,  
152 1962, p. 244). Numerous stable complexes of anions from solubilizing acids ( $\text{HCl}$ ,  $\text{HF}$ ,  $\text{HNO}_3$ ,  
153  $\text{H}_2\text{SO}_4$ ,  $\text{HClO}_4$ ) contribute to the dissolution of other radionuclides, such as americium, cobalt,  
154 technetium, thorium, uranium, and zirconium (see Section 14.10, “Radiochemical Equilibrium”).

155 The process of fusion with sodium carbonate to solubilize uranium samples is also based on the  
156 formation of  $\text{UO}_2(\text{CO}_3)_2$ <sup>4</sup> after the metal is oxidized to  $\text{U}^{+6}$  (Grindler, 1962, p. 256).

### 157 **13.2.5 Equilibrium: Carriers and Tracers**

158 Carriers and tracers that are required for radiochemical separation and detection procedures  
159 usually are added to samples before dissolution in order to subject them to the same chemical  
160 treatment as the analyte. Addition as soon as practical promotes equilibration with the analyte.  
161 The dissolution process tends to bring the carrier and tracers to the same oxidation state as the  
162 analyte and ensures intimate mixing of all the components in solution. Acid mixtures also create  
163 a large hydrogen-ion concentration that minimizes the tendency of cations to hydrolyze and  
164 subsequently form insoluble complexes. Detailed discussions of carriers and tracers as well as  
165 radiochemical equilibration are found in Section 14.9, "Carriers and Tracers" and Section 14.10,  
166 "Radiochemical Equilibration." Knowledge of the behavior of carriers and tracers and of the  
167 principles behind radiochemical equilibrium is very important, because the final form of the  
168 analyte in solution is crucial to understanding their behavior, not only during solubilization of the  
169 sample but also in the separation and detection steps of the analysis. During each of the steps in  
170 the method, the analyst should be aware of the expected oxidation states of the analyte and its  
171 tendency to hydrolyze, polymerize, and form complexes and radiocolloids, and other issues  
172 during each step of the procedure. Knowledge of these processes will ensure that the analyst will  
173 be able to recognize and address problems if they arise.

## 174 **13.3 Fusion Techniques**

175 Sample decomposition through fusion is most employed often for samples that are difficult to  
176 dissolve in acids such as soils, sludges, silicates, and some mineral oxides. Fusion is accomp-  
177 lished by heating a salt (the flux) mixed with a small amount of sample. The mixture is heated to  
178 a temperature above the melting point of the salt, and the sample is allowed to react in the molten  
179 mixture. When the reaction is completed, the mixture is allowed to cool to room temperature.  
180 The fused sample is then dissolved, and the analysis is continued. Any residue remaining may be  
181 treated by repeating the fusion with the same salt, performing a fusion with a different salt, wet  
182 ashing, or any combination of the three.

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

188 Samples to be fused should be oven-dried to remove moisture. Charring to remove organic  
 189 material is not usually necessary because samples with significant amounts of organic material  
 190 are typically dry ashed or wet ashed before fusion. Solid samples are ground mesh size to  
 191 increase the surface area, allowing the fusion process to proceed more readily. The sample must  
 192 be thoroughly mixed with the flux in an appropriate ratio. Generally, the crucible should never be  
 193 more than half-filled at the outset of the fusion process. Fusions may be performed using sand or  
 194 oil baths on a hot plate, in a muffle furnace, or over a burner. Crucibles are made of platinum,  
 195 zirconium, nickel, or porcelain (Table 13.1). The choice of heat source and crucible material  
 196 generally depends on the salt used for the fusion.

TABLE 13.1 — Common fusion fluxes

Flux (mp, °C)	Fusion Temperature, °C	Type of Crucible	Types of Sample Decomposed
Na <sub>2</sub> S <sub>2</sub> O <sub>7</sub> (403) or K <sub>2</sub> S <sub>2</sub> O <sub>7</sub> (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 <sub>2</sub> CO <sub>3</sub> (853) or K <sub>2</sub> CO <sub>3</sub> (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 <sub>2</sub> O <sub>2</sub>	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 <sub>3</sub> BO <sub>3</sub> (169)		Pt	For analysis of sand, aluminum silicates, titanite, natural aluminum oxide (corundum), and enamels.
Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> (878)	1,000-1,200	Pt	For Al <sub>2</sub> O <sub>3</sub> ; ZrO <sub>2</sub> and zirconium ores, minerals of the rare earths, Ti, Nb, and Ta, aluminum-containing materials; iron ores and slags.
Li <sub>2</sub> B <sub>4</sub> O <sub>7</sub> (920) or LiBO <sub>2</sub> (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 <sub>2</sub> and nearly all minerals.
NH <sub>4</sub> HF <sub>2</sub> (125) NaF (992) KF (857) or KHF <sub>2</sub> (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.

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

219 Fusions are heated slowly and evenly to prevent ignition of the sample before the reaction with  
 220 the molten salt can begin. It is especially important to raise the temperature slowly when using a

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221 gas flame because the evolution of water and gases is a common occurrence at the beginning of  
222 the fusion, and hence a source of spattering. The crucible can be covered with a lid as an added  
223 precaution. Sand and oil baths provide the most even source of heat, but they are difficult to  
224 maintain at very high temperatures. Muffle furnaces provide an even source of heat, but when  
225 using them it is difficult to monitor the progress of the reaction and impossible to work with the  
226 sample during the fusion. Burners are used often as a convenient heat source although they make  
227 it difficult to heat the sample evenly.

228 The maximum temperature employed varies considerably and depends on the sample and the  
229 flux. In order to minimize attack of the crucible and decomposition of the flux, excessive  
230 temperatures should be avoided. Once the salt has melted, the melt is swirled gently to monitor  
231 the reaction. The fusion continues until visible signs of reaction are completed (e.g., formation of  
232 gases, foaming, fumes). It is frequently difficult to decide when heating should be discontinued.  
233 In ideal cases, a clear melt serves to indicate the completeness of sample decomposition. In other  
234 cases, it is not as obvious, and the analyst must base the heating time on past experience with the  
235 sample type.

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

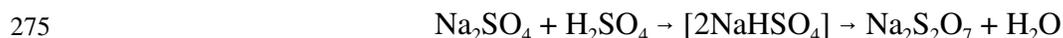
239 After the sample has returned to room temperature, the fused material is dissolved. The solvent is  
240 usually warm water or a dilute acid solution, depending on the salt. For example, dilute acid  
241 typically would not be used to dissolve a carbonate fusion because of losses to spray caused by  
242 release of CO<sub>2</sub>. The aqueous solution from the dissolution of the fusion melt should be examined  
243 carefully for particles of undissolved sample. If undissolved particles are present, they should be  
244 separated from solution by centrifugation or filtration, and a second fusion should be performed.

245 Several types of materials are used for crucibles, but platinum, other metals (Ni, Zr, Ag), and  
246 graphite are most common. Graphite crucibles are a cost-effective alternative to metal crucibles;  
247 they are disposable, which eliminates the need for cleaning and the possibility of cross-sample  
248 contamination. Graphite crucibles are chemically inert and heat-resistant, although they do  
249 oxidize slowly at temperatures above 430 °C. Graphite is not recommended for extremely  
250 lengthy fusions or for reactions where the sample may be reduced. Platinum is probably the most  
251 commonly used crucible material. It is virtually unaffected by any of the usual acids, including  
252 hydrofluoric, and it is attacked only by concentrated phosphoric acid at very high temperatures,  
253 and by sodium carbonate. However, it dissolves readily in mixtures of hydrochloric and nitric  
254 acids (aqua regia), nitric acid containing added chlorides, or chlorine water or bromine water.

255 Platinum offers adequate resistance toward molten alkali metal, borates, fluorides, nitrates, and  
256 bisulfates. When using a platinum crucible, one should avoid using aqua regia, sodium peroxide,  
257 free elements (C, P, S, Ag, Bi, Cu, Pb, Zn, Se, and Te), ammonium, chlorine and volatile  
258 chlorides, sulfur dioxide, and gases with carbon content. Platinum crucibles can be cleaned in  
259 boiling HCl, by hand cleaning with sea sand, or by performing a blank fusion with sodium  
260 hydrogen sulfate.

