

## 15.5 Sample Digestion Methods

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### 15.5.1 Introduction

Knowledge of the chemical and isotopic composition of samples is a prerequisite for understanding their characteristics. The major task of sample digestion is to convert the form of sample into one suitable for chemical analysis. Generally, after the sample is digested, the component of interest is in the solution as a soluble salt. The major advantage of the solution is its excellent homogeneity. It represents the original solution composition even in microliter volume. Despite a considerable amount of new research on sample introduction techniques, solution sampling remains the preferred method for most modern instrumental techniques, such as inductively coupled plasma mass spectrometry (ICP-MS)/inductively coupled plasma atomic emission spectrometry (ICP-AES). If the sample is a liquid or soluble in a liquid, then the sample dissolution is relatively simple. For example, water samples for which the

further normal treatment necessary is to stabilize dissolved elements by the addition of small amounts of acid. However, most solid geologic samples cannot be dissolved in water, and sample digestion methods, such as acid digestion, fusion, or ashing, are required. Sample digestion is thus a fundamental and critical stage in the process of sample analysis, and it is often the limiting factor for sample throughput, especially with the rapid development of modern multielement measurement instrumentation (Chao and Sanzalone, 1992; Eggins et al., 1997; Jarvis, 1988; Longrich et al., 1990; Navarro et al., 2008).

The complexity of sample materials makes it necessary to choose a sample digestion method that is compatible with the specific objective of the analysis (Chao and Sanzalone, 1992). In reality, the choice of a digestion method should consider and be consistent with the chemical and physical composition and properties of the sample, the elements to be analyzed, the sample size required, the precision and accuracy desired, the

sample throughput needed, the suitability of the resulting digestion matrix for the analysis method, the apparatus and laboratory facilities available, the economic aspects including the reagent and labor consumption, and the safety considerations. There is an extensive literature on the various digestion methods for geologic and environmental samples (Chao and Sanzolone, 1992; Jarvis, 1992; Jeffery, 1975; Johnson and Maxwell, 1981; Matusiewicz, 2003; Nóbrega et al., 2006; Potts, 1987; Potts and Robinson, 2003; Šulcek and Povondra, 1989; Walsh et al., 1997). Despite numerous studies, the solution chemistry involved in many digestion methods is not well understood, and the knowledge in this area lags far behind developments in analytical instrumentation (Jarvis, 1992; Makishima et al., 2009; Tanaka et al., 2003; Yokoyama et al., 1999; Yu et al., 2001). Sample digestion thus remains a popular research theme for analytical geochemists.

This chapter provides a brief overview of digestion methods for the analysis of geologic samples. The authors do not attempt to discuss all dissolution methods; rather, many methods that are routinely used in the laboratory are presented.

## 15.5.2 General Considerations

### 15.5.2.1 Mineral Acids

Strong mineral acids ( $\text{HNO}_3$ ,  $\text{HCl}$ ,  $\text{HF}$ ,  $\text{HClO}_4$ ,  $\text{H}_2\text{SO}_4$ , and  $\text{H}_3\text{PO}_4$ ) are generally used for sample dissolution, and appropriate combinations of acids have been used successfully to decompose various geologic samples, such as rocks, minerals, soils, sediments, and ores (Chao and Sanzolone, 1992; Jarvis, 1992; Johnson and Maxwell, 1981; Potts, 1987; Potts and Robinson, 2003; Šulcek and Povondra, 1989). All of these acids are corrosive in nature, especially when heated and concentrated, and should be handled with extreme caution to prevent injury and accidents. Concentrated acids with the requisite high degree of purity are commercially available, and they can be further purified using subboiling distillation methods if needed (Yuan et al., 2000). The physical properties of the common mineral acids used in sample preparation are summarized in Table 1.

#### 15.5.2.1.1 Hydrofluoric acid

Hydrofluoric acid (HF) is the most effective mineral acid for breaking up strong Si–O bonds to form  $\text{SiF}_6^{-2}$  ions in acidic solution. Silicates are converted to volatile  $\text{SiF}_4$ , which will be lost in open vessel digestion procedures. HF by itself is more effective in the digestion of silicate rock minerals than when mixed with another acid. However, HF is rarely used as the sole reagent because some salts are poorly soluble in this acid

(Potts, 1987). HF is almost always mixed with other oxidizing acids such as  $\text{HNO}_3$  and/or  $\text{HClO}_4$  to ensure complete dissolution and to produce uniformly high oxidation states in the final solutions. Even diluted HF solutions will etch glass, so plastic labware (preferably PTFE or Teflon) is essential. It should also be noted that HF is one of the most hazardous mineral acids used in the laboratory, and it is both highly corrosive and toxic. Any HF spills on the skin should be immediately washed with copious cold water, and the affected area should be treated with a gel containing monosodium glutamate (Potts, 1987). Contact with HF does not cause an immediate burning sensation or pain but readily penetrates deep tissue and causes intense pain after an hour or more. HF will cause irreparable damage to the skin and eyes and should never be used without full safety precautions. Recently,  $\text{NH}_4\text{F}$  has been proposed to replace HF for the acid digestion of geologic and environmental samples (Hu et al., 2010; Mariet et al., 2008). A clear advantage of  $\text{NH}_4\text{F}$ -assisted acid digestion is that it does not require handling the very corrosive and toxic HF. Notably, the conventional subboiling purification procedure is not effective at removing As impurities in HF. This limit may be related to the presence of volatile As species such as  $\text{AsF}_3$  (boiling point of  $63^\circ\text{C}$ ). To remove this volatile As species, it is recommended to employ a boiling procedure for hydrofluoric acid prior to the conventional subboiling purification procedure (Hu et al., 2005).

#### 15.5.2.1.2 Nitric acid

Nitric acid ( $\text{HNO}_3$ ) is one of the most widely used digestion reagents and the most widely used primary oxidant for the decomposition of organic matter. Hot and concentrated  $\text{HNO}_3$  (16 M and 68%) is a strong oxidizing agent that will liberate trace elements from many materials as highly soluble nitrate salts. The oxidizing properties of nitric acid are lost when it is diluted below approximately 2 M. The most important application of  $\text{HNO}_3$  in rock analysis is to decompose both carbonate and sulfide minerals (usually in association with  $\text{HCl}$ ). Nitric acid matrices are the best acid medium for ICP-MS analysis. Its constituents ( $\text{H}_2$ ,  $\text{N}_2$ , and  $\text{O}_2$ ) are already present in air entrained by the plasma, and the range of polyatomic ions are not increased significantly by the addition of an  $\text{HNO}_3$  matrix (Gray, 1986; Tan and Horlick, 1986), and it also does not interfere with most determinations. Additionally, nitric acid is available commercially in sufficient purity.

#### 15.5.2.1.3 Aqua regia

A fresh mixture of concentrated  $\text{HNO}_3$  (16 M) and  $\text{HCl}$  (12 M) in a volume ratio of 1:3 produces a particularly useful reagent known as aqua regia. This reagent has much stronger oxidizing

**Table 1** General physical properties of common mineral acids

Mineral acids	Formula	Concentration (%)	Molarity (M)	Density ( $\text{kg l}^{-1}$ )	Boiling point ( $^\circ\text{C}$ )	Comments
Nitric acid	$\text{HNO}_3$	68	16	1.42	122	68% $\text{HNO}_3$ , azeotrope
Hydrochloric acid	$\text{HCl}$	36	12	1.19	110	20.4% $\text{HCl}$ , azeotrope
Hydrofluoric acid	$\text{HF}$	48	29	1.16	112	38.3% $\text{HF}$ , azeotrope
Perchloric acid	$\text{HClO}_4$	70	12	1.67	203	72.4% $\text{HClO}_4$ , azeotrope
Sulfuric acid	$\text{H}_2\text{SO}_4$	98	18	1.84	338	98.3% $\text{H}_2\text{SO}_4$
Phosphoric acid	$\text{H}_3\text{PO}_4$	85	15	1.71	213	Decomposes to $\text{HPO}_3$

and dissolving powers than  $\text{HNO}_3$  alone. The effectiveness of this reagent is most likely due to the complexing power of the  $\text{Cl}^-$  combined with the catalytic effects of free  $\text{Cl}_2$  and  $\text{NOCl}$  (Jarvis, 1992). This reagent should be freshly prepared before use. Aqua regia is mainly used for the decomposition of metals, alloys, sulfides, silicates (in association with HF), and other ores and is well known for its ability to dissolve Au, Pt, and Pd.

#### 15.5.2.1.4 Hydrochloric acid

Concentrated hydrochloric acid (HCl) is the most frequently used halogen acid for the dissolution of geologic samples. Unlike  $\text{HNO}_3$ , HCl is a weak reducing acid and is not generally used to digest organic materials. It is an excellent solvent for carbonates, phosphates, many metal oxides, and metals. For example, due to its reducing properties and the complexing ability of  $\text{Cl}^-$ , HCl is a better solvent for dissolving iron and manganese oxides than  $\text{HNO}_3$ . For silicate analysis, HCl is generally used in combination with other acids, such as HF and  $\text{HNO}_3$ , although some basic silicate minerals can be completely or partially decomposed by HCl alone. At elevated temperatures and pressures, many silicates and other refractory oxides, sulfates, and fluorides are attacked by HCl to produce soluble salts. HCl is the preferred acid medium to dissolve residues that remain after acid digestion or melts of alkali fusion for later analysis using atomic absorption spectrometry (AAS) (Potts, 1987). Unlike atomic absorption techniques, HCl is not a suitable sample matrix for ICP-MS analysis because chloride-bearing polyatomic ions cause major interferences (e.g.,  $\text{ArCl}$ ,  $\text{ClO}$ , and  $\text{ClOH}$ ) with As and V ( $^{75}\text{As}$  and  $^{51}\text{V}$ ) and with many other trace elements (Cr, Fe, Ga, Ge, Se, Ti, and Zn) to a lesser extent (Jarvis, 1992). Hydrochloric acid can be effectively removed from sample solutions by repeated evaporation to incipient dryness with  $\text{HNO}_3$  because the boiling point of the HCl azeotrope (110 °C) is below that of the  $\text{HNO}_3$  azeotrope (122 °C). However, it should be noted that there may be potential losses of the volatile metal chlorides (As, Sb, Sn, Se, Ge, and Hg) if HCl is used in acid digestion procedures.

#### 15.5.2.1.5 Perchloric acid

Perchloric acid ( $\text{HClO}_4$ ) is one of the strongest mineral acids. Hot and concentrated perchloric acid has powerful oxidizing and dehydrating properties, and it will react explosively with organic compounds. For this reason, it is best to pretreat geologic samples containing organic material or organic samples with  $\text{HNO}_3$  or an  $\text{HNO}_3$ - $\text{HClO}_4$  mixture. Perchlorate salts are generally highly soluble and stable in aqueous solutions, but some alkali (K, Rb, and Cs) perchlorates are exceptions to this general rule. The high boiling point of the acid ensures a more efficient attack of refractory minerals by improving the efficiency of HF and the more complete removal of HF during evaporation stages. Unlike HCl, chlorine ions introduced during the digestion procedure in the form of  $\text{HClO}_4$  are difficult to be removed by evaporation and will be harmful to the determination of low levels of As and V in ICP-MS (Jarvis, 1992). Some salts of  $\text{HClO}_4$  are spontaneously flammable in the anhydrous form. Therefore,  $\text{HClO}_4$  must be used in a specially designed hood that is equipped with washdown facilities for cleaning after use (Chao and Sanzalone, 1992; Potts, 1987).