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

270 SULFATE FUSION is useful for the conversion of ignited oxides to sulfates, but is generally an  
271 ineffective approach for silicates. Sulfate fusion is particularly useful for BeO, Fe<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>,  
272 MoO<sub>3</sub>, TeO<sub>2</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub>, Nb<sub>2</sub>O<sub>5</sub>, Ta<sub>2</sub>O<sub>5</sub>, PuO<sub>2</sub>, and rare earth oxides (Bock, 1979, pp. 77-82).  
273 Pyrosulfate fusions are prepared routinely in the laboratory by heating a mixture of sodium or  
274 potassium sulfate with a stoichiometric excess of sulfuric acid:



278 The rate of heating is increased with time until the sulfuric acid has volatilized and a clear  
279 pyrosulfate fusion is obtained. It is important to note that pyrosulfate fusions are reversible and,  
280 if needed, the fusion can be cooled, additional sulfuric acid added, and the fusion repeated as  
281 many times as needed to dissolve the sample. The analyst must distinguish between insoluble  
282 material that has not yet or will not dissolve, and material that has precipitated during the final  
283 stages of a prolonged pyrosulfate fusion. In the latter situation the fusion must be cooled,  
284 additional sulfuric acid added, and the sample refluxed until the precipitated material redissolves  
285 and a clear melt is obtained. Otherwise, the precipitated material will be extremely difficult, if  
286 not impossible, to dissolve in subsequent steps. Platinum or quartz crucibles are recommended

287 for this type of fusion, with quartz being preferred for analysis of the platinum group metals.  
288 After the melt is cooled and solidified, it should be dissolved in dilute sulfuric or hydrochloric  
289 acid rather than in water to avoid hydrolysis and precipitation of Ti, Zr, etc. Niobium and  
290 tantalum may precipitate even in the presence of more concentrated acid. In order to avoid  
291 precipitation of Nb or Ta, concentrated sulfuric acid, tartaric acid, ammonium oxalate, hydrogen  
292 peroxide, or hydrofluoric acid must be used. Mercury and the anions of volatile acids are largely  
293 volatilized during these fusion procedures.

### 294 13.3.1 Alkali-Metal Hydroxide Fusions

295 Alkali metal hydroxide fusions are used for silicate analysis of ash and slag; for decomposition of  
296 oxides, phosphates, and fluorides (Bock, 1979, pp. 102-108); and for dissolution of soils for  
297 actinide analyses (Smith et al., 1995). Sodium hydroxide (NaOH) generally is used because of its  
298 lower melting point, but potassium hydroxide (KOH) is just as effective. These fusions generally  
299 are rapid, the melts are easy to dissolve in water, and the losses because of volatility are reduced  
300 because of the low temperature of the melt. Nickel, silver, or glassy carbon crucibles are  
301 recommended for this type of fusion. The maximum suggested temperature for nickel crucibles is  
302 600 °C, but silver crucibles can be used up to 700 °C. Generally, crucibles made of platinum,  
303 palladium, and their alloys should not be used with hydroxide fusions because the crucibles are  
304 easily attacked in the presence of atmospheric oxygen. The weight ratio of fusion salt to sample  
305 is normally 5-10:1. Typically, these fusions are carried out below red heat at 450 to 500 °C for  
306 15 to 20 minutes, or sometimes at higher temperatures between 600 to 700 °C for 5 to 10  
307 minutes. The solidified melt dissolves readily in water; and therefore, this step may be carried out  
308 directly in the crucible, or alternatively in a nickel dish. Under no circumstances should the  
309 dissolution be carried out in a glass vessel because the resulting concentrated hydroxide solution  
310 attacks glass quite readily.

311 FUSION WITH SODIUM CARBONATE (Na<sub>2</sub>CO<sub>3</sub>) is a common procedure for decomposing silicates  
312 (clays, rocks, mineral, slags, glasses, etc.), refractory oxides (magnesia, alumina, beryllia,  
313 zirconia, quartz, etc.), and insoluble phosphates and sulfates (Bogen, 1978). The fusion may  
314 result in the formation of a specific compound such as sodium aluminate, or it may simply  
315 convert a refractory oxide into a condition where it is soluble in hydrochloric acid—this is the  
316 method of choice when silica in a silicate is to be determined, because the fusion converts an  
317 insoluble silicate into a mixture that is easily decomposed by hydrochloric acid (“M” represents a  
318 metal in the equations below):



320 followed by acidification to form a more soluble chloride salt,



322 Carbonate fusions provide an oxidizing melt for the analysis of chromium, manganese, sulfur,  
323 boron, and the platinum group metals. Organic material is destroyed, sometimes violently.  
324  $\text{Na}_2\text{CO}_3$  generally is used because of its lower melting point. However, despite its higher melting  
325 point and hygroscopic nature,  $\text{K}_2\text{CO}_3$  is preferred for niobium and tantalum analyses because the  
326 resulting potassium salts are soluble, whereas the analogous sodium salts are insoluble.

327 The required temperature and duration of the fusion depend on the nature of the sample as well  
328 as particle size. In the typical carbonate fusion, 1 g of the powdered sample is mixed with 4 to 6 g  
329 of sodium carbonate and heated at 900 to 1,000 °C for 10 to 30 minutes. Very refractory  
330 materials may require heating at 1,200 °C for as long as 1 to 2 hours. Silica will begin to react at  
331 500 °C, while barium sulfate and alumina react at temperatures above 700 °C. Notably, volatility  
332 is a problem at these temperatures. Mercury and thallium are lost completely, while selenium,  
333 arsenic, and iodine suffer considerable losses. Non-silicate samples should be dissolved in water,  
334 while silicate samples should be treated with acid (Bock, 1979, p. 111).

335 Platinum crucibles are recommended, even though there is a 1 to 2 mg loss of platinum per  
336 fusion. Attack on the crucible can be reduced significantly by covering the melt with a lid during  
337 the fusion process, or virtually eliminated by working in an inert atmosphere. Moreover, nitrate is  
338 often added to prevent the reduction of metals and the subsequent alloying with the platinum  
339 crucibles. The platinum crucibles may be seriously attacked by samples containing high  
340 concentrations of  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Sn}^{4+}$ ,  $\text{Pb}^{2+}$ , and compounds of Sb and As, because these ions are  
341 reduced easily to the metallic state and then form intermetallic alloys with platinum that are not  
342 easily dissolved in mineral acids. This problem is especially prevalent when fusion is carried out  
343 in a gas flame. Porcelain crucibles are corroded rapidly and should be discarded after a single  
344 use.

### 345 **13.3.2 Boron Fusions**

346 Fusions with boron compounds are recommended for analysis of sand, slag, aluminum silicates,  
347 alumina ( $\text{Al}_2\text{O}_3$ ), iron and rare earth ores, zirconium dioxide, titanium, niobium, and tantalum.  
348 Relatively large amounts of flux are required for these types of fusions. The melts are quite  
349 viscous and require swirling or stirring, so they should not be performed in a furnace. Platinum  
350 crucibles should be used for these fusions because other materials are rapidly attacked by the  
351 melt, even though some platinum is lost in each fusion.

## *Sample Dissolution*

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352 BORIC ACID ( $\text{H}_3\text{BO}_3$ ) can be used to fuse a number of otherwise rather inert substances such as  
353 sand, aluminum silicates, titanite, natural aluminum oxide (corundum), and enamels. Boric acid  
354 fusions generally require 4 to 8 times as much reagent as sample. Initially, the mixture should be  
355 heated cautiously while water is being driven off, then more strongly until gas evolution is  
356 completed, and then more vigorously if the sample has yet to be fully decomposed. Normally, the  
357 procedure is complete within 20 to 30 minutes. The cooled and solidified melt usually is  
358 dissolved in dilute acid. Additionally, boric acid has one great advantage over all other fluxes in  
359 that it can be completely removed by addition of methanol and subsequent volatilization of the  
360 methyl ester.

361 Because MOLTEN SODIUM TETRABORATE ( $\text{Na}_2\text{B}_4\text{O}_7$ ) dissolves so many inorganic compounds, it is  
362 an important analytical tool for dissolving very resistant substances. Fusions with sodium  
363 tetraborate alone are useful for  $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$  and zirconium ores, minerals of the rare earths,  
364 titanium, niobium, and tantalum, aluminum-containing materials, and iron ores and slags (Bock,  
365 1979). Relatively large amounts of borax are mixed with the sample, and the fusion is carried out  
366 at a relatively high temperature (1,000 to 1,200 °C) until the melt becomes clear. Thallium,  
367 mercury, selenium, arsenic, and the halogens are volatilized under these conditions. Boric acid  
368 can be removed from the melt as previously described. By dissolving the melt in dilute  
369 hydrofluoric acid, calcium, thorium, and the rare earths can be separated from titanium, niobium,  
370 and tantalum as insoluble fluorides.

371 Fluxes of LITHIUM TETRABORATE ( $\text{Li}_2\text{B}_4\text{O}_7$ ) are well suited for dissolving basic oxides such as  
372 alumina ( $\text{SiO}_2$ ) and some resistant silicates. However, lithium metaborate,  $\text{LiBO}_2$ , (or a mixture  
373 of meta- and tetraborate) is more basic and better suited for dissolving acidic oxides such as  
374 silica or titanium dioxide, although it is capable of dissolving nearly all minerals (Dean, 1995).  
375 Platinum dishes normally are used for this type of fusion, but occasionally graphite crucibles are  
376 advantageous because they can be heated rapidly by induction heating and because they are not  
377 wetted by  $\text{Li}_2\text{B}_4\text{O}_7$  melts. The fusion melt typically is dissolved in dilute acid, usually nitric but  
378 sometimes sulfuric. When easily hydrolyzed metal ions are present, it is recommended that  
379 dissolution be carried out in the presence of EDTA or its sodium salt in 0.01 M HCl (Bock, 1979,  
380 p. 92). Moreover, when titanium is present, hydrogen peroxide can be used to help maintain the  
381 titanium in solution.