#### 15.5.2.1.6 Sulfuric acid

Concentrated sulfuric acid ( $\text{H}_2\text{SO}_4$ ) has dehydrating and mildly oxidizing abilities and the highest boiling point (338 °C for the 98.3% acid) of the mineral acids. Cold concentrated sulfuric acid has an extremely high affinity for water, and it will produce a significant amount of heat when diluted. Therefore, this acid must always be added slowly to excess water and not vice versa. Sulfuric acid is a highly effective reagent in combination with HF for the decomposition of most resistant minerals, such as zircon, chromite, monazite, cryolite, and many naturally occurring fluorides (Potts and Robinson, 2003; Yu et al., 2001). Unfortunately, some inorganic sulfates have low solubilities (e.g., Ba, Ca, Pb, and Sr), and volatilization of trace elements (Ag, As, Ge, Hg, Re, and Se) may occur during the digestion of some samples (Šulcek and Povondra, 1989). Furthermore,  $\text{H}_2\text{SO}_4$  is very difficult to remove by evaporation (several days) due to its high boiling point (338 °C). The viscosity of this acid results in transport effects during sample introduction in ICP-MS. This acid also causes severe sulfur polyatomic ion interferences and attacks the nickel sampler cones in the ICP-MS instrument. For these reasons,  $\text{H}_2\text{SO}_4$  has not been widely used for the decomposition of geologic samples.

#### 15.5.2.1.7 Phosphoric acid

Phosphoric acid ( $\text{H}_3\text{PO}_4$ ) is somewhat limited in its use in analytical chemistry because phosphate ions can cause interferences by complexing or precipitating some of the elements to be analyzed (Chao and Sanzalone, 1992). Possible difficulties encountered in ICP-MS analysis are the presence of polyatomic species of P, transport effects induced by the high viscosity of the acid, and rapid erosion of the nickel sampler cone.  $\text{H}_3\text{PO}_4$  undergoes a series of condensation reactions to form condensed phosphoric acid upon heating. Condensed phosphoric acid alone or with  $\text{HClO}_4$  can decompose 70 natural minerals among sulfides, oxides, silicates, and carbonates (Hannaker and Hou, 1984). Further investigations are needed to explore the full potential of  $\text{H}_3\text{PO}_4$  as an acid decomposition agent.

### 15.5.2.2 Digestion Vessel Materials

Many different vessel materials are used to handle samples during sample digestion in laboratories. The vessel material must be chosen carefully according to its nature (e.g., resistance to acids and alkalis, heat resistance and conductance, surface properties, reactivity, mechanical strength, and contamination), the sample components to be analyzed, and the analytical requirements. Table 2 lists the preferred vessel materials for sample digestion. These materials have gained considerable popularity for use in the handling of samples.

### 15.5.2.3 Contamination from the Digestion Process

The influence of contamination on the analytical results becomes increasingly important with decreasing concentrations of the analyte. Modern analytical methods and instrumentation make possible the measurement of extremely low concentrations of elements in complex matrices. In many

**Table 2** Preferred vessel materials for sample digestion

Materials	Maximum temperature (°C)	Comments
Borosilicate glass	800	Resistant to most acids, but should not be used with HF or boiling H <sub>3</sub> PO <sub>4</sub> or alkaline solutions
Porcelain	1100	Popular material used for ashing purpose
Quartz	1200	The most suitable material for the wet digestion of organic materials
Platinum	1500	Resistant to attack by most acids and fusion reagents. Heats up and cools down rapidly, making it excellent for ash determinations
Glassy carbon	500	An inexpensive material for alkaline fusions with low melting point agents
Polytetrafluorethylene (PTFE)	250	Generally used for closed digestion vessels
Perfluoroalkoxy (PFA)	250	Commonly used in microwave digestion vessels
High-density polyethylene (HDPE)	120	Typically used for containment of the diluted sample digestion solution
Low-density polyethylene (LDPE)	80	
Polypropylene (PP)	135	

cases, the blank level determines the lower limit of detection, which has increased the importance of digesting samples in a manner that keeps them as contamination-free as possible.

Contamination can occur from the reagents, the vessel materials, and the environment during the digestion process and is often an unforeseen barrier in sample analyses that can lead to false results. Liquid reagents, such as water and acids, are most important for sample preparation, and they are generally available in high-purity grades. If required, these reagents also can be further purified using subboiling distillation. In contrast, solid reagents are difficult to purify and result in comparatively high blank levels. Many different vessel materials have been used to handle samples during sample preparation. Contaminants can be desorbed from impurities on the surfaces of the vessels or leached out from the vessel materials. It has been reported that the degree of contamination from the commonly used vessel materials is in the following order: polyethylene (low density) < fluorocarbons (e.g., Teflon, PTFE, and Tefzel) < quartz (synthetic) < polyethylene (high density) < quartz (natural) < platinum < borosilicate (Gaines, 2012; Moody and Lindstrom, 1977; Murphy, 1974). Although containers made of linear polyethylene or Teflon introduce the least amount of contamination for most trace element analysis, these containers should be carefully cleaned with HCl and HNO<sub>3</sub> before use (Moody and Lindstrom, 1977). Simple acid washing of the bottles prior to use does not solve the contamination problem for all elements. For example, Ta contamination from perfluoroalkoxy (PFA) Teflon<sup>®</sup> vessels (Makishima et al., 1999), Ba, Zn, and Cr contamination from high-density polyethylene bottles (Reimann et al., 1999, 2007) and Sb contamination from polyethylene terephthalate bottles (Shotyk et al., 2006) occur via leaching of the contaminants from the containers. Reimann et al. (2010) reported that dark-colored containers leach more materials than clear containers do for most elements, and this observation is independent of the container material. Therefore, great care is required when choosing containers, reagents, and the apparatuses used for sample digestion. Environmental contamination is caused by airborne particles and gaseous matter. To keep contamination risks low during chemical treatment in open systems, work should be performed in clean rooms equipped with laminar-flow clean benches (Gaines, 2012; Knapp and Schramel, 2003; Tschöepel and Toelg, 1982; this volume, Chapter 15.6).

#### 15.5.2.4 Assessing a Digestion Procedure

Quality assurance, which is aimed at obtaining the correct result, is extremely important in analytical chemistry. Long-term experience has shown that precise sample digestion is the most critical part of an analysis because it is responsible for the largest and most often hidden sources of errors (Hoenig, 2001). For quality control in sample digestion, it is necessary to measure and record certain parameters exactly to be able to subsequently trace the course of the digestion process (Matusiewicz, 2003). Precision and accuracy are the two most important parameters for the quality control of sample digestion. Precision is defined as an estimation of the reproducibility of a sample digestion method, which is normally calculated from the standard deviation of the analyses of duplicate digestions of the same sample. Accuracy refers to a measure of how closely the analytical data agree with the 'true' composition of the sample. For the sample digestion procedures, the use of an adequate certified reference material (CRM) is strongly recommended for quality assurance and for method development. A CRM is a substance for which one or more analytes have certified values, which are produced by a technically valid procedure and are accompanied with a traceable certificate and issued by an appropriate certifying agency (see Chapter 15.3 in this volume). CRMs are available from many distributors and for a wide range of matrices (see Chapter 15.3 in this volume). Selecting an appropriate test portion of the sample materials before digestion is also an important part of quality assurance. Since the 1980s, when using a particle size level of 200 mesh (74 μm), it has been recommended to use 100 mg as a minimum test portion size to assure representative subsampling, which is a compromise between sample size and detection limits. However, for modern high-sensitivity analytical techniques, such as ICP-MS, the practical sampling mass is much less than 100 mg. Thus, a significant challenge to use the minimum sampling mass of sample materials has emerged with the development of modern analytical techniques (Wang et al., 2004). Similarly, the added amount of digestion reagents should be appropriated for the selected test portion of the sample materials. For example, 1–2 ml of HF and 0.5–1 ml of HNO<sub>3</sub> are typically used for the digestion of 50–100 mg silicate materials in closed vessels. In addition, procedural blanks should always be prepared for each batch of samples, which are very helpful for tracing the sources of errors.

### 15.5.3 Sample Digestion Methods

#### 15.5.3.1 Open Vessel Acid Digestions

Open vessel acid digestions have long been a popular and simple method for the digestion of inorganic and organic sample materials in chemical laboratories. It refers to acid attack in open containers or screw-top vials (low pressure) placed on a hot plate. This method is an extremely important value for routine analysis because of its flexibility in the control of digestion parameters, such as temperature, time, and the addition of reagents. However, the maximum digestion temperatures are limited by the ambient-pressure boiling point of the corresponding acid or acid mixture. Other disadvantages of open vessel digestions are the potential risk of contamination from the laboratory air and the large amounts of reagents that are required and the potential loss of trace elements. Therefore, open vessel acid digestion has not been considered to be a state-of-the-art technology in trace and ultratrace sample preparation (Matusiewicz, 2003).

For the digestion of geologic samples, HF in combination with other mineral acids (most commonly nitric and perchloric acids) in an open vessel is routinely used (Chao and Sanzalone, 1992; Jarvis, 1990, 1992; Jenner et al., 1990; Johnson and Maxwell, 1981; Potts, 1987; Potts and Robinson, 2003; Robinson et al., 1999; Šulcek and Povondra, 1989). Silicon is quantitatively removed as the volatile silicon tetrafluoride  $\text{SiF}_4$ , which reduces the total amount of dissolved solid in the solutions and makes the solution far more stable because Si in the solution tends to hydrolyze and precipitate to form undissolved polysilicic acid. Evaporation using a mineral acid in addition to hydrofluoric acid also facilitates the removal of fluorine ions and ensures that insoluble fluorides are converted to more soluble salts. For example, the high boiling point of  $\text{HClO}_4$  (203 °C) compared with that of HF (112 °C) ensures the complete removal of fluorides and the more efficient attack of refractory minerals due to the increased boiling temperature of the reaction mixture and the high solubility of perchlorates (Potts and Robinson, 2003; Totland et al., 1992). The order of effectiveness in removing residual amounts of fluorine decreases in the order of sulfuric acid, perchloric acid, and nitric acid. Langmyhr (1967) reported that double evaporation with  $\text{HClO}_4$  at 180 °C gives about the same trace residue of fluoride as one evaporation with  $\text{H}_2\text{SO}_4$  at 250 °C. However, as mentioned in Section 15.5.2.1,  $\text{HClO}_4$  is preferred to  $\text{H}_2\text{SO}_4$  in analytical practice. The choice of the accompanying acid or the optimum combination of acid mixtures is determined by many factors, such as the nature of the sample, the elements to be analyzed, and the suitability of the resulting digest matrix for the analysis method. There is also some disagreement in the literature regarding the optimum combination of acids and the role of the second acid (Langmyhr and Sveen, 1965; Tang et al., 1992). For example, Langmyhr and Sveen (1965) reported that hydrofluoric acid alone is more effective as a decomposition agent for the digestion of minerals than a mixture containing HF with another mineral acid. Tang et al. (1992) analyzed 11 Chinese geologic reference materials and found no significant difference between HF/ $\text{HNO}_3$ / $\text{HClO}_4$ , HF/aqua regia/ $\text{HClO}_4$ , and HF/ $\text{HClO}_4$  in an open acid digestion.

During sample decomposition using HF, stable insoluble Mg–Ca–Al fluorides are usually produced, which differentially incorporate trace elements into their lattices during

precipitation and lead to negative errors in the analysis (Boer et al., 1993; Croudace, 1980; Langmyhr and Kringstad, 1966; Makishima et al., 2009; Yokoyama et al., 1999). Not only do insoluble fluorides form with elements, such as rare earth elements (REEs) and Th, but some soluble elements, such as Rb, Cs, and U, also coprecipitate with these fluorides (Boer et al., 1993; Hu et al., 2010; Yokoyama et al., 1999). It is clear that the analysis of trace elements in the presence of insoluble fluorides will yield erroneous results and misleading conclusions, especially in terms of Rb–Sr, La–Ce, Sm–Nd, U–Th–Pb systematics, or REE patterns. To remove these fluorides, repeated evaporation of sample solutions with  $\text{HClO}_4$  has been commonly used (Langmyhr, 1967; Yokoyama et al., 1999). Yokoyama et al. (1999) obtained 100% recovery of the incompatible elements Rb, Sr, Y, Cs, Ba, REEs, Pb, Th, and U by using larger amounts of  $\text{HClO}_4$  and evaporating the sample to dryness in a stepwise fashion. However, the high-field strength elements (HFSE), such as Ti, Zr, Nb, Hf, and Ta, were lost as insoluble oxides. The complete removal of fluoride from sample solutions is not always straightforward and is often difficult to accomplish (Chao and Sanzalone, 1992; Croudace, 1980; Makishima et al., 2009; Takei et al., 2001; Tanaka et al., 2003). For example, the presence of rastonite (Boer et al., 1993; Croudace, 1980),  $\text{NaUZr}_2\text{F}_{12}$  (Boer et al., 1993), and  $\text{AlF}_3$  (formed at 205 °C in the bombs) (Takei et al., 2001) remains a problem because these phases do not dissolve in acids. Therefore, it is very important to suppress the formation of insoluble fluorides. To prevent the formation of insoluble fluorides, the use of small quantities of a sample (not exceeding 100 mg) is recommended (Hu et al., 2010; Potts and Robinson, 2003; Yokoyama et al., 1999; Zhang et al., 2012). It has also been proposed that during sample digestion, treated powders, after acid attack, should not be allowed to dry completely, a step that apparently can minimize the formation of insoluble compounds (Croudace, 1980; Dulski, 2001; Navarro et al., 2008). Takei et al. (2001) and Tanaka et al. (2003) found that the bulk rock proportions of Ca:Al:Mg have a significant effect on the formation of insoluble fluorides. They have developed the novel ‘Al-addition’ and ‘Mg-addition’ methods to overcome these problems.

The main drawbacks of open vessel acid digestions for the digestions of geologic samples are the incomplete dissolution of refractory minerals, such as chromite, corundum, cassiterite, spinel, garnet, magnetite, monazite, rutile, and zircon, and the potential loss of some elements (e.g., As, B, Ge, Sb, Se, Hg, Te, Re, Os, and Ru) (Chao and Sanzalone, 1992; Hall and plant, 1992; Potts, 1987; Révillon and Hureau-Mazaudier, 2009; Roy et al., 2007; Šulcek and Povondra, 1989; Walsh et al., 1997; Yu et al., 2001). Elements such as Zr, Hf, Cr, Sn, Mo, Y, Ba, and HREEs are often present in these refractory minerals, and their recovery may be low (Hall and plant, 1992; Révillon and Hureau-Mazaudier, 2009; Roy et al., 2007; Šulcek and Povondra, 1989; Tang et al., 1992). To overcome this drawback, the residue that remains after open acid digestion is sometimes filtered and decomposed using alkali fusion or closed vessel digestion (Dupta, 1994; Jarvis and Jarvis, 1988; Pin and Joannon, 1997). However, the lack of ultrapure reagents precludes the use of alkali fusion methods for the analysis of geologic samples with low trace abundances. Recently, a new method using a Siliconit furnace was developed to accomplish the

flux-free fusion of silicate rock prior to HF–HClO<sub>4</sub> digestion in a Teflon beaker in preparation for bulk analysis using ICP-MS (Shimizu et al., 2011). This method is especially effective for felsic samples that contain refractory minerals, such as zircon and tourmaline.

Open vessel acid digestions are a well-established method incorporating the sample into the solution and are very successful for samples without refractory minerals. However, the digestion recipe used by each laboratory varies. Table 3 lists a selection of typical sample treatment procedures for open vessel acid digestions.

### 15.5.3.2 Closed Vessel Digestions

An important advance in acid dissolution procedures was made with the introduction of the closed acid digestion bomb that was popularized by Langmyhr and Paus (1968) and Bernas (1968). The complete digestion of a sample is a prerequisite to achieve reproducible and accurate results in routine analysis. Digestions performed in closed vessel devices benefit from the synergic effects of temperature and pressure,

in which digestions reach higher temperatures because the boiling point of the reagents is raised by the pressure generated within the vessel. The principal advantages of digestion in a closed system can be summarized as follows (Chao and Sanzalone, 1992; Jackwerth and Gomiscek, 1984; Jarvis, 1992; Šulcek and Povondra, 1989):

1. This method enables the rapid digestion of refractory phases, which are not decomposed or are only partially decomposed in an open vessel.
2. The digestion time is significantly shortened.
3. Smaller reagent volumes are required.
4. Losses of volatile elements, such as As, B, Cr, Cd, Hg, Sb, Se, Sn, and Pb, are prevented.
5. Contamination is reduced by lowering the reagent volumes and excluding the possible introduction of airborne particles during the decomposition.

Due to these advantages, closed vessel digestions are particularly suitable for trace and ultratrace analyses, especially when the supply of the sample is limited. However, if silicon is to be determined, boric acid is normally added to complex the excess

**Table 3** A selection of typical sample treatment procedures for open vessel acid digestions

Material	Determined elements and instruments	Sample treatment	References
Acid, intermediate and basic rocks, sediments, shales, limestones	Y, Zr, Nb, Hf, Ta, Pb, Th, U, REEs (ICP-MS)	(1) A 0.2 g aliquot of the sample is placed in a beaker and moistened with 2 ml of water. (2) After the addition of 10 ml of HF and 8 ml of HClO <sub>4</sub> , the sample is evaporated to dryness at 200 °C. (3) Step 2 is typically repeated 3–4 times. (4) An additional 5 ml of HClO <sub>4</sub> is added, and the sample is evaporated to dryness. (5) The sample is heated for 10 min following the addition of 10 ml of 5N HNO <sub>3</sub> . (6) The sample is transferred to 100 ml volumetric flasks	Jarvis (1990)
Serpentinite, limestone, dolomite, andesite, basalt, granite, shale, syenite	Ti, Al, Fe, Mg, Mn, Ca, Ba, Cr, Cu, Ni, Sr, V, Y, Zn, Zr (ICP-AES); Ba, Be, Co, Cr, Cs, Cu, Hf, Mo, Nb, Ni, Pb, Rb, Sb, Sc, Sn, Sr, Ta, Th, Tl, U, W, Y, Zn, Zr, REEs (ICP-MS)	(1) An aliquot of 0.500 g of the sample is placed in a beaker and moistened with a few milliliters of water. (2) Next, 10 ml of HF and 4 ml of HClO <sub>4</sub> are added, and the sample is evaporated to dryness at 200 °C. (3) Step 2 is typically repeated 3–4 times. (4) The sample is evaporated to dryness after the addition of 4 ml of HClO <sub>4</sub> . (5) A 10 ml portion of 5N HNO <sub>3</sub> is added, and the sample is heated gently. (6) The sample is transferred to 50 ml volumetric flasks	Totland et al. (1992)
A range of basalt, granite, and ironstone geologic reference materials	Sc, Rb, Y, Zr, Nb, Mo, Sn, Cs, Ba, REEs, Hf, Ta, Pb, Th, U (ICP-MS)	(1) A 100 mg aliquot of the sample is placed in Teflon vials and wetted with a few drops of water. (2) The addition of 2 ml of HF and 0.5 ml of HNO <sub>3</sub> is followed by digestion at 130–150 °C for 48 h and evaporation to dryness. During the digestion, the vial is removed from the hot plate twice and placed in an ultrasonic bath for a couple of minutes. (3) The evaporation is repeated twice more after adding 1 ml of HNO <sub>3</sub> each time. (4) Next, 2 ml of HNO <sub>3</sub> and 3–5 ml of water are added. (5) The sample is then diluted to 100 ml with water	Robinson et al. (1999) and Yu et al. (2001)
Stream and lake sediment	Sc, Ti, V, Cr, Mn, Co, Ni, Cu, Ga, Zn, Rb, Y, Zr, Nb, Cs, Ba, REEs, Hf, Ta, Pb, Th, U (HR-ICP-MS)	(1) A 100 mg aliquot of the sample is placed in PFA Teflon beakers. (2) After the addition of 3 ml of HF and 1 ml of HNO <sub>3</sub> , the sample is agitated for 20 min in an ultrasonic bath. (3) The sample is then digested at 130 °C for 48 h and evaporated to dryness at 80–120 °C. (4) The sample is mixed with 1 ml of HCl, heated for 12 h, and evaporated to dryness. (5) The dried residue is then dissolved in another solution of 40 ml of HCl (3 mol l <sup>-1</sup> )	Révillon and Hureau-Mazaudier (2009)

fluoride. The addition of boric acid permits the retention of Si and other volatile fluorides and prevents the precipitation of insoluble fluorides (Bernas, 1968; Langmyhr and Paus, 1968; Van Eenbergen and Bruninx, 1978). Because the resulting solution still attacks glassware, it should not be aspirated into the conventional sample introduction systems of ICP-MS/ICP-AES. In addition, the increased amount of dissolved solids significantly hinders the analysis of trace elements. Thus, the application of this technique is limited in routine sample analysis. For the analysis of trace elements, it is better to remove silicate as the volatile  $\text{SiF}_4$  on a hot plate after opening the vessel.

Many types of vessels are available for sample digestion in a closed system. The different vessels have different temperature limits. Polypropylene and polycarbonate bottles can be used up to 130 °C, and PTFE-lined pressure vessels can withstand temperatures in the range of 150–250 °C (Bernas, 1968; Langmyhr and Paus, 1968). Decompositions in closed systems at elevated temperatures started to develop successfully only after the introduction of fluorinated hydrocarbon polymers (PTFE and Teflon®) as the materials for the autoclave internal vessels (Šulcek and Povondra, 1989). Modern conventional acid digestion bombs consist of a PTFE beaker with a lid, which fits tightly into an outer stainless-steel pressure jacket. The outer jacket has a screw-top lid, which, when tightened, forms a gas-tight high-pressure seal between the beaker and its lid. These bombs produce very high pressures (7–12 MPa) when the sample and acids are subjected to high temperatures (110–250 °C) (Jarvis, 1992; Potts and Robinson, 2003). At any temperature, the pressure developed within the closed vessel depends on the partial pressure of the solvents under nonequilibrium conditions and the gaseous decomposition products formed during the decomposition. To avoid explosive rupturing of the vessels, organic material should not be mixed with strong oxidizing agents in closed vessels, and samples and reagents should never constitute more than 20% of the total vessel volume. It is also essential that the closed vessel is not opened until it has completely returned to room temperature.