### 382 **13.3.3 Fluoride Fusions**

383 Fluoride fusions are used for the removal of silicon, the destruction of silicates and rare earth  
384 minerals, and the analysis of oxides of niobium, tantalum, titanium, and zirconium. Sill et al.  
385 (1974) and Sill and Sill (1995) has described a method using potassium fluoride/potassium

386 pyrosulfate fusion for determining alpha-emitting nuclides in soil (see Sect. 13.8). Sulcek and  
387 Povondra (1989) describe the isolation of the rare earth elements (REE) and thorium from  
388 silicate materials and their minerals, especially monazite, through potassium hydrofluoride  
389 fusion. The silicate matrix is first degraded by evaporation with HF, then the residue is fused  
390 with tenfold excess flux, and finally the melt is digested with dilute acid. The resulting fluorides  
391 (REE + Th + Ca + U) are filtered off, dissolved, and further separated by chromatography.

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

### 397 **13.4 Wet Ashing and Acid Dissolution Techniques**

398 “Wet ashing” and “acid dissolution” are terms used to describe sample decomposition using hot,  
399 concentrated acid solutions. Because many inorganic matrices such as oxides, silicates, nitrides,  
400 carbides, and borides can be difficult to dissolve completely, geological or ceramic samples can  
401 be particularly challenging. Therefore, different acids are used alone or in combination to  
402 decompose specific compounds that may be present in the sample. Few techniques will  
403 completely decompose all types of samples. Many decomposition procedures use wet ashing to  
404 dissolve the major portion of the sample but leave a minor fraction as residue. Whether or not  
405 this residue requires additional treatment (by wet ashing or fusion) depends on the amount of  
406 residue and whether it is expected to contain the radionuclides of interest. The residue should not  
407 be discarded until all of the results have been reviewed and determined to be acceptable.

#### 408 **13.4.1 Acids and Oxidants**

409 Numerous acids are commonly used in wet ashing procedures. Table 13.2 lists several acids and  
410 the types of compounds they generally react with during acid dissolution. The electromotive  
411 force series (Table 13.3) is a summary of oxidation-reduction half-reactions arranged in  
412 decreasing oxidation strength and is also useful in selecting reagent systems (Dean, 1995). The  
413 table allows one to predict which metals will dissolve in nonoxidizing acids, such as  
414 hydrochloric, hydrobromic, hydrofluoric, phosphoric, dilute sulfuric, and dilute perchloric acid  
415 The dissolution process is simply a replacement of hydrogen by the metal (Dean, 1995). In  
416 practice, however, what actually occurs is influenced by a number of factors, and the behavior of  
417 the metals cannot be predicted from the potentials alone. Generally, metals below hydrogen in  
418 Table 13.3 displace hydrogen and dissolve in nonoxidizing acids with the evolution of hydrogen.

Sample Dissolution

419 Notable exceptions include the very slow dissolution by hydrochloric acid of lead, cobalt, nickel,  
 420 cadmium, and chromium. Also, lead is insoluble in sulfuric acid because of the formation of a  
 421 surface film of insoluble lead sulfate.

422 **TABLE 13.2 — Examples of acids used for wet ashing**

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

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

434	Half-Reaction	E <sup>0</sup> (volts)
435	Ag <sup>2+</sup> + e <sup>-</sup> = Ag <sup>+</sup> . . . . .	1.980
436	S <sub>2</sub> O <sub>8</sub> <sup>2-</sup> + 2e <sup>-</sup> = 2SO <sub>4</sub> <sup>2-</sup> . . . . .	1.96
437	HN <sub>3</sub> + 3H <sup>+</sup> + 2e <sup>-</sup> = NH <sub>4</sub> <sup>+</sup> + N <sub>2</sub> . . . . .	1.96
438	Ce <sup>4+</sup> + e <sup>-</sup> = Ce <sup>3+</sup> . . . . .	1.72
439	MnO <sub>4</sub> <sup>-</sup> + 4H <sup>+</sup> + 3e <sup>-</sup> = MnO <sub>2</sub> (c) + 2H <sub>2</sub> O . . . . .	1.70
440	2HClO + 2H <sup>+</sup> + 2e <sup>-</sup> = Cl <sub>2</sub> + 2H <sub>2</sub> O . . . . .	1.630
441	2HBrO + 2H <sup>+</sup> + 2e <sup>-</sup> = Br <sub>2</sub> + 2H <sub>2</sub> O . . . . .	1.604
442	NiO <sub>2</sub> + 4H <sup>+</sup> + 2e <sup>-</sup> = Ni <sup>2+</sup> + 2H <sub>2</sub> O . . . . .	1.593
443	Bi <sub>2</sub> O <sub>4</sub> (bismuthate) + 4H <sup>+</sup> + 2e <sup>-</sup> = 2BiO <sup>+</sup> + 2H <sub>2</sub> O . . . . .	1.59
444	MnO <sub>4</sub> <sup>-</sup> + 8H <sup>+</sup> + 5e <sup>-</sup> = Mn <sup>2+</sup> + 4H <sub>2</sub> O . . . . .	1.51
445	2BrO <sub>3</sub> <sup>-</sup> + 12H <sup>+</sup> + 10e <sup>-</sup> = Br <sub>2</sub> + 6H <sub>2</sub> O . . . . .	1.478
446	PbO <sub>2</sub> + 4H <sup>+</sup> + 2e <sup>-</sup> = Pb <sup>2+</sup> + 2H <sub>2</sub> O . . . . .	1.468
447	Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup> + 14H <sup>+</sup> + 6e <sup>-</sup> = 2Cr <sup>3+</sup> + 7H <sub>2</sub> O . . . . .	1.36
448	Cl <sub>2</sub> + 2e <sup>-</sup> = 2Cl <sup>-</sup> . . . . .	1.3583
449	2HNO <sub>2</sub> + 4H <sup>+</sup> + 4e <sup>-</sup> = N <sub>2</sub> O + 3H <sub>2</sub> O . . . . .	1.297