Closed vessel acid digestion may result in the decomposition of many refractory minerals and compounds that are not decomposed or are only partially decomposed in an open vessel (Bernas, 1968; Hu and Gao, 2008; Langmyhr and Sveen, 1965; Maqueda and Rodriguez, 1986; Olive et al., 2001; Pretorius et al., 2006; Qi and Grégoire, 2000; Qi et al., 2000). Beryl, chalcopyrite, kyanite, pyrite, pyrrhotite, and staurolite are only partially decomposed at 95 °C in an open vessel by HF/HClO<sub>4</sub>, but they are completely dissolved in a Teflon-lined bomb at 250 °C (Langmyhr and Sveen, 1965). Topaz is a significant exception, which may require alkali fusion to be brought into the solution. Pyrophyllite is not attacked by HF/HClO<sub>4</sub>/HNO<sub>3</sub> in an open vessel, but it is dissolved completely in PTFE-lined sealed vessel (Maqueda and Rodriguez, 1986). Refractory compounds, such as titanium dioxide, niobium dioxide, and silicate nitride, were also successfully decomposed at 170 °C using closed vessel digestion (Bernas, 1968). Felsic rocks are known to be very difficult to dissolve because of the presence of refractory minerals, such as zircon, tourmaline, magnetite, and monazite. Recent results show that felsic rocks, such as granites and granodiorites, can be completely decomposed using closed vessel acid digestion at the temperatures of 190–200 °C for 12 h to several days (Hu et al., 2010; Pretorius

et al., 2006; Qi et al., 2000; Yu et al., 2001). Currently, closed vessel acid digestion is one of the most successful and popular sample preparation techniques, and it has been widely used to decompose various geologic samples (e.g., felsic rocks, ultramafic rocks, sediments, and soils) for multielement determinations, such as REEs and HFSE (Begum et al., 2007; Diegor et al., 2001; Dulski, 2001; Hu and Gao, 2008; Hu et al., 2010; Navarro et al., 2008; Olive et al., 2001; Pretorius et al., 2006; Qi and Grégoire, 2000; Qi et al., 2000; Révillon and Hureau-Mazaudier, 2009; Yu et al., 2000, 2001; Zhang et al., 2012).

To decompose silicate materials, acid mixtures such as HF/HNO<sub>3</sub> (Diegor et al., 2001; Hu and Gao, 2008; Navarro et al., 2008; Qi and Grégoire, 2000; Qi et al., 2000; Zhang et al., 2012), HF/HClO<sub>4</sub> (Dulski, 2001; Olive et al., 2001; Yu et al., 2000, 2001), HF/H<sub>2</sub>SO<sub>4</sub> (Münker, 1998; Yu et al., 2001), HF/HNO<sub>3</sub>/HCl (Roy et al., 2007), and HF/HClO<sub>4</sub>/HNO<sub>3</sub> (Pretorius et al., 2006; Révillon and Hureau-Mazaudier, 2009; Xie and Kerrich, 1995) have been used extensively in closed vessel digestions for multielement analysis. Different reliable digestion procedures have been described by these authors. Regardless of the different acid mixture used, the final sample uptake is routinely performed with HNO<sub>3</sub> in most geochemical laboratories. Sometimes, in order to stabilize HFSE in the solution, a final sample uptake procedure using HCl or HNO<sub>3</sub>/HCl has also been proposed (Dulski, 2001; Münker, 1998; Yu et al., 2000, 2001). The choice of acid mixtures is critical for sample digestion in some circumstance. For example, the use of HF/HClO<sub>4</sub> is preferred to the use of HF/HNO<sub>3</sub> or HF/HNO<sub>3</sub>/HCl for trace elements in ultramafic rocks in which spinel-group minerals are effectively decomposed (Olive et al., 2001; Potts and Robinson, 2003). In contrast to HF/HNO<sub>3</sub> digestion in high-pressure bombs, the use of HF/HClO<sub>4</sub>/HNO<sub>3</sub> has resulted in superior recoveries and better precision for the bulk of the trace elements analyzed in felsic rocks (Pretorius et al., 2006). Yu et al. (2001) reported that HF/H<sub>2</sub>SO<sub>4</sub> is more powerful for digesting granites and ironstones than HF/HClO<sub>4</sub>. However, the high boiling point of H<sub>2</sub>SO<sub>4</sub> (338 °C) dictates a minimum of 4 days of evaporation time (Yu et al., 2001). Ito (1962) reported that HF is more powerful for digesting zircon than HF/H<sub>2</sub>SO<sub>4</sub>. Zhang et al. (2012) reported that the addition of HNO<sub>3</sub> inhibited the digestion capabilities of HF for zircon. Table 4 lists a selection of typical sample treatment procedures for closed vessel acid digestion.

### 15.5.3.3 Microwave Digestions

In 1975, Abu-Samra et al. (1975) described one of the first uses of microwave heating for the rapid wet acid digestion of biological materials. This discovery stimulated the long-term development of microwave technology for the preparation of all types of samples for analysis (Bettinelli et al., 1989; Chao and Sanzalone, 1992; Chen et al., 2008; Kingston and Haswell, 1997; Kingston and Jassie, 1988; Kuss, 1992; Lamble and Hill, 1998; Matusiewicz and Sturgeon, 1989; Nadkarni, 1984; Smith and Arsenaault, 1996; Srog, 2006; Suzuki and Sensui, 1991). Currently, microwave technology is being applied not only in analytical chemistry but also in organic synthesis, inorganic reactions, preparation of catalysts, and other fields (Chen et al., 2008; Kingston and Haswell, 1997; Kingston and Jassie, 1988). This technology has now advanced to the point where it is

**Table 4** A selection of typical sample treatment procedures for closed vessel acid digestion

Material	Determined elements and instruments	Sample treatment	References
Granite, andesite, basalt, sediments, sandstone, shale, limestone, and soil	Li, Sc, V, Cr, Co, Ni, Cu, Zn, Ga, Rb, Sr, Y, Zr, Nb, Mo, Cs, Ba, REEs, Hf, Ta, W, Pb, Th, U (HR-ICP-MS)	(1) A 100 mg aliquot of the sample is placed in a PTFE bomb. (2) Next, 1 ml of HF and 0.5 ml of HNO <sub>3</sub> are added, and the sample is evaporated to dryness on a hot plate. (3) The addition of 1 ml of HF and 0.5 ml of HNO <sub>3</sub> is followed by heating to 200 °C for 12 h under pressure. (4) After cooling, 1 ml of a 1 µg ml <sup>-1</sup> Rh solution is added as an internal standard, and the sample is evaporated to dryness at 150 °C. (5) Next, 1 ml of HNO <sub>3</sub> is added, and the sample is evaporated to dryness. (6) Repeat step 5 one time. (7) Approximately 6–8 ml of 40% v/v HNO <sub>3</sub> is added, and the bombs are resealed and heated to 110–140 °C for 3 h. (8) The sample is then diluted to 100 ml with ultrapure water	Qi et al. (2000) and Qi and Grégoire (2000)
Ninety reference materials of different matrix compositions	Rb, Sr, Y, Zr, Cs, Ba, REEs, Hf, Pb, Th, U (ICP-MS)	(1) A 100 mg aliquot of the sample is placed in a PTFE bomb and wetted with a few drops of water. (2) Next, 3 ml of HF and 3 ml of HClO <sub>4</sub> are added, and the sample is heated to 180 °C for 16 h under pressure. (3) After cooling, the sample is evaporated to near dryness at 180 °C. (4) A 5 ml portion of HCl is then added, and the sample is evaporated to incipient dryness. (5) After the addition of 5 ml of HCl, the sample is heated to 130 °C for 12 h under pressure. (6) After cooling, the sample is evaporated to near dryness and redissolved in 2 ml of HCl and 10 ml of water. (7) The sample is then diluted to 50 ml with ultrapure water	Dulski (2001)
Granite, granodiorite	Li, Sc, V, Co, Ni, Cu, Zn, Ga, Rb, Sr, Y, Zr, Nb, Mo, Cd, Sn, Sb, Cs, Ba, REEs, Hf, Ta, W, Pb, Bi, Th, U (HR-ICP-MS)	(1) A 100 mg aliquot of the sample is placed in a PTFE bomb. (2) Next, 5 ml of HF, 0.714 ml of HClO <sub>4</sub> , and 0.714 ml of HNO <sub>3</sub> are added, and the sample is heated to 190 °C for 5 days under pressure. (3) After cooling, the sample is evaporated to dryness, redissolved in 6 ml of 6 mol l <sup>-1</sup> HCl, and heated to 190 °C for 24 h. (4) The sample is then transferred to a Savillex <sup>®</sup> vial and evaporated to dryness. (5) The sample is placed on a hot plate for 24 h after the addition of 1 ml of HNO <sub>3</sub> . (6) The sample is then evaporated to dryness and stored until dilution for analysis	Pretorius et al. (2006)
Leucogranite, diorite, granodiorite, granite, andesite, basalt, sandstone, shale, limestone, graywacke, pelite, and loess	Li, Be, B, Sc, V, Cr, Co, Ni, Cu, Zn, Ga, Ge, As, Rb, Sr, Y, Zr, Nb, Mo, Cd, In, Sn, Sb, Te, Cs, Ba, REEs, Hf, Ta, W, Ti, Pb, Bi, Th, U (ICP-MS)	(1) A 50 mg aliquot of the sample is placed in a PTFE bomb. (2) Next, 1 ml of HNO <sub>3</sub> and 1 ml of HF are added, and the sample is heated to 190 °C for 48 h under pressure. (3) After cooling, the bomb is opened, and the sample is evaporated to incipient dryness at 120–150 °C. (4) After the addition of 1 ml of HNO <sub>3</sub> , the sample is evaporated to dryness. (5) Step 4 is then repeated. (6) An additional 1.5 ml of HNO <sub>3</sub> and 2.50 ml of ultrapure water are added. (7) The bomb is then resealed and heated to 150 °C overnight. (8) The sample is then diluted to 50 ml with ultrapure water	Hu and Gao (2008)

revolutionizing chemical sample preparation and chemical synthesis (Chen et al., 2008; Kingston and Haswell, 1997; Smith and Arsenault, 1996).

Microwave digestion makes use of electromagnetic radiation with a typical frequency of 2450 MHz to generate heat (Matusiewicz and Sturgeon, 1989). Compared with classical heating, microwave heating is many times more efficient. When irradiated by microwave energy, polar molecules and ions are energized via mechanisms of dipole rotation and ion conductance, respectively (Gilman and Engelhart, 1989; Neas and Collins, 1988). The radiating energy is absorbed by both

the digestion medium and the sample molecules, which enhances the chemical reaction that completes the decomposition of the sample. Furthermore, localized internal heating of individual sample particles can cause these particles to burst, thus allowing new surfaces to come into contact with reagents increasing the dissolution rate (Nadkarni, 1984). The high dielectric constant of the reagent facilitates the absorption of the radiating energy. Aqueous solutions of acids absorb microwave radiation to a lesser extent than water alone does. It has been shown that the efficiency of absorption of MW radiation decreases according to the following series: nitric, hydrofluoric,



sulfuric, and hydrochloric acids (Kingston and Jassie, 1986; Šulcek and Povondra, 1989). Microwaves only heat the liquid phase, while vapors do not absorb microwave energy. Thus, very high temperatures can be reached at relatively low pressures, which is a key advantage of microwave technology (Matusiewicz, 2003). The vessel material also plays a significant role in microwave dissolution techniques. Glassy carbon and platinum vessels cannot be used with this method, but quartz glass and plastics, such as Teflon PFA and polycarbonate, are suitable because they cause no loss of energy to the vessel and allow for quick and efficient heating. Modern microwave digestion systems monitor both the pressure and temperature in the container. The electronic controls of these systems allow for very reproducible digestion conditions, which also reduces the need for operator attention.