	Half-Reaction	E <sup>0</sup> (volts)
450	$\text{MnO}_2 + 4\text{H}^+ + 2\text{e}^- = \text{Mn}^{2+} + 2\text{H}_2\text{O}$	1.23
451	$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- = 2\text{H}_2\text{O}$	1.229
452	$\text{ClO}_4^- + 2\text{H}^+ + 2\text{e}^- = \text{ClO}_3^- + \text{H}_2\text{O}$	1.201
453	$2\text{IO}_3^- + 12\text{H}^+ + 10\text{e}^- = \text{I}_2 + 3\text{H}_2\text{O}$	1.195
454	$\text{N}_2\text{O}_4 + 2\text{H}^+ + 2\text{e}^- = 2\text{HNO}_3$	1.07
455	$2\text{ICl}_2 + 2\text{e}^- = 4\text{Cl}^- + \text{I}_2$	1.07
456	$\text{Br}_2 (\text{lq}) + 2\text{e}^- = 2\text{Br}^-$	1.065
457	$\text{N}_2\text{O}_4 + 4\text{H}^+ + 4\text{e}^- = 2\text{NO} + 2\text{H}_2\text{O}$	1.039
458	$\text{HNO}_2 + \text{H}^+ + \text{e}^- = \text{NO} + \text{H}_2\text{O}$	0.996
459	$\text{NO}_3^- + 4\text{H}^+ + 3\text{e}^- = \text{NO} + 2\text{H}_2\text{O}$	0.957
460	$\text{NO}_3^- + 3\text{H}^+ + 2\text{e}^- = \text{HNO}_2 + \text{H}_2\text{O}$	0.94
461	$2\text{Hg}^{2+} + 2\text{e}^- = \text{Hg}_2^{2+}$	0.911
462	$\text{Cu}^{2+} + \text{I}^- + \text{e}^- = \text{CuI}$	0.861
463	$\text{OsO}_4 (\text{c}) + 8\text{H}^+ + 8\text{e}^- = \text{Os} + 4\text{H}_2\text{O}$	0.84
464	$\text{Ag}^+ + \text{e}^- = \text{Ag}$	0.7991
465	$\text{Hg}_2^{2+} + 2\text{e}^- = 2\text{Hg}$	0.7960
466	$\text{Fe}^{3+} + \text{e}^- = \text{Fe}^{2+}$	0.771
467	$\text{H}_2\text{SeO}_3 + 4\text{H}^+ + 4\text{e}^- = \text{Se} + 3\text{H}_2\text{O}$	0.739
468	$\text{HN}_3 + 11\text{H}^+ + 8\text{e}^- = 2\text{NH}_4^+$	0.695
469	$\text{O}_2 + 2\text{H}^+ + 2\text{e}^- = \text{H}_2\text{O}_2$	0.695
470	$\text{Ag}_2\text{SO}_4 + 2\text{e}^- = 2\text{Ag} + \text{SO}_4^{2-}$	0.654
471	$\text{Cu}^{2+} + \text{Br}^- + \text{e}^- = \text{CuBr} (\text{c})$	0.654
472	$2\text{HgCl}_2 + 2\text{e}^- = \text{Hg}_2\text{Cl}_2 (\text{c}) + 2\text{Cl}^-$	0.63
473	$\text{Sb}_2\text{O}_5 + 6\text{H}^+ + 4\text{e}^- = 2\text{SbO}^+ + 3\text{H}_2\text{O}$	0.605
474	$\text{H}_3\text{AsO}_4 + 2\text{H}^+ + 2\text{e}^- = \text{HAsO}_2 + 2\text{H}_2\text{O}$	0.560
475	$\text{TeOOH}^+ + 3\text{H}^+ + 4\text{e}^- = \text{Te} + 2\text{H}_2\text{O}$	0.559
476	$\text{Cu}^{2+} + \text{Cl}^- + \text{e}^- = \text{CuCl} (\text{c})$	0.559
477	$\text{I}_2 + 2\text{e}^- = 3\text{I}^-$	0.536
478	$\text{I}_2 + 2\text{e}^- = 2\text{I}^-$	0.536
479	$\text{Cu}^+ + \text{e}^- = \text{Cu}$	0.53
480	$4\text{H}_2\text{SO}_3 + 4\text{H}^+ + 6\text{e}^- = \text{S}_4\text{O}_6^{2-} + 6\text{H}_2\text{O}$	0.507
481	$\text{Ag}_2\text{CrO}_4 + 2\text{e}^- = 2\text{Ag} + \text{CrO}_4^{2-}$	0.449
482	$2\text{H}_2\text{SO}_3 + 2\text{H}^+ + 4\text{e}^- = \text{S}_2\text{O}_3^{2-} + 3\text{H}_2\text{O}$	0.400
483	$\text{UO}_2^+ + 4\text{H}^+ + \text{e}^- = \text{U}^{4+} + 2\text{H}_2\text{O}$	0.38
484	$\text{Cu}^{2+} + 2\text{e}^- = \text{Cu}$	0.340
485	$\text{VO}^{2+} + 2\text{H}^+ + \text{e}^- = \text{V}^{3+} + \text{H}_2\text{O}$	0.337
486	$\text{BiO}^+ + 2\text{H}^+ + 3\text{e}^- = \text{Bi} + \text{H}_2\text{O}$	0.32
487	$\text{UO}_2^{2+} + 4\text{H}^+ + 2\text{e}^- = \text{U}^{4+} + 2\text{H}_2\text{O}$	0.27
488	$\text{Hg}_2\text{Cl}_2 (\text{c}) + 2\text{e}^- = 2\text{Hg} + 2\text{Cl}^-$	0.2676

Sample Dissolution

	Half-Reaction	E <sup>0</sup> (volts)
489	AgCl + e <sup>-</sup> = Ag + Cl <sup>-</sup> .....	0.2223
490	SbO <sup>+</sup> + 2H <sup>+</sup> + 3e <sup>-</sup> = Sb + H <sub>2</sub> O .....	0.212
491	CuCl <sub>3</sub> <sup>2-</sup> + e <sup>-</sup> = Cu + 3Cl <sup>-</sup> .....	0.178
492	SO <sub>4</sub> <sup>2-</sup> + 4H <sup>+</sup> + 2e <sup>-</sup> = H <sub>2</sub> SO <sub>3</sub> + H <sub>2</sub> O .....	0.158
493	Sn <sup>4+</sup> + 2e <sup>-</sup> = Sn <sup>2+</sup> .....	0.15
494	CuCl + e <sup>-</sup> = Cu + Cl <sup>-</sup> .....	0.121
495	TiO <sup>2+</sup> + 2H <sup>+</sup> + e <sup>-</sup> = Ti <sup>3+</sup> + H <sub>2</sub> O .....	0.100
496	S <sub>4</sub> O <sub>6</sub> <sup>2-</sup> + 2e <sup>-</sup> = 2S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> .....	0.08
497	2H <sup>+</sup> + 2e <sup>-</sup> = H <sub>2</sub> .....	0.0000
498	Hg <sub>2</sub> I <sub>2</sub> + 2e <sup>-</sup> = 2Hg + 2I <sup>-</sup> .....	-0.0405
499	Pb <sup>2+</sup> + 2e <sup>-</sup> = Pb .....	-0.125
500	Sn <sup>2+</sup> + 2e <sup>-</sup> = Sn .....	-0.136
501	AgI + e <sup>-</sup> = Ag + I <sup>-</sup> .....	-0.1522
502	V <sup>3+</sup> + e <sup>-</sup> = V <sup>2+</sup> .....	-0.255
503	Ni <sup>2+</sup> + 2e <sup>-</sup> = Ni .....	-0.257
504	Co <sup>2+</sup> + 2e <sup>-</sup> = Co .....	-0.277
505	PbSO <sub>4</sub> + 2e <sup>-</sup> = Pb + SO <sub>4</sub> <sup>2-</sup> .....	-0.3505
506	Cd <sup>2+</sup> + 2e <sup>-</sup> = Cd .....	-0.4025
507	Cr <sup>3+</sup> + e <sup>-</sup> = Cr <sup>2+</sup> .....	-0.424
508	Fe <sup>2+</sup> + 2e <sup>-</sup> = Fe .....	-0.44
509	H <sub>3</sub> PO <sub>3</sub> + 2H <sup>+</sup> + 2e <sup>-</sup> = HPH <sub>2</sub> O <sub>2</sub> + H <sub>2</sub> O .....	-0.499
510	U <sup>4+</sup> + e <sup>-</sup> = U <sup>3+</sup> .....	-0.52
511	Zn <sup>2+</sup> + 2e <sup>-</sup> = Zn .....	-0.7626
512	Mn <sup>2+</sup> + 2e <sup>-</sup> = Mn .....	-1.18
513	Al <sup>3+</sup> + 3e <sup>-</sup> = Al .....	-1.67
514	Mg <sup>2+</sup> + 2e <sup>-</sup> = Mg .....	-2.356
515	Na <sup>+</sup> + e <sup>-</sup> = Na .....	-2.714
516	K <sup>+</sup> + e <sup>-</sup> = K .....	-2.925
517	Li <sup>+</sup> + e <sup>-</sup> = Li .....	-3.045
518	Source: Dean, 1995.	

519 Oxidizing acids, such as nitric acid, hot concentrated sulfuric acid, or hot concentrated perchloric  
 520 acid, are used to dissolve metals above hydrogen. For nitric acid, the potential of the nitrate ion-  
 521 nitric oxide couple can be employed as a rough estimate of the solvent power. For aqua regia, the  
 522 presence of free chlorine ions allows one to make predictions based upon the potential of the  
 523 chlorine-chloride couple, although NOCl also plays a significant role. Some oxidizing acids  
 524 exhibit a passivating effect with transition elements such as chromium and pure tungsten,  
 525 resulting in a very slow attack because of the formation of an insoluble surface film of the oxide

526 in the acid (Bogen, 1978). Moreover, oxides are often resistant to dissolution in oxidizing acids  
527 and, in fact, dissolve much more readily in nonoxidizing acids. A common example is ferric  
528 oxide, which is readily soluble in hydrochloric acid but is relatively inert in nitric acid.

529 However, insoluble oxides of the lower oxidation states of an element sometime dissolve in  
530 oxidizing acids with concurrent oxidation of the element. For example,  $\text{UO}_2$  and  $\text{U}_3\text{O}_8$  dissolve  
531 readily in nitric acid to produce a solution of uranyl ion ( $\text{UO}_2^{+2}$ ).

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



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



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

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550 polymeric depolymerize to form reactive monomeric species suitable for further analytical  
551 operations. Formation of colloidal solutions is avoided and the stability of solutions is increased  
552 even with compounds of elements that are easily hydrolyzed in aqueous solution (e.g., Si, Sn, Ti,  
553 Zr, Hf, Nb, Ta, and Pa).

554 HF should never be used or stored in glass containers. Platinum containers are preferred, and  
555 Teflon is acceptable as long as the temperature does not exceed 250 °C; the constant boiling

## Sample Dissolution

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556 azeotrope boils at 112 °C. HF works most effectively when used alone. Samples should be  
557 ground to a fine powder to increase the surface area and moistened with water to prevent losses  
558 as dust and spray when the acid is added to the sample. After the addition of HF, the sample is  
559 allowed to stand overnight to dissolve the silicates. However, the reaction can be sped up by  
560 heating the solution. Because it is such a strong complexing agent, excess fluoride ion can cause  
561 problems with many chemical reactions. Residual fluoride is usually removed by evaporation to  
562 fumes in a low-volatility acid (e.g., H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, HClO<sub>4</sub>) or, in extreme cases, excess fluoride  
563 ion can be removed by fusing the residue with K<sub>2</sub>S<sub>2</sub>O<sub>7</sub> or by the addition of quartz (SiO<sub>2</sub>).