The microwave digestion system has been used with both open and closed vessels. Moreover, it is also suitable for on-line digestion in continuous-flow systems (Chen et al., 2008; Pichler et al., 1999; Smith and Arsenault, 1996). Open vessel microwave-assisted digestion is a suitable and rapid alternative to conventional hot plate digestion for mafic geologic, environmental, and biological materials (Bettinelli et al., 1989; Lambie and Hill, 1998; Nna-Mvondo et al., 2008; Taylor et al., 2002). Microwave heating is also particularly applicable to closed vessel digestion because it offers the advantages of a more vigorous digestion at elevated temperatures and pressures, a reduced likelihood of contamination, the retention of volatile elements, very rapid heating and cooling compared with conventional PTFE-lined stainless-steel bombs, and improved safety measures (Matusiewicz, 1994; Matusiewicz and Sturgeon, 1989; Pichler et al., 1999; Smith and Arsenault, 1996).

The microwave digestion technique has been widely used in the digestion of soils, sediments, coals, airborne particulates, sludge, and organic environmental and biological samples for which easily dissolved elements are required (Bettinelli et al., 1989, 2000; McGrath, 1998; Nandy et al., 2008; Sen Gupta and Bouvier, 1995; Srogi, 2007; Sun et al., 2001a,b; Tuzen et al., 2004; Wang et al., 1996, 2006; Xu et al., 2005). However, it should be noted that the relatively short digestion times (within 1 h) in a microwave system are insufficient to decompose all minerals, which is in contrast to the long digestion times (up to several days) used in conventional PTFE-lined stainless-steel bombs (Navarro et al., 2008; Potts and Robinson, 2003; Yu et al., 2001). Many authors found that microwave digestion did not always allow the measurement of elements, such as Cr, Zr, Hf, and HREEs, especially when refractory mineral phases (e.g., zircon, chromite, rutile, corundum, and cassiterite) were present (Lamothe et al., 1986; Navarro et al., 2008; Sen Gupta and Bertrand, 1995a,b; Totland et al., 1992; Wu et al., 1996; Yoshida et al., 1996; Yu et al., 2001).

#### 15.5.3.4 Partial Dissolutions

In some special geochemical studies, such as mineral exploration and environmental monitoring programs, only the elements of interest need to be analyzed in the rocks, soils, sediments, sludges, oils, and other samples. The elements of interest are not thought to be present in the undissolved fraction (or the part present in the insoluble substrate is not of interest) and can be totally dissolved by an acid or combination of acids without

HF. Partial dissolution may also be useful for selectively removing unwanted components of rock samples to eliminate bias (Walsh et al., 1997). For these purposes, complete digestion is often unnecessary. Due to partial acid attack without HF for sample digestion, the resulting solution can be used directly for measurements without evaporating to dryness on a hot plate, and such methods are simple, fast, and economical.

The purpose of partial dissolution is to save time and to simplify the sample digestion procedure. The procedure for different sample types is variable. To leach the total contents of elements of interest in samples, the results of a partial dissolution method should be compared with those of the total dissolution with HF to evaluate the validity of the proposed method (Sastre et al., 2002). To leach the elements of interest in one phase of the samples, the elements in the residue of the samples should not be leached. For example, 5% HNO<sub>3</sub> was used to leach off the trace elements in the carbonate mineral phase of seep carbonates to separate the carbonate mineral phase from the residue phase (Chen et al., 2005; Feng et al., 2009).

HCl, HNO<sub>3</sub>, and HClO<sub>4</sub> are generally used when searching ore deposits in which base metals and sulfides are of interest. Partial dissolution using HNO<sub>3</sub> and HClO<sub>4</sub> is useful for analyzing heavy metals in soils and sediments for environmental geochemistry studies (Duzgoren-Aydin et al., 2006; Lee et al., 2006; Luo et al., 2011). Partial leach procedures using aqua regia and cyanide are often used for gold exploration because a very large sample mass can be digested to measure very low concentrations of gold. Aqua regia is often used for the rapid dissolution sulfide phases (Church et al., 1987), soils, and sediments (Balaram et al., 1999; Bettinelli et al., 2000). In comparison with HF and fusion techniques, aqua regia dissolution invariably results in the retention of volatile elements (As, Hg, S, Sb, Se, etc.) in the dissolved solution (Potts and Robinson, 2003). The use of aqua regia and HNO<sub>3</sub> leaches in a high-pressure microwave system on sediments, soils, and sludges, and environmental samples for the determination of Cd, Co, Cr, Cu, Hg, Ni, Pb, and Zn were compared by Florian et al. (1998). The element recoveries obtained using the aqua regia procedures were superior to those obtained using the nitric acid procedures. When a nitric acid procedure was applied, the extraction efficiency strongly depended on the applied leaching parameters and varied for certain elements among different materials. For samples with a high content of organic matter, digestion with HNO<sub>3</sub> can substitute for total digestion with HF (Sastre et al., 2002).

An important problem encountered in analyses based on the partial dissolution of the material is that there are few recognized reference materials available that can be used for method validation (Walsh et al., 1997).

#### 15.5.3.5 Dry Ashing Techniques

Dry ashing techniques are especially suitable for samples with a high organic matter content, such as biological tissues, plants, or food. The organic matter can be completely eliminated using a muffle furnace equipped with temperature control programs and with atmospheric oxygen serving as the oxidizing agent, and all the associated elements in the samples are typically transformed to carbonate or oxide forms in the

residue. The characteristics of the carbonate or oxide forms in ash after dry ashing differ: some will be stable to subsequent acid attack, whereas others will be digested readily with no loss of the analytes. The selection of an appropriate ashing temperature (typical ashing temperatures are 450–550 °C) and ashing vessels is important to ensure quantitative decomposition of the organic matter without loss of interest by volatilization, the formation of refractory oxides that are difficult to dissolve by normal digestion, or reactions with the crucible materials.

Porcelain, vitreous silica, quartz, and platinum crucibles are commonly used as ashing vessels. Porcelain and vitreous silica contain some K, Na, Al, Fe, Ca, Mg, and Ti oxide impurities, which may react with the sample ash to produce a complex silicate and result in contamination and loss of the analytes. A quartz crucible has a relatively higher melt point than a vitreous silica crucible and much lower impurity levels. The best vessel for dry ashing is the platinum crucible, which is unaffected by any of the usual acids, except concentrated, high-temperature phosphoric acid and aqua regia. Although the cost of platinum is higher than that of porcelain and quartz crucibles, its lifetime is unlimited, and it does not induce contamination.

The typical procedure for dry ashing is as follows (Hoening, 2003): 0.2–2.0 g of dried sample (105 °C) is accurately weighed into a platinum crucible and then placed into a cold muffle furnace and progressively heated to 450 °C over 8 h; the sample is maintained at this temperature for 5 h. After cooling, the resulting ash, if it is of white or light gray color and without silicates in its matrix (e.g., animal tissues, milk, fruit juices, or blood), is dissolved in 1 ml of HNO<sub>3</sub> and 20 ml of water and heated to a gentle boil. The solution is subsequently transferred to a calibrated flask or tube and made up to an appreciate volume for measurement. If the sample contains silicates (e.g., plants, sludges, soils, or sediments), 0.5–2.0 ml of water is added at the wall of the crucible to moisten the residue and avoid loss of the fly ash. Then, 1.0–3.0 ml of HNO<sub>3</sub> and 0.5–2.0 ml of HF are added, and the sample is evaporated slowly to dryness on a hot plate. This step is repeated two times, and the residue is then dissolved, as described previously. Good recoveries for most major and trace elements (except volatile elements, such as As, Se, Hg, and S) are obtained for environmental, biological, and food samples. The addition of HF is necessary for quantitative release of the analytes into the solution when the sample contains silicates.

The main advantage of dry ashing is the possibility to treat large masses of samples and to dissolve the resulting ash in a small volume of acid to preconcentrate the trace elements in the final solution. Because of the heterogeneity of many biological materials, the ability to process larger masses of sample using dry ashing helps minimize errors in the results. Compared to wet digestion methods, the sample matrix is simplified, and the resulting ash is completely free of organic matter; consequently, the influence of residual carbon or some undigested organic molecules on ICP-MS or ICP-AES measurements is minimized. However, the charring process may have both oxidizing and reducing conditions during the combustion process, and the temperature, in some cases, may be several hundred degrees greater than that of a muffle furnace because of the combustion of the organic materials, which may result in poor recoveries of some volatile elements. It is therefore recommended that the whole procedure must first be

validated using CRMs with compositions similar to those of the samples to be analyzed (Hoening, 2003).

Numerous studies about the determination of major and trace elements in biological tissues, plants, and food samples using dry ashing techniques have been published in the past several decades. Heanes (1981) measured Co and Mo in plants. Dixon et al. (1980), Harju et al. (1997), and Lee et al. (1986) used the dry ashing technique to determine trace metals in proteins, oily foodstuffs, and trunk wood. Arnaud et al. (1992) used dry ashing to determine Zn in human milk. An interlaboratory study of a method for the determination of Pb, Cd, Zn, Cu, Fe, Cr, and Ni in foodstuffs after dry ashing at 450 °C that involved 16 laboratories was reported by Jorhem (1993). Kucera and Soukal (1995) reported that only 7% of Cd losses were observed after dry ashing at temperatures less than 500 °C and 30% when the temperature was increased to 900 °C. The most appreciable Cd losses (up to 35%) occurred when sulfuric acid was used on wet ashing due to Cd retention in the CaSO<sub>4</sub> precipitate formed. Mader et al. (1997) reported that, in the absence of an ashing aid, a temperature of approximately 500 °C was necessary for complete decomposition of plant tissues, whereas the more resistant animal tissues required significantly higher temperatures. Ming and Bing (1998) used dry ashing, microwave-oven digestion, and traditional open vessel acid digestion methods to determine REEs in human hair, and the results for the three digestion methods were comparable. Quantitative recoveries (>95%) were obtained for the determination of Fe, Cu, Zn, and Mn in pig-feed sample by dry ashing (Van Paemel et al., 2005). A dry ashing temperature in the 500–550 °C range was found to produce ashes with an organic carbon content of less than 1 wt%, which allowed the recovery of a significant proportion of the elements present in the original biomass (Llorente and Garcia, 2006). Fish, baby food, and honey were decomposed by dry ashing at 450 °C for 4–16 h, with subsequent recoveries of approximately 95% for Al, Cd, Co, Cr, Cu, Fe, Mn, Se, and Zn (Saracoglu et al., 2007; Tuzen, 2003; Tuzen et al., 2007). Khuder et al. (2010) used an improved dry ashing method to determine K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Rb, and Sr in bee honey samples. Borosova et al. (2010) used the dry ashing technique to measure Ni in the hair. Wang and Li (2010) used microwave-assisted decomposition and dry ashing methods to measure 27 elements in 16 Chinese rice samples and 11 Japanese rice samples. The dry ashing technique was also used to determine boron isotopes in plant tissues (Rosner et al., 2011; Vogl et al., 2011).

Although the dry ashing technique has been successfully used for various samples and different elements, as previously described, it is still a problematic technique for sample decomposition, especially with respect to the determination of trace contents of heavy metals, halogenides, S, As, Sb, Se, Te, and Bi. Saarela et al. (1995) reported that dry ashing is a sensitive and reliable technique for the determination of elements with atomic numbers greater than 20 in biological materials with a low ash content; however, they also reported that volatile elements, such as halogenides and sulfur, can be partly lost depending on the composition of the material studied. Mader et al. (1998) studied the retention of Cd, Cr, Cu, Mn, Pb, and Zn in solid residue when 1.5% HNO<sub>3</sub> was used as a leaching medium after the classical dry ashing of ten materials. Their

results showed that the addition of HF was necessary for quantitative release of the analytes into the solution. Koh et al. (1999) investigated the losses of trace elements in plant samples after dry ashing at 105–600 °C for 0.5–24 h in a muffle furnace. The amounts of Cl and Br decreased over the temperature range of 200–400 °C in all samples, especially in stem samples. Although arsenic is very problematic, Ybanez et al. (1992) successfully used dry ashing and hydride generation AAS to measure As in mussel from seafood products. Vassileva et al. (2001) reported results obtained by dry ashing of plants of terrestrial origin without As and Se losses that did not require a separate preparation methodology for As and Se analysis; however, they observed significant losses of As and Se for aquatic plants. Sahayam et al. (2010) added palladium nitrate ( $\text{Pd}(\text{NO}_3)_2$ ) to avoid the loss of volatile As during dry ashing. The recovery of both As(III) and As(V) was found to be nearly quantitative; the results were in good agreement with the certified values and were comparable with results obtained using closed microwave digestion. Oxidizing reagents, such as high-purity magnesium nitrate and magnesium oxide, are commonly used as ashing aids to prevent the volatilization of analytes (e.g., As, Se, Sb, Te, and Bi) and also to speed up the ashing process (Gorsuch, 1970; Hoenig, 2001; Matos-Reyes et al., 2010; Mindak and Dolan, 1999). However, the addition of an ashing aid significantly increases the content of inorganic salts, which might be a problem for the subsequent determination of trace elements and might also contribute to contamination (Korn et al., 2008).

Because numerous researchers doubt the validity of dry ashing decomposition, comparisons between dry ashing and wet digestion have been reported since the appearance of commercial wet digestion microwave heating devices for trace element analysis. The wet digestion methods were generally faster than the dry ashing methods but required the use of large amounts of reagents and, therefore, gave higher blank contributions for some elements (Adeloju, 1989). Some researchers have reported that microwave digestion methods give higher recoveries for many elements in comparison with dry ashing methods (Aydin, 2008; Bakircioglu et al., 2011; Demirel et al., 2008; Guldaz, 2008; Kaya et al., 2008; Soylak et al., 2004; Yaman and Cokol, 2004; Zachariadis et al., 1995). However, other researchers have found no significant differences between dry ashing and microwave digestion for the determination of major and trace elements in organic matter (Moreno et al., 2008), pine needles (Vaisanen et al., 2008), plant samples (Masson et al., 2010), and human hair (Dogan and Kaya, 2010; Ming and Bing, 1998). Based on these observations, it may be stated that dry ashing techniques also permit good recoveries for most major, minor, and trace elements in various organic materials under suitable conditions. Dry ashing techniques ensure the best simplification of the matrix through the efficient elimination of organic matter, which is a prerequisite for ensuring accuracy with some analytical techniques. This technique will undoubtedly remain an important and unique alternative method for the decomposition of organic materials in the near future.

### 15.5.3.6 Alkali Fusions

Alkali fusion is generally used to decompose geologic samples that contain refractory minerals that are difficult to digest with

acids, and this method ensures the complete quantitative attack and subsequent dissolution of all elements in the solution. NaOH, KOH,  $\text{Na}_2\text{O}_2$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{LiBO}_2$ , and  $\text{Li}_2\text{B}_4\text{O}_7$  are typically used for this type of fusion. Alkali fusion is traditionally used to analyze the major elements in geologic samples. Due to its relatively high blank level and the large amount of total dissolved solids in the final solution, this method is rarely used for trace element analysis in geologic samples recently.

#### 15.5.3.6.1 Fusion with NaOH and KOH

NaOH and KOH are well-known extremely efficient fluxes for the decomposition of silicate minerals. This decomposition occurs at relatively lower temperatures (500–700 °C) and requires less time (10–30 min) than fusion with  $\text{Na}_2\text{CO}_3$  and  $\text{LiBO}_2$  does. Molten alkalis are particularly corrosive, and the fusion procedures using these materials should be performed at the lowest temperature as possible. The amount of NaOH and KOH used is generally at least five times the sample mass for fusion in a muffle furnace or spirit lamp. The sample powder must be well mixed with the fluxes to avoid any incomplete decomposition during the fusion; otherwise, the fluxes will not be in contact with the sample, thus resulting in a partial decomposition and difficulty dissolving the alkali cake after fusion. The muffle furnace is normally heated to approximately 300 °C for 30 min to remove the water in the alkali fluxes and, thus, to prevent 'alkali creep' over the edge of the crucible. The temperature is then increased to 650–700 °C and maintained for approximately 15–30 min. The alkali cake can be rapidly dissolved with hot water and then acidified with HCl or  $\text{HNO}_3$ . A silver, nickel, iron, or graphite crucible can be used for NaOH and KOH fusion; the use of a silver crucible is quite common.

#### 15.5.3.6.2 Sinter or fusion with $\text{Na}_2\text{O}_2$

Sodium peroxide is a strongly oxidizing alkali flux. Most of the minerals in silicate rocks can be rapidly decomposed by sinter with  $\text{Na}_2\text{O}_2$  at a temperature of  $480 \pm 20$  °C, and a sample-to- $\text{Na}_2\text{O}_2$  ratio of 1:4 is usually used (Raftar, 1950; Seelye and Raftar, 1950). Lower temperatures (below the melting point of  $\text{Na}_2\text{O}_2$ ) result in less corrosion of the decomposition vessel. The sample powder must be fine and well mixed with  $\text{Na}_2\text{O}_2$  before heating.  $\text{Na}_2\text{O}_2$  is particularly useful in mineral analyses, and it is the only flux that can easily be used for the complete decomposition of zircon, tourmaline, cassiterites, or chromites.

Platinum, gold, zirconium, silver, nickel, and iron crucibles can be used for  $\text{Na}_2\text{O}_2$  sinter experiments. Nickel or iron crucibles may need to be discarded after a few uses due to the strong corrosion of the crucible materials. To avoid excessive attack of the crucible materials, a thick layer of fused anhydrous sodium carbonate is used before adding and mixing the sample with the  $\text{Na}_2\text{O}_2$  flux, and the duration of the subsequent fusion should be limited. Zirconium crucibles have been shown to have superior resistance to molten  $\text{Na}_2\text{O}_2$  flux, and the temperature can be increased to 700 °C for the fusion process (Belcher, 1963). The temperature must be precisely controlled at 510–520 °C for sintering in silver, nickel, and iron crucibles to prevent excessive corrosion of the crucible materials. For platinum crucibles, the fusion can be conducted at 540 °C without introducing Pt into the solution.

The reaction of  $\text{Na}_2\text{O}_2$  cake with water is violent and may give rise to local overheating and spitting of the alkali solution. For silicon analyses, the use of glass beakers must be avoided because the beaker materials may be corroded. The use of a PTFE beaker is suggested for dissolution of the alkali cake. After cooling, water is carefully added to the crucible to leach the contents, and then, the alkali solution is dissolved with HCl or  $\text{HNO}_3$ . REEs, Sc, Y, Th, and Sr can be analyzed using this technique (Robinson et al., 1986). Yu et al. (2001) reported poor recoveries for Rb, Zr, Nb, Mo, Sn, Sb, Cs, Ba, Hf, Ta, Tl, Pb, and Bi in nine reference rocks, but Meisel et al. (2002) reported a reproducibility of 5–10% for REEs, Y, Zr, Hf, Ta, and Nb.

#### 15.5.3.6.3 Fusion with $\text{LiBO}_2$ and $\text{Li}_2\text{B}_4\text{O}_7$

$\text{LiBO}_2$  is a nonoxidative alkali flux. Fusions can be performed at 950–1050 °C with sample-to-flux ratios of 1:3–1:5 in Pt crucibles for approximately 15 min.  $\text{LiBO}_2$  is readily available as a highly pure reagent and can decompose all forming minerals and most accessory minerals in rocks (Ingamell, 1970).  $\text{LiBO}_2$  is the flux that most commonly replaces NaOH and  $\text{Na}_2\text{O}_2$  fusion. The major advantage of  $\text{LiBO}_2$  fusion is that all of the major elements can be analyzed with one sample preparation. The disadvantages of this method are that loss of K and Na may occur at relatively high temperatures, a long time is required for sample fusion, and the alkali cake is difficult to leach off for dissolution. Ultrasonication has been suggested to accelerate the cake dissolution (Ohlweile et al., 1973).

$\text{Li}_2\text{B}_4\text{O}_7$  has a higher melting point (930 °C) than that of  $\text{LiBO}_2$  (845 °C) and is slower to dissolve.  $\text{Li}_2\text{B}_4\text{O}_7$  is better for ultramafic rocks, whereas  $\text{LiBO}_2$  is preferred for mafic and acidic rocks. A HF/ $\text{HNO}_3$  mixture was used to digest the melt to remove some of the Si and B as volatile fluorides to reduce the matrix in the solution (Panteeva et al., 2003; Yu et al., 2001).

#### 15.5.3.6.4 Fusion with $\text{Na}_2\text{CO}_3$

Anhydrous sodium carbonate can decompose many silicate materials in platinum crucibles when heated to 1000–1200 °C for approximately 1 h at a sample-to-flux ratio of 1:3 or 1:5 for acidic rocks and up to 1:15 for ultramafic rocks (less than 40%  $\text{SiO}_2$ ) (Šulcek and Povondra, 1989). Volatile elements, such as As, Se, Tl, and Hg, are lost during this type of fusion. Some refractory minerals cannot be decomposed by  $\text{Na}_2\text{CO}_3$ . The addition of an oxidizer, such as  $\text{KNO}_3$ ,  $\text{Na}_2\text{O}_2$ , or  $\text{KClO}_3$ , enhances the decomposition.  $\text{Na}_2\text{CO}_3$  together with NaOH or  $\text{Na}_2\text{O}_2$  decomposes accessory phases, such as zircon, cassiterite, corundum, ilmenite, and monazite, and melts at much lower temperatures than do  $\text{Na}_2\text{CO}_3$  fluxes (Potts, 1987). A platinum crucible may become iron-stained after a few uses for the  $\text{Na}_2\text{CO}_3$  fusion of rocks, indicating that some iron has been reduced to its metallic state and became alloyed with platinum. The iron can be removed by heating with 6N HCl or fusing with potassium pyrosulfate in the crucibles.