564 HYDROCHLORIC ACID (HCl) is one of the most widely used acids for wet ashing samples because  
565 of the wide range of compounds it reacts with and the low boiling point of the azeotrope (110  
566 °C); after a period of heating in an open container, a constant boiling 6M solution remains. HCl  
567 forms strong complexes with gold (III), titanium (III), and mercury (II). The concentrated acid  
568 will also complex iron (III), gallium (III), indium (III), and tin (IV). Most chloride compounds are  
569 readily soluble in water except for silver chloride, mercury chloride, titanium chloride, and lead  
570 chloride. HCl can be oxidized to form chlorine gas by manganese dioxide, permanganate, and  
571 persulfate. While HCl dissolves many carbonates, oxides, hydroxides, phosphates, borates,  
572 sulfides, and cement, it does not dissolve the following:

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

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

582 “The rate of decomposition of oxidic uranium ores depends on the U(VI)/U(IV) ratio. The so-  
583 called uranium blacks with minimal contents of U(IV) are even dissolved in dilute  
584 hydrochloric acid. Uraninite (UO<sub>2</sub>) requires an oxidizing mixture of hydrochloric acid with  
585 hydrogen peroxide, chlorate, or nitric acid for dissolution. Uranium and thorium compounds  
586 cannot be completely leached from granites by hydrochloric acid. Natural and synthetic  
587 thorium dioxides are highly resistant toward hydrochloric acid and must be decomposed in a  
588 pressure vessel. Binary phosphates of uranyl and divalent cations, e.g., autunite and tobernite,  
589 are dissolved without difficulties. On the other hand, phosphates of thorium, tetravalent

590 uranium, and the rare earths (monazite and xenotime) are only negligibly attacked, even with  
591 the concentrated acid.”

592 Arsenic (III), antimony (III), germanium (III), and selenium (IV) are easily volatilized in HCl  
593 solutions, while mercury (II), tin (IV), and rhenium (VII) are volatilized in the latter stages of  
594 evaporation. Glass is the preferred container for HCl solutions.

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

599 HYDROIODIC ACID (HI) is readily oxidized and often appears as a yellowish-brown liquid  
600 because of free iodine. HI is most often used as a reducing agent during dissolutions. HI also  
601 dissolves tin (IV) oxide, and complexes and dissolves mercury (II) sulfide. HI forms an azeotrope  
602 with water containing 56.9 percent w/w of HI, boiling at 127 °C.

603 SULFURIC ACID (H<sub>2</sub>SO<sub>4</sub>) is another widely used acid for sample decomposition. Part of its  
604 effectiveness is due to its high boiling point (about 340 °C). Oxides, hydroxides, carbonates, and  
605 sulfide ores can be dissolved in H<sub>2</sub>SO<sub>4</sub>. The boiling point can be raised by the addition of sodium  
606 or potassium sulfate to improve the attack on ignited oxides, although silicates will still not  
607 dissolve. H<sub>2</sub>SO<sub>4</sub> is not appropriate when calcium is a major constituent because of the low  
608 solubility of CaSO<sub>4</sub>. Other inorganic sulfates are typically soluble in water, with the notable  
609 exceptions of strontium, barium, radium, and lead.

610 Dilute H<sub>2</sub>SO<sub>4</sub> does not exhibit oxidizing properties, but the concentrated acid will oxidize many  
611 elements and almost all organic compounds. Oxidation of organic compounds in H<sub>2</sub>SO<sub>4</sub> is a slow  
612 reaction with a tendency to form indestructible charred residues. Moreover, because of the high  
613 boiling point of H<sub>2</sub>SO<sub>4</sub>, there is an increased risk of losses because of volatilization. Iodine can  
614 be distilled quantitatively, and boron, mercury, selenium, osmium, ruthenium, and rhenium may  
615 be lost to some extent. The method of choice is to oxidize the organic substances with HNO<sub>3</sub>,  
616 volatilize the nitric acid, add H<sub>2</sub>SO<sub>4</sub> until charred, followed by HNO<sub>3</sub> again, repeating the process  
617 until the sample will not char with either HNO<sub>3</sub> or H<sub>2</sub>SO<sub>4</sub>. Dissolution is then continued with  
618 HClO<sub>4</sub>.

619 Glass, quartz, platinum, and porcelain are resistant to H<sub>2</sub>SO<sub>4</sub> up to the boiling point. Teflon  
620 decomposes at 300 °C, below the boiling point, and, therefore, is not recommended for  
621 applications involving H<sub>2</sub>SO<sub>4</sub> that require elevated temperature.

## *Sample Dissolution*

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622 PHOSPHORIC ACID ( $\text{H}_3\text{PO}_4$ ) seldom is used for wet ashing because the residual phosphates  
623 interfere with many procedures.  $\text{H}_3\text{PO}_4$  attacks glass, although glass containers are usually  
624 acceptable at temperatures below 300 °C. Alumina, chromium ores, iron oxide ores, and slags  
625 can be dissolved in  $\text{H}_3\text{PO}_4$ . The acid also has been used to dissolve silicates selectively without  
626 attacking quartz.

627 NITRIC ACID ( $\text{HNO}_3$ ) is one of the most widely used oxidizing acids for sample decomposition.  
628 Most metals and alloys are oxidized to nitrates, which are usually very soluble in water, although  
629 many metals exhibit a pronounced tendency to hydrolyze in nitric acid solution. Nitric acid does  
630 not attack gold, hafnium, tantalum, zirconium, and the metals of the platinum group (except  
631 palladium). Aluminum, boron, chromium, gallium, indium, niobium, thorium, titanium, calcium,  
632 magnesium, and iron form a layer of insoluble oxide when treated with  $\text{HNO}_3$  and are thereby  
633 pacified and do not dissolve in the concentrated acid. However, calcium, magnesium, and iron  
634 will dissolve in more dilute acid.

635 Complexing agents (e.g.,  $\text{Cl}^-$ ,  $\text{F}^-$ , citrate, tartrate) can assist  $\text{HNO}_3$  in dissolving most metals. For  
636 example, Sulcek and Povondra (1989) describe the decomposition of thorium and uranium  
637 dioxides in nitric acid, which is catalytically accelerated by the addition of 0.05 to 0.1 M HF.  
638 They report that a solid solution of the mixed oxides ( $\text{Pu, U}$ ) $\text{O}_2$  or  $\text{PuO}_2$  ignited at temperatures  
639 below 800 °C behaves analogously.

640 Although nitric acid is a good oxidizing agent, it usually boils away before sample oxidation is  
641 complete. Oxidation of organic materials proceeds slowly and is usually accomplished by  
642 repeatedly heating the solution to  $\text{HNO}_3$  fumes. Refluxing in the concentrated acid can help  
643 facilitate the treatment, but  $\text{HNO}_3$  is seldom used alone to decompose organic materials.

644 PERCHLORIC ACID ( $\text{HClO}_4$ ). Hot concentrated solutions of  $\text{HClO}_4$  act as a powerful oxidizer, but  
645 dilute aqueous solutions are not oxidizing. Hot concentrated  $\text{HClO}_4$  will attack nearly all metals  
646 (except gold and platinum group metals) and oxidize them to the highest oxidation state, except  
647 for lead and manganese, which are oxidized only to the +2 oxidation state. Perchloric acid is an  
648 excellent solvent for stainless steel, oxidizing the chromium and vanadium to the hexavalent and  
649 pentavalent acids, respectively. Many nonmetals also will react with  $\text{HClO}_4$ . Because of the  
650 violence of the oxidation reactions,  $\text{HClO}_4$  is rarely used alone for the destruction of organic  
651 materials.  $\text{H}_2\text{SO}_4$  or  $\text{HNO}_3$  are used to dilute the solution and break down easily oxidized material  
652 before  $\text{HClO}_4$  becomes an oxidizer above 160 °C.

653 The concentrated acid is a dangerous oxidant that can explode violently. The following are  
654 examples of some reactions with  $\text{HClO}_4$  that *should never be attempted*:

- 655 • Heating Bi metal and alloys with concentrated acid.
- 656 • Dissolving metals (e.g., steel) in concentrated acid when gas-phase hydrogen becomes  
657 heated.
- 658 • Heating uranium turnings or powder in concentrated acid.
- 659 • Heating finely divided aluminum and silicon in concentrated acid.
- 660 • Heating antimony or antimony (III) compounds in HClO<sub>4</sub>.
- 661 • Mixing HClO<sub>4</sub> with hydrazine or hydroxylamine.
- 662 • Mixing HClO<sub>4</sub> with hypophosphates.
- 663 • Mixing HClO<sub>4</sub> with fats, oils, greases, or waxes.
- 664 • Evaporating solutions of metal salts to dryness in HClO<sub>4</sub>.
- 665 • Evaporating alcoholic filtrates after collection of KClO<sub>4</sub> precipitates.
- 666 • Heating HClO<sub>4</sub> with cellulose, sugar, and polyhydroxy alcohols.
- 667 • Heating HClO<sub>4</sub> with N-heterocyclic compounds.
- 668 • Mixing HClO<sub>4</sub> with any dehydrating agent.