The alkali fusion technique is traditionally used for the analysis of major elements in silicate rocks (Jeffery, 1975). When NaOH, KOH, and  $\text{Na}_2\text{O}_2$  have been used for this purpose, Na and K were unable to be detected, and large quantities of a given element may result in polyatomic interferences during ICP-MS analyses (Jarvis, 1992). Different combinations of the reagents for a flux mentioned earlier can be used for different types of samples. For example, the combinations of

$\text{Na}_2\text{CO}_3$  and  $\text{H}_3\text{BO}_3$  (Watanabe, 2001; Watanabe and Otsuki, 2008),  $\text{Na}_2\text{CO}_3$  and  $\text{Na}_2\text{B}_4\text{O}_7$  (Mitsumata and Aoki, 2004), and KOH and  $\text{H}_3\text{BO}_3$  (Mutsuga et al., 2011) are used for the decomposition of SiC, silicate, blue phosphor, and titanium dioxide, respectively. One advantage of the alkali fusion method is the rapid decomposition of geologic samples containing refractory minerals compared with acid digestion. Almost all minerals and accessory minerals can be completely dissolved. For example, platinum group elements (PGEs) in mafic and ultramafic rocks (Jarvis et al., 1997; Meisel et al., 2003b; Qi et al., 2003; Stone and Crocket, 1993; Totland et al., 1995), graphite and silicon carbide (Yamaguchi et al., 2000), barium sulfate (using ammonium hydrogen sulfate for the decomposition) (Matsumoto and Koura, 2001), ceramic materials (using a mixture of  $\text{Na}_2\text{CO}_3$  and ZnO for the decomposition) (Mihaljevic et al., 2001), zircon (Jain et al., 2001; Yamagata et al., 2008), and chromitites (Potts et al., 1992) can all be dissolved.

The main disadvantage of using fusion for the decomposition of rocks and minerals is the relatively high blank level and the high level of total dissolved solids in the final solution, which affects modern instrumental methods of analysis (e.g., ICP-MS and ICP-AES). For example, when the alkali fusion technique is used, the dilution factor for ICP-MS is 5–10 times higher than that of acid digestion (at least 1000), resulting in a deterioration in the detection limits and the need for frequent cleaning of the cones, nebulizer, and spray chamber. When  $\text{LiBO}_2$  has been used, it can be difficult to determine Li or B in subsequent acid digestion runs due to high background levels left in the ICP-MS. Thus, the relatively high blank level and high salt concentration in the solution after alkali fusion limit the application of the alkali fusion technique for trace element analysis, which has resulted in a limited number of papers reporting the use of alkali fusion for the detection of major to ultratrace elements in samples using ICP-AES or ICP-MS (Awaji et al., 2006; Fujimori et al., 2001; Sekimoto et al., 2002; Wei and Haraguchi, 1999). Wang et al. (2003) used  $\text{LiBO}_2$  fusion to decompose geologic samples. After the fusion and the subsequent dissolution with  $\text{HNO}_3$ , the elements Ti, Mn, Co, Sr, Y, Nb, Ta, Zr, Hf, In, Ba, Th, and REEs can be quantitatively precipitated using 50% NaOH to adjust the solution to strong alkaline. This method can effectively decompose samples containing high concentrations of Al, Nb, Ta, Zr, and Hf, which are difficult to decompose using acid digestion. The matrix from the flux is removed, and the detection limits are improved with this method, but only 26 elements can be determined.

Volatile elements, such as Sn, Sb, Tl, Pb, and Zn, may be lost when  $\text{LiBO}_2$  or  $\text{Na}_2\text{CO}_3$  fusion is used at high temperatures (Totland et al., 1992; Yu et al., 2001). However, alkali fusion is often used to prepare samples of some volatile elements that can easily evaporate by acid digestion, such as fluorine and chlorine (Anazawa et al., 2001; Malde et al., 2001; Tarafder et al., 1997), boron (Terashima et al., 1998), boron isotope (Tonarini et al., 1997), and iodine (Yamada et al., 1996).

In summary, the alkali fusion technique is used primarily to analyze major elements, decompose refractory minerals, and prepare samples of some volatile elements that can easily evaporate by acid digestion. Unlike the PTFE high-pressure bomb technique, hazardous reagents, such as HF or  $\text{HClO}_4$ , are not used for alkali fusion. However, it is difficult to purify

the alkali flux, which results in relatively high blank levels and larger dilution factors for modern instrumental analysis. Although the decomposition time in the fusion method is short compared with that of acid digestion, the fusion method is labor intensive and more difficult to apply with large numbers of geologic samples. An automated fusion system has been reported to simplify the alkali fusion procedure (Govindaraju and Mevelle, 1987).

### 15.5.3.7 Fire Assays

Fire assay (FA) technique is normally used for preconcentration and separation of the precious metals, including PGEs, Au, and Ag, from a large amount of complex matrices, such as Cu-Ni-PGE ores, mafic and ultramafic rocks, minerals, and soils. PGEs are known to be sensitive indicators for understanding several fundamental aspects of the origin and evolution of the Earth and mantle-derived magmas, such as the core segregation, core-mantle interaction, degree of partial melting, the extent of sulfide segregation and silicate fractionation, and melt-rock reactions, and thus are important for understanding the petrogenesis of mantle-derived rocks (Crocket and Paul, 2004; Ely and Neal, 2003; Lightfoot and Keays, 2005). Consequently, the FA technique is important for geochemical studies. A large amount of sample mass (5–100 g) is typically taken to obtain better accuracy, precision, and lower limits of detection and to avoid the ‘nugget effect.’ Two types of collector are currently used to collect precious metals from the matrix: lead FA (Pb-FA) and nickel sulfide FA (NiS-FA).

#### 15.5.3.7.1 Lead fire assay

For Pb-FA, PGEs are extracted from sample matrix by reductive fusion and are collected in a lead button (Bugbee, 1957; Farago et al., 1996; Haffty et al., 1977; Hall and Pelchat, 1994; Van Loon and Barefoot, 1991). The fluxes comprise sodium carbonate, borax, litharge, and a reducing agent, such as flour or charcoal, and are fused at 1000 °C in a clay crucible. The exact composition of the flux largely depends on the nature of the sample. Silver is normally added to the flux as powder or as a solution to increase the recoveries of PGEs. The ratio of Ag to Au + PGE is approximately 20:1. The precious metals are partitioned into a Pb button that settles to the bottom of the crucible. The matrix elements react with the flux component to form a slag that is subsequently discarded. After cooling, this button is separated and cupelled (i.e., oxidized) in a furnace to give a noble-metal prill, which can be dissolved for the quantitative analysis of Au, Pt, and Pd. Rhodium, Ir, Ru, and Os are partially lost (Hall and Pelchat, 1994; Van Loon and Barefoot, 1991). The molten lead and slag are poured into iron molds and are allowed to solidify. The slag is removed, and the lead button is subsequently cupelled by being placed in a cupel made of bone ash or MgO and heated to approximately 960 °C in an oxidizing atmosphere. Most of the molten lead is absorbed (as PbO) by the cupel or is volatilized, which leaves a Ag prill that contains Au, Pt, Pd, and Rh. Osmium is completely lost during the cupellation procedure as a volatile oxide, and Ru and Ir are partially lost as oxides into the cupel. The silver prill can be measured by instrumental neutron activation analysis or dissolved in acid and measured by AAS, ICP-AES, or ICP-MS.

Pb-FA is normally used for the determination of Au, Pt, and Pd in geologic samples. Detection limits of 2, 0.1, and 0.5 ppb for Au, Pt, and Pd, respectively, have been reported. Further improvements in the detection limits through purification of the flux components have been suggested (Hall and Pelchat, 1994). Compared with the NiS-FA technique, the Pb-FA technique has lower recoveries and higher detection limits (Juvonen et al., 1994), and only Au, Pt, and Pd can be determined using this method.

#### 15.5.3.7.2 Nickel fire assay

The NiS-FA method is capable of collecting all of the PGEs in different types of samples and has been studied extensively over the past 20 years (Balaram et al., 2006; Bedard and Barnes, 2002; Bedard and Barnes, 2004; Farago et al., 1996; Frimpong et al., 1995; Gros et al., 2002; Haffty et al., 1977; Hall and Pelchat, 1994; Jackson et al., 1990; Jarvis et al., 1995; Jorge et al., 1998; Juvonen et al., 1994; 2002; Li and Ebihara, 2003; Li and Tong, 1995; Morcelli et al., 2004; Plessen and Erzinger, 1998; Ravizza and Pyle, 1997; Sun and Sun, 2005; Van Loon and Barefoot, 1991; Wichmann and Bahadir, 2001; Zereini et al., 1994; Zhou et al., 2001). In a typical NiS-FA, approximately 15 g of finely ground rock sample is mixed with 5 g of Ni, 3 g of S, 20 g of sodium tetraborate, 10 g of sodium carbonate, and 5 g of quartz in a clay crucible and is heated to 1100–1200 °C for approximately 75 min. During fusion, two phases are formed in the melt: the siliceous phase and the sulfide phase in which PGEs and Au are concentrated. Covering the crucible can prevent the possible contamination during fusion, and the size of the NiS button is increased because less of the sulfide is oxidized during fusion. The NiS button can be measured directly by laser ablation (LA)-ICP-MS (Jarvis et al., 1995). Alternatively, it can be dissolved in HCl to separate Ni from PGEs and then measured using the solution ICP-MS. The button is dissolved in HCl in an Erlenmeyer flask at approximately 90 °C, and this process is usually performed overnight. The insoluble PGE sulfides, along with the dissolved PGEs, are then collected by Te coprecipitation, which can effectively collect all of the PGEs in the form of a black precipitate (Jackson et al., 1990; Oguri et al., 1999; Sun et al., 1993); a good recovery of Os has even been reported (Gros et al., 2002).

Different sample type may require different fusion compositions for NiS-FA. Incomplete fusion has been observed in the case of chromite-bearing samples using normal FA techniques, with recoveries of PGEs ranged from 76% to 85% (Asif and Parry, 1991). Juvonen et al. (2002) changed the composition of the flux by adding oxidant to the fusion flux for black shale and a reducing reagent in the case of magnetite samples to improve the outcome of the fusion. Carbon can be oxidized either by roasting the sample prior to fusion (700 °C for 2 h) or by adding potassium nitrate to the fusion. For magnetite, a reducing agent (flour or potassium tartrate) is required. Base metals, As, Cu, Fe, Sb, and Zn, can also be collected with Ni into the sulfide button. If present in large quantities, these metals will lead to the formation of an unusually large sulfide button that is difficult to dissolve in HCl and that will remain with the PGEs in the final solution and cause interference in the ICP-MS determination.

Frimpong et al. (1995) found that the recovery of Ir, Os, and Au from a komatiite sample did not significantly depend

on the mass of the collector used; recoveries of Ru, Rh, Pd, and Pt, however, were reproducible and dependent upon the collector mass. The partition coefficients were found to depend upon the PGE concentrations. They concluded that, when PGE concentrations are determined at low levels, the NiS-FA collection method may cause significant biases.