669 Perchloric acid vapor should never be allowed to come in contact with organic materials such as  
670 rubber stoppers. The acid should be stored only in glass bottles. Splashed or spilled acid should  
671 be diluted with water immediately and mopped up with a woolen cloth, never cotton. HClO<sub>4</sub>  
672 should only be used only in specially designed fume hoods incorporating a washdown system.

673 Acid dissolutions involving HClO<sub>4</sub> should only be performed by analysts experienced in working  
674 with this acid. When any procedure is designed, the experimental details should be recorded  
675 exactly. These records are used to develop a detailed SOP that must be followed exactly to  
676 ensure the safety of the analyst (Schilt, 1979).

## *Sample Dissolution*

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677 AQUA REGIA. One part concentrated HNO<sub>3</sub> and 3 parts concentrated HCl (volume/volume) are  
678 combined to form aqua regia:



680 However, the interaction of these two acids is much more complex than indicated by this simple  
681 equation. Both the elemental chlorine and the trivalent nitrogen of the nitrosyl chloride exhibit  
682 oxidizing effects, as do other unstable products formed during the reaction of these two acids.  
683 Coupled with the catalytic effect of Cl<sub>2</sub> and NOCl, this mixture combines the acidity and  
684 complexing power of the chloride ions. The solution is more effective if allowed to stand for 10  
685 to 20 minutes after it is prepared.

686 Aqua regia dissolves sulfides, phosphates, and many metals and alloys including gold, platinum,  
687 and palladium. Ammonium salts are decomposed in this acid mixture. Aqua regia volatilizes  
688 osmium as the tetroxide; has little effect on rhodium, iridium, and ruthenium; and has no effect  
689 on titanium. Oxidic uranium ores with uraninite and synthetic mixed oxides (U<sub>3</sub>O<sub>8</sub>) are dissolved  
690 in aqua regia, with oxidation of the uranium (VI) to UO<sub>2</sub><sup>2+</sup> ions (Sulcek and Povondra, 1989).  
691 However, this dissolution procedure is insufficient for poor ores; the resistant, insoluble fraction  
692 must be further attacked (e.g., by sodium peroxide or borate fusion) or by mixed-acid digestion  
693 with HF, HNO<sub>3</sub>, and HClO<sub>4</sub>.

694 Oxysalts, such as KMnO<sub>4</sub> (potassium permanganate) and K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (potassium dichromate), are  
695 commonly not used to solubilize or wet ash environmental samples for radiochemical analysis  
696 because of their limited ability to oxidize metals and the residue that they leave in the sample  
697 mixture. These oxysalts are more commonly used to oxidize organic compounds.

698 POTASSIUM PERMANGANATE (KMnO<sub>4</sub>) is a strong oxidizer whose use is limited primarily to the  
699 decomposition of organic substances and mixtures, although it oxidizes metals such as mercury  
700 to the ionic form. Oxidation can be performed in an acid, neutral, or basic medium; near-neutral  
701 or basic solutions produce an insoluble residue of manganese dioxide (MnO<sub>2</sub>) that can be  
702 removed by filtration. Oxidation in acid media leaves the manganese (II) ion in solution, which  
703 might interfere with additional chemical procedures or analyses. Extreme caution must be taken  
704 when using this reagent because KMnO<sub>4</sub> reacts violently with some organic substances such as  
705 acetic acid and glycerol, with some metals such as antimony and arsenic, and with common  
706 laboratory reagents such as hydrochloric acid and hydrogen peroxide.

707 POTASSIUM DICHROMATE (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) is a strong oxidizing agent for organic compounds but is not  
708 as strong as KMnO<sub>4</sub>. K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> has been used to determine carbon and halogen in organic

709 materials, but the procedure is not used extensively.  $K_2Cr_2O_7$  is commonly mixed with sulfuric  
710 acid and heated. The chromium (III) ion remains after sample oxidation and this might interfere  
711 with other chemical procedures or analyses.  $K_2Cr_2O_7$  can react violently with certain organic  
712 substances such as ethanol and might ignite in the presence of boron. Caution also must be  
713 observed in handling this oxidizing agent because of human safety concerns, particularly with the  
714 hexavalent form of chromium.

715 SODIUM BROMATE ( $NaBrO_3$ ) is an oxidizing agent for organic compounds but is not used for  
716 metals. Unlike  $KMnO_4$  and  $K_2Cr_2O_7$ , the bromate ion can be removed from solution after sample  
717 oxidation by boiling with excess HCl to produce water and  $Br_2$ . Caution must be observed when  
718 using this oxidizing agent because it can react violently with some organic and inorganic  
719 substances.

#### 720 **13.4.2 Acid Digestion Bombs**

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

729 These sealed pressure vessels are lined with Teflon, which offers resistance to cross-  
730 contamination between samples and to attack by HF. In all reactions, the bomb must never be  
731 completely filled; there must be adequate vapor space above the contents. When working with  
732 inorganic materials, the total volume of sample plus reagents must never exceed two-thirds of the  
733 capacity of the bomb. Moreover, many organic materials can be treated satisfactorily in these  
734 bombs, but critical attention must be given to the nature of the sample as well to possible  
735 explosive reactions with the digestion media.

#### 736 **13.4.3 Is it Dissolved?**

737 Following aggressive acid digestion and even fusion, the analyst often must determine if the  
738 sample has indeed been dissolved. This determination is first made through visual inspection for  
739 particulate matter in the acid leachate or dissolved fusion melt. If a residue is observed, this  
740 residue can be physically separated and subsequently fused or treated in an acid digestion bomb

741 to determine if any analyte was left behind. Sometimes these residues are inconsequential and  
742 contain no analyte of interest. In other cases, residues may consist of materials such as zircons or  
743 other minerals that can contain trapped uranium, thorium, etc. Even if no particles are readily  
744 observed, small undissolved particles that are invisible to the naked eye may be present.  
745 Therefore, the analyst may choose to filter the sample through a 0.22 to 0.45  $\mu\text{m}$  filter, and then  
746 count the filter for gross  $\alpha$ ,  $\beta$ , and  $\gamma$  activity to determine if any activity has been left behind in  
747 the residue. However, this approach is applicable only for samples that contain elevated levels of  
748 radioactivity. Finally, for those cases where the laboratory has decided to perform an acid  
749 digestion rather than a total dissolution fusion, it is advisable to perform a total dissolution on a  
750 subset of the samples and compare the results to those obtained from the acid digestion. This  
751 check will help to substantiate that the acid digestion approach is adequate for the particular  
752 sample matrix.

### 753 **13.5 Microwave Digestion**

754 Microwave energy as a heat source for sample digestion was first described more than 20 years  
755 ago (Abu-Samra et al., 1975). Its popularity is derived from the fact that it is faster, cleaner, more  
756 reproducible, and more accurate than traditional hot-plate digestion. However, until recently, this  
757 technology has had limited application in the radiochemical laboratory because of constraints on  
758 sample size resulting from vessel pressure limitations. Because of this drawback, microwave  
759 dissolution was not practical for many radiochemical procedures where larger sample sizes are  
760 dictated to achieve required detection limits. However, recent advances in vessel design and  
761 improved detection methods, such as ICP-MS (inductively coupled plasma-mass spectrometry)  
762 and ion chromatography have eliminated this disadvantage, and microwave dissolution is  
763 becoming an important tool for today's radiochemists (Smith and Yaeger, 1996; Alvarado et al.,  
764 1996). A series of articles in the journal *Spectroscopy* describes recent advances in microwave  
765 dissolution technology (Kammin and Brandt, 1989; Grillo, 1989 and 1990; Gilman and  
766 Engelhardt, 1989; Lautenschlager, 1989; Noltner et al., 1990), and Dean (1995) presents a  
767 synopsis of current microwave theory and technology in the *Analytical Chemistry Handbook*.  
768 Moreover, *Introduction to Microwave Sample Preparation: Theory and Practice* by Kingston  
769 and Jassie (1988) and *Microwave-Enhanced Chemistry—Fundamentals, Sample Preparation,  
770 and Applications* by Kingston and Haswell (1997), are excellent resources for this topic.