Because of difficulties in establishing conditions for the complete fusion of all chromite grains, Zereini et al. (1994) reported that the best results were obtained when a 1:1 mixture of the lithium tetraborate and sodium tetraborate in flux was used. Bedard and Barnes (2004) reported a procedure based on the addition of sodium metaphosphate to the fusion mixture for the determination of PGEs in chromites. The optimum composition of the fusion mixture was found to be 10 g of sodium metaphosphate, 9 g of silica, 15 g of sodium carbonate, 30 g of lithium tetraborate, 7.5 g of nickel, and 4.5 g of sulfur for 10 g of sample to achieve complete dissolution of the chromite grains. The addition of sodium metaphosphate improved chromite dissolution in the flux and appeared to improve recoveries of the PGEs.

To accelerate the dissolution process, NiS buttons are crushed or pulverized before treatment with acid. However, this method introduces both the possibility of cross-contamination between samples and the possibility of losses of NiS together with PGEs during this step. Boisvert et al. (1991) reported that crushing buttons in a shatter-box resulted in losses of up to 20% of the NiS buttons. Some researchers crush the NiS buttons in plastic bags with a hammer to avoid mechanical losses (McDonald et al., 1994).

One disadvantage for samples that contain low levels of PGEs and Au is the contamination caused by reagent blanks as a result of the large amount of chemicals used as fluxes. Nickel produced by the carbonyl process must be used. Reagent blanks for PGEs and Au were reduced significantly when a much smaller quantity (0.5 g) of nickel was used. Because the high reagent blank of NiS-FA was found to originate primarily from the nickel, Sun et al. (1998) developed a method to purify the nickel oxide. They dissolved 500 g of nickel in HCl. The solution was then purified to be free of PGEs by Te coprecipitation or through the use of anion-exchange resin. The purified solution was neutralized with  $\text{Na}_2\text{CO}_3$ , and the precipitate by centrifugation of the solution was subsequently rinsed with water. The precipitate was finally ignited at 700 °C for approximately 2 h. The procedure blank was significantly reduced.

Because the recoveries of PGEs for a single FA are approximately 90%, approximately 10% of the PGEs still remain in the slag. Oguri et al. (1999) developed a duplicate NiS-FA technique to enhance the recovery of PGEs to better than 96.7%. Isotope dilution (ID) was also used for NiS-FA to compensate the loss and improve the accuracies of PGEs, especially Os (Ravizza and Pyle, 1997).

When dissolving the NiS bead in an open beaker, the Ru and Pd can possibly escape as chlorides at low temperatures. Sun et al. (1993) used a closed beaker to prevent the loss of HCl during dissolution of the NiS button. Gros et al. (2002) designed a semiopen system that combines the advantages of the open system and those of the closed-beaker system. They also found that the S/Ni ratio in the NiS button is very important. An increase in the S/Ni ratio results in the formation of nickel disulfide ( $\text{NiS}_2$ ). This compound is poorly soluble in hot

hydrochloric acid but is readily soluble in aqua regia. A decrease in the S/Ni ratio to 0.5 results in the formation of  $\text{Ni}_{1-x}\text{S}$  in the NiS button, which is theoretically soluble in hot hydrochloric acid. This change in the S/Ni ratio significantly reduces the formation of insoluble nickel sulfide but does not alter the efficiency of PGE collection in the bead.

Sun and Sun (2005) reported an improved NiS-FA method that involves the addition of Fe to the flux. The Fe assay buttons are disintegrated into powder in water and then dissolved in HCl. This improved technique for the preconcentration of all six PGEs not only overcomes the problems of cross-contamination between samples and button losses at the mechanical crushing step but also speeds up the dissolution of the button. The button can be manipulated more easily than can a conventional sulfide button.

As previously reported, Re is poorly recovered by the NiS-FA technique (Frimpong et al., 1995). Sun et al. (2009) reported an improved Fe-Ni sulfide FA method in which  $\text{Na}_2\text{B}_4\text{O}_7$  was used instead of  $\text{Na}_2\text{CO}_3$  in the flux for the determination of Re, PGE, and Os isotopic ratios. Recovery of Re, to as high as 75%, was achieved, whereas it was less than 10% when  $\text{Na}_2\text{CO}_3$  was used. When  $\text{Na}_2\text{CO}_3$  is absent, the alkalinity of the slag phase is decreased, which favors the formation of  $\text{Re}^{4+}$ . The radius of  $\text{Re}^{4+}$  (0.77 Å) is virtually identical to that of  $\text{Fe}^{2+}$ . Consequently,  $\text{Re}^{4+}$  tends to occur in the Fe-Ni sulfide phase that contains FeS and thereby increasing Re recovery.

In summary, all of the PGEs can be collected using the NiS-FA technique. Large sample masses can be used to reduce the nugget effect. The NiS button can be analyzed directly by LA inductively coupled plasma mass spectrometry (LA-ICP-MS). The main disadvantage of NiS-FA is the relatively large mass of reagents used, which increase the reagent blanks of the PGEs, especially from the used Ni powder. Carbonyl nickel or purified nickel is preferred for fusion. Osmium may be lost as volatile  $\text{OsO}_4$  during the fusion and the recovery of Au is usually low. Ru and Pd may be lost as chlorides or Cl-bearing complexes during the dissolution of the NiS bead with HCl. Finally, it must be borne in mind that fire assaying is a technique that requires skill on the part of the operator; different types of samples require the composition of the flux to be varied, and considerable operator experience is required to obtain good results.

### 15.5.3.8 Carius Tube and High-Pressure Asher (HPA-S)

The use of a sealed glass tube for the digestion of organic materials with concentrated nitric acid under elevated temperatures of 250–300 °C was first described in 1860 and is often referred to as the Carius tube technique. The glass tube is typically a thick-walled quartz ampule in which the sample and the acid have been mixed, and the tube has been subsequently sealed. The tube is transferred to a jacket and heated for several hours for digestion. The modern redesign and application of the Carius tube for the digestion of some refractory materials was accomplished at the US National Bureau of Standards during the 1940s (Gordon, 1943; Gordon et al., 1944; Wichers et al., 1944).

Since the 1990s, the Carius tube technique has been mainly used to determine PGEs and Re-Os isotopes in geologic samples. Shirey and Walker (1995) used the Carius tube technique to determine Re-Os in geologic samples. In a typical analysis,

sample powders are introduced via a glass funnel into the tube. Spikes and aqua regia are added through a funnel and allowed to freeze in the bottom of the tube. As a precaution against bursting, at least half of the tube volume should be left empty. The lower parts of the tubes are immersed in an ethanol-dry ice slush to reduce the vapor pressure of the reagents and to make the sealing of the tube easier and more reliable. This process precludes the possibility of Re or Os loss during loading before sealing, because the reagents can oxidize both Re and Os, which may form moderately volatile oxides. While the bottom parts of the tubes are still frozen, the tube is sealed and then placed in a stainless-steel jacket. The internal volume of the stainless-steel jacket is about twice the external volume of the Carius tube, so that if it bursts, the jacket will not become overpressurized. The tubes are then heated in an oven at 220–260 °C for approximately 12 h. Agitation between multiple heating cycles can aid in sample digestion. It should be noted that, once heated, the inside of the tube may be under high pressure even when the temperature is reduced to room conditions. Thus, the tubes should be treated gently. Protective face and body shields should be worn during subsequent handling.

To avoid the problem of loss of mechanical stability at high temperatures, vessels made of quartz are used in the high-pressure ashing (HPA) technique, the digestion principles of which are similar to those of the Carius tube. This pressure digestion system has not only reduced the effective digestion time but has also enabled digestion of extremely resistant materials, such as carbon, carbon fibers, mineral oils, organic waste materials, and PGEs (Knapp, 1984, 1985). Nitric acid alone or combined with HCl is a sufficiently powerful reagent for a variety of samples. The maximum digestion temperature for high-pressure digestion is as high as 320 °C at a pressure of approximately 13 MPa. A commercial pressure digestion system, the HPA-S High Pressure Asher (Anton Paar GmbH, Austria), is available. The HPA-S technique is substantially safer than the use of Carius tubes, but its costs are higher.

The Carius tube technique has proven to be useful for Re–Os chronological dating and Os isotopes (Birck et al., 1997; Brauns, 2001; Cohen and Waters, 1996; Malinovsky et al., 2002; Meisel et al., 2001b, 2003b; Pearson and Woodland, 2000; Qi et al., 2010; Qu et al., 2008; Shirey and Walker, 1995; Sun et al., 2001a,b; Yang et al., 2005) and for the dissolution of most or all Re and PGEs from refractory platinum group minerals in geologic samples (Jensen et al., 2003; Meisel and Moser, 2004a, 2004b; Meisel et al., 2001a, 2003a; Norman et al., 2002; Pearson and Woodland, 2000; Pretorius et al., 2003; Qi and Zhou, 2008; Qi et al., 2007; Rehkamper et al., 1998). Because samples are dissolved in aqua regia under high temperatures (220–240 °C for Carius tubes and 300 °C for HPA-S), all the PGEs are at their highest oxidation state with complete equilibrium between spikes and samples. A total of 1–2 g of sample is commonly used in a Carius tube and HPA-S, with aqua regia added to less than one-third the total volume of the Carius tube to avoid a possible explosion. The total procedural blanks of HPA-S technique are as low as 0.04 ng for Pt and 0.005 ng for other PGEs (Meisel et al., 2003a) because small volumes of reagents are used and because all of the reagents can be purified. Osmium can be separated by normal distillation (Fritsche and Meisel, 2004; Malinovsky et al., 2002; Qi and Zhou, 2008;

Qi et al., 2007; Shirey and Walker, 1995; Sun et al., 2001a,b), in situ distillation (Brauns, 2001; Qi et al., 2010), or solvent extraction (Birck et al., 1997; Cohen and Waters, 1996). Recently, the use of HPA-S to fully dissolve rock samples with HF and ultimately to quantify REEs and HFSEs has also been reported (Cotta and Enzweiler, 2012). The HPA-S technique enables faster dissolution of samples that contain refractory phases (several hours), which otherwise require several days to digest in PTFE bombs.

Rehkamper et al. (1998) reported a modified Carius tube technique. The Carius tube was incorporated into a liner of high-purity quartz glass that retained the sample and acids during the digestion procedure. This technique achieves total procedural blanks at the 1–15 pg g<sup>-1</sup> level for PGEs and lowers the blank values by a factor of 10–100 compared to the standard NiS-FA technique. The quartz vessel of HPA-S is stabilized during the digestion process by subjecting it to an external pressure roughly equivalent to or higher than the internal pressure by using N<sub>2</sub> to pressurize the exterior of the vessel to 13 MPa; the vessel is thus protected from explosion (Meisel et al., 2001a). Becker et al. (2006) used a steel pressure vessel that contained 20 g dry ice to digest 2–3 g of peridotite in a quartz glass Carius tubes at 345 °C. The CO<sub>2</sub> pressure that builds up inside the pressure vessel upon warming supports the internal pressure in the Carius tube. They demonstrated that the spinels in peridotites were either completely dissolved or oxidized. Qi et al. (2007, 2008) reported a modified Carius tube method that utilizes a sealed stainless-steel high-pressure autoclave filled with water to prevent possible explosion of the tube. This technique allows a higher temperature (up to 300 °C), a greater volume of aqua regia (up to two-thirds of the total volume of the Carius tube), and thus a larger sample mass (12 g) compared to the normal Carius tube