771 Some example protocols for various media are given in ASTM standards: "Standard Practice for  
772 Acid-Extraction from Sediments Using Closed Vessel Microwave Heating" (ASTM D5258)  
773 describes the decomposition of soil and sediment samples for subsequent analyte extraction;  
774 "Standard Practice for Sample Digestion Using Closed Vessel Microwave Heating Technique for  
775 the Determination of Total Metals in Water" (ASTM D4309) addresses the decomposition of

776 surface, saline, domestic, and industrial waste water samples; and “Standard Practice for  
777 Microwave Digestion of Industrial Furnace Feedstreams for Trace Element Analysis” (ASTM  
778 D5513) covers the multistage decomposition of samples of cement raw feed materials, waste-  
779 derived fuels, and other industrial feedstreams for subsequent trace metal analysis. A method for  
780 acid digestion of siliceous and organically based matrices is given in EPA (1996).

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

### 786 **13.5.1 Focused Open-Vessel Systems**

787 A focused open-vessel system has no oven but consists of a magnetron to generate microwaves, a  
788 waveguide to direct and focus the microwaves and a cavity to contain the sample (Grillo, 1989).  
789 Because of the open-vessel design, there is no pressure buildup during processing, and reagents  
790 may be added during the digestion program. These systems are quite universal in that any reagent  
791 and any type of vessel (glass, Perfluoroalcoholoxil™ [PFA], or quartz) can be used.

792 The waveguide ensures that energy is directed only at the portion of the vessel in the path of the  
793 focused microwaves thereby allowing the neck of the vessel and refluxer to remain cool and  
794 ensuring refluxing action. Because of this refluxing action, the system maintains all elements,  
795 even selenium and mercury. The focused microwaves cause solutions to reach higher  
796 temperatures faster than with conventional hotplates or block-type digesters and do so with  
797 superior reproducibility. An aspirator removes excess acid vapors and decomposition gases.  
798 Depending on the system, up to 20 g of solids or 50 to 100 mL of liquids can be digested within  
799 10 to 30 minutes on average.

### 800 **13.5.2 Low-Pressure, Closed-Vessel Systems**

801 These systems consist of a microwave oven equipped with a turntable, a rotor to hold the sample  
802 vessels, and a pressure-control module (Grillo, 1990). The PFA vessels used with these systems  
803 are limited to approximately 225 °C, and, therefore, low-boiling reagents or mixtures of reagents  
804 should be used. However, waste is minimized in these systems because smaller quantities of acid  
805 are required. Moreover, because little or no acid is lost during the digestion, additional portions  
806 of acid may not be required and blank values are minimized. Additionally, these sealed vessels  
807 are limited to 100 to 300 psi, depending on the model thereby limiting the size of organic

808 samples utilized. However, inorganic materials such as metals, water and waste waters, minerals,  
809 and most soils and sediments are easily digested without generating large amounts of gaseous by-  
810 products. Typical sample sizes are on the order of 0.5 g for solids and 45 mL for waters.

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

### 818 **13.5.3 High-Pressure, Closed-Vessel Systems**

819 Recent advances in vessel design have produced microwave vessels capable of withstanding  
820 pressures on the order of 1,500 psi (Lautenschlager, 1989), allowing for larger sample sizes on  
821 the order of 1 to 2 g for soil (Smith and Yaeger, 1996) or 0.5 to 3 g for vegetation (Alvarado et  
822 al., 1996) and, consequently, better detection limits. These high-pressure vessels are used to  
823 digest organic and inorganic substances, such as coals, heavy oils, refractories, and ceramic  
824 oxides, which cannot easily be digested with other techniques. Additionally, vessel composition  
825 continues to improve. Noltner et al. (1990) have demonstrated that Tetrafluorometoxil™ (TFM)  
826 vessels exhibit significantly lower blank background values from residual contamination and  
827 reuse than vessels produced with the more traditional PFA. This lower “memory” results in lower  
828 detection limits, a clear advantage for environmental laboratories.

## 829 **13.6 Special Matrix Considerations**

### 830 **13.6.1 Liquid Samples**

#### 831 13.6.1.1 Aqueous Samples

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

835 13.6.1.2 Nonaqueous Samples

836 Most radiochemical analyses are performed in aqueous solutions. Because nonaqueous liquids  
837 are incompatible with this requirement, these samples must be converted into an aqueous form.  
838 In most cases, the nonaqueous liquid is simply a solvent that does not contain the radionuclide of  
839 interest, and the nonaqueous solvent simply can be removed and the residue dissolved as  
840 described in Sections 13.3 and 13.4.

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

854 **13.6.2 Solid Samples**

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

858 **13.6.3 Filters**

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

867 dissolve the sample. In these cases, the sample may be dry ashed to destroy the filter and the  
868 residue subjected to fusion or other decomposition of oxides in the sample.

#### 869 **13.6.4 Wipe Samples**

870 If oxides and silicates are not present in wipe samples, acid dissolutions are generally acceptable  
871 for sample decomposition. In many cases, it is not the sample but the material from which the  
872 wipe is constructed that causes problems with acid dissolution. Paper wipes are decomposed  
873 easily in sulfuric-nitric solutions or in perchloric nitric solutions or by combustion, and it may be  
874 necessary to dry ash the sample before dissolution. If volatile isotopes are expected, precautions  
875 must be taken to prevent loss when heating (see Section 14.5, “Volatilization and Distillation”).  
876 “Sticky” smears can be more difficult to dissolve—the glue can be especially troublesome and  
877 should be watched closely if perchloric acid is used. Other materials used for wipe samples  
878 should be evaluated on an individual basis to determine the best method for sample  
879 decomposition. In some cases, the sample will be a problem to decompose as well. Oil and  
880 grease are often collected on wipe samples from machinery, and these samples are usually dry  
881 ashed before acid dissolution to remove the organic material. If large amounts of solid material  
882 (i.e., soil, dust, etc.) are collected with the wipe, it is recommended that the sample be treated as  
883 a solid (the analytical protocol specification or the project manager should be consulted before  
884 removing the wipe and simply analyzing the solid sample).

#### 885 **13.6.5 Liquid Scintillation Samples**

886 Sample oxidation is used in association with liquid scintillation counting to enhance the  
887 solubility of samples, decolorize samples to limit quenching, separate radionuclides, concentrate  
888 the analyte from bulk material, or for a combination of these reasons.

##### 889 13.6.5.1 Wet Oxidation

890 Wet oxidation reagents are used to liberate  $^{14}\text{CO}_2$ ,  $^3\text{H}_2\text{O}$ , and  $^{35}\text{SO}_3$  from samples containing  $^{14}\text{C}$ ,  
891  $^3\text{H}$ , and  $^{35}\text{S}$ , respectively, with limited success (Gibbs et al., 1978; Peng, 1977). Nitric acid, nitric  
892 acid with perchloric acid, fuming sulfuric acid with periodate and chromic acid, and perchloric  
893 acid with hydrogen peroxide are employed. However, a consequence of using these strong  
894 reagents is the production of chemiluminescence. Moreover, these reagents also suppress  
895 counting efficiency because they are strong quenching agents.

896 13.6.5.2 Dry Oxidation

897 Dry oxidation refers to combustion of the sample in an oxygen atmosphere to yield the highest  
898 oxides, e.g., H<sub>2</sub>O, CO<sub>2</sub>, SO<sub>3</sub>. Sample oxidizers are currently available for liquid scintillation  
899 based upon this approach. The current system uses a continuous flow of oxygen to ensure  
900 complete oxidation of the sample and to force the gaseous products through the H<sub>2</sub>O and CO<sub>2</sub>  
901 collection regions and any untrapped gases to vented waste. The sample is loaded into a  
902 platinum-rhodium wire basket and then is sealed into the combustion flask. Oxygen begins to  
903 flow as an electric current passes through the wire basket to ignite the sample. The continuous  
904 flow of O<sub>2</sub> sweeps the gaseous combustion products into the air-cooled condenser. The collection  
905 of the combustion products consists of two consecutive stages. First, the water produced in the  
906 combustion process is condensed at 2 °C and collected. Second, the CO<sub>2</sub> produced in the  
907 combustion is isolated by a CO<sub>2</sub> absorber. Each fraction is then mixed with liquid scintillation  
908 cocktail and counted. This instrument is designed to give highly reproducible recoveries of <sup>3</sup>H  
909 and <sup>14</sup>C while eliminating chemiluminescence and various quenching problems.

910 **13.7 Total Dissolution and Leaching**

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

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

927 **13.7.1 Acid Leaching**

928 “Acid leaching” has no accepted definition, but will be defined here as the use of nitric or  
929 hydrochloric acid to put the radionuclide into solution. The acid concentration may vary up to  
930 and include concentrated acid. Normally, the use of hydrofluoric acid and aqua regia are not  
931 included in this definition. Sample size is usually relatively much larger than that used for fusion.  
932 Although mineral acids might not totally break down all matrices, they have been shown to be  
933 effective leaching solvents for metals, oxides, and salts in some samples. In some cases, leaching  
934 requires fewer chemicals and less time to accomplish than complete sample dissolution. For  
935 matrices amenable to leaching, multiple samples are easily processed simultaneously using a  
936 hotplate or microwave system, and excess reagents can be removed through evaporation.  
937 Complete dissolution of a sample is not necessary if it can be demonstrated confidently that the  
938 radionuclide of interest is completely leached from the sample medium. However, if complete  
939 dissolution of the analyte cannot be so demonstrated, then it may be necessary to compare  
940 leaching data with data from totally dissolved samples in order for the analyst to determine the  
941 appropriate method for total analyte content of a specific set of samples. When leaching is a  
942 viable option for analyte removal, as an alternative to complete dissolution, the samples can be  
943 treated with strong acids to leach all or a large fraction of the radionuclides of interest from solid  
944 media. It may be possible to complete the dissolution of leach residue with hot aqua regia and  
945 then followed by hot hydrofluoric acid. The use of these acids is usually used on relatively small  
946 sample residues and may also be used on small samples.

947 Sill and Sill (1995) point out that:

948 “In many cases, the mono-, di-, and small tervalent elements can be leached fairly  
949 completely from simple solids by boiling with concentrated hydrochloric or nitric acids.  
950 However, even these elements cannot necessarily be guaranteed to be dissolved  
951 completely by selective leaching. If they are included in a refractory matrix, they will not  
952 be removed completely without dissolution of the matrix. If the samples have been  
953 exposed to water over long periods of time, such as with sediments in a radioactive waste  
954 pond, small ions such as divalent cobalt will have diffused deeply into the rock lattice  
955 from which they cannot be removed without complete dissolution of the host matrix. In  
956 contrast, because of its large size, ionic cesium has a marked tendency to undergo  
957 isomorphous replacement in the lattice of complex silicates from which it too cannot be  
958 removed completely. In some unpublished work by the present authors, 15% of the <sup>137</sup>Cs  
959 and 5% of the <sup>60</sup>Co in some pond sediments remained in the residue after extensive  
960 leaching, and could not be removed by further boiling for two hours with either

961 concentrated nitric or hydrochloric acids. The fraction remaining in the residue was  
962 obviously much greater with shorter, more reasonable leaching times.”

### 963 **13.7.2 Total Dissolution through Fusion**

964 There are those within the radiochemistry community who maintain that leaching techniques are  
965 always inadequate. Sill and Sill (1995), longtime proponents of total dissolution, state, “Any  
966 procedure that fails to obtain complete sample dissolution for whatever reasons of economy,  
967 speed, sample load, or other expediency is untrustworthy at best, and will inevitably give low and  
968 erratic results.” They go on to support their argument:

969 “The large ter-, quadri-, and pentavalent elements are extremely hydrolytic and form  
970 hydroxides, phosphates, silicates, carbides, etc., that are very insoluble and difficult to  
971 dissolve in common acids, particularly if they have been heated strongly and converted to  
972 refractory forms. For example, eight samples of soil taken in the vicinity of a plutonium-  
973 handling facility were analyzed in the facility’s own laboratory for <sup>239</sup>Pu by their routine  
974 procedure involving leaching with nitric acid in the presence of <sup>236</sup>Pu tracer. The insoluble  
975 residues were then analyzed for the same radionuclide by one of the present authors using  
976 a procedure involving complete dissolution in a potassium fluoride fusion in the presence  
977 of <sup>236</sup>Pu tracer. Four of the residues contained more <sup>239</sup>Pu than the corresponding  
978 leachates, three residues contained about half as much as the leachates, and only one  
979 contained as little as 22%, largely because that sample contained relatively high activity  
980 of the radionuclide (Sill, 1981). None of the water-soluble <sup>236</sup>Pu tracer used in the original  
981 leach determination was present in any of the residues, showing that heterogeneous  
982 exchange did not occur (Sill, 1975). The original results from leaching were, therefore,  
983 grossly inaccurate.”

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

995 **13.7.3 Acid Digestion — Fusion Combined Approach**

996 Clearly, the sample history, as well as the analytical protocol specifications of a study, should  
997 play a significant role in the choice of analytical method. The analyst must be certain that the  
998 chosen dissolution technique will provide adequate data for the problem at hand, whether it be  
999 through acid leaching or total dissolution. However, as a compromise, it is common practice to  
1000 employ a combination of the two approaches when the majority of the material to be analyzed is  
1001 acid-soluble. First, an acid leach is applied to the bulk of the sample. Then any undecomposed  
1002 residue is isolated by filtration and fused with a relatively small quantity of suitable flux. Finally,  
1003 the melt is dissolved and combined with the rest of the sample.

1004 Through this approach, the total matrix is decomposed, but the problems, such as reagent  
1005 quantity, and sample and fusion vessel size (commonly associated with fusions), are limited. The  
1006 quantities of added salt are less; therefore, the sources of contamination or of subsequent  
1007 chemical interferences are reduced. Moreover, losses because of volatility tend to be less because  
1008 only a small fraction of the sample is exposed to the high temperatures associated with the fusion  
1009 process.

1010 **13.8 Examples of Decomposition Procedures**

1011 DECOMPOSITION OF ORGANIC MATERIAL WITH SULFURIC AND NITRIC ACIDS. Add  $\text{H}_2\text{SO}_4$  to the  
1012 sample and heat to fumes in a Kjeldahl flask. Add concentrated  $\text{HNO}_3$  by drops to the flask,  
1013 allowing the reaction to subside after each addition. Periodically heat to fuming to remove water  
1014 and to keep the temperature high. When the solution is clear and colorless, the reaction is  
1015 complete. Very reactive material can be left overnight in a 1:1 solution of the acids. Red or white  
1016 fuming nitric acid can be used to speed up the reaction, if necessary.

1017 DECOMPOSITION OF ORGANIC MATERIAL WITH PERCHLORIC AND NITRIC ACIDS. The acids can be  
1018 added to the sample as a mixture or the sample can be treated with concentrated  $\text{HNO}_3$  first to  
1019 destroy any highly reactive material. The solution is heated to drive off the  $\text{HNO}_3$  and to raise the  
1020 temperature to  $160^\circ\text{C}$ , where the  $\text{HClO}_4$  begins to oxidize the organic material. The reaction is  
1021 generally accompanied by foaming, and  $\text{HNO}_3$  is used to cool the solution and to control the  
1022 formation of foam. The solution should be cooled immediately if any layer of material begins to  
1023 separate and turn brown.  $\text{HNO}_3$  is added to the sample before it is returned to the hot plate. The  
1024 transition into  $\text{HClO}_4$  continues until the foaming is completed and dense white fumes are  
1025 evolved, indicating that  $\text{HClO}_4$  is being evaporated. The volume is reduced and the solution  
1026 converted to  $\text{HNO}_3$  by repeated addition of  $\text{HNO}_3$  and evaporation to near dryness.

1027 DECOMPOSITION OF A SAMPLE OF UNKNOWN COMPOSITION (Noyes and Bray, 1927/1943; Bock,  
1028 1979, Appendix 1). First, destroy the organic material with perchloric and nitric acids and then  
1029 perform an oxidizing dissolution with HBr and Br<sub>2</sub>. Separate the residue and oxidize it with nitric  
1030 acid. Subsequently, heat to fumes with perchloric acid and HF to destroy any silicates present.  
1031 Combine with the HBr solution and distill off the bromides of arsenic, germanium, and selenium.  
1032 Oxidize the residue with nitric acid, add sodium peroxide, and distill off osmium as the tetroxide.  
1033 Add perchloric acid and distill off ruthenium as the tetroxide. Reduce the contents of the flask  
1034 with formic acid. Separate the residue, and leach with HF to dissolve niobium, tantalum, and  
1035 tungsten. Separate the residue, and fuse with sodium carbonate to convert fluorides to carbonates;  
1036 then dissolve the melt in dilute perchloric acid. Separate the residue, and treat with aqua regia to  
1037 dissolve the gold group metals. Separate the residue, and treat with ammonia to dissolve silver.  
1038 Separate the residue, and fuse with K<sub>2</sub>S<sub>2</sub>O<sub>7</sub>; then dissolve the melt in water. Separate the residue,  
1039 and fuse with sodium peroxide.

1040 DECOMPOSITION OF SOIL FOR ACTINIDE ANALYSIS (Sill et al., 1974; Sill and Sill, 1995). Sill has  
1041 described a potassium fluoride-potassium pyrosulfate fusion technique that can be used before  
1042 elemental separation for the alpha-emitting nuclides of radium through californium. The organic  
1043 matter of the soil is initially destroyed by heating the sample with nitric acid in a platinum  
1044 crucible. To a 1 g sample, potassium fluoride is added and mixed well. The potassium fluoride  
1045 fusion is carried out using a blast burner at approximately 900 °C. After the melt is cooled,  
1046 concentrated sulfuric acid is added, and the mixture is heated to decompose the potassium  
1047 fluoride cake, with the simultaneous volatilization of hydrogen fluoride and silicon tetrafluoride.  
1048 After the cake is completely transformed, anhydrous sodium sulfate is added and the pyrosulfate  
1049 fusion is performed. The resultant cake is then dissolved in dilute HCl before subsequent  
1050 elemental separation.

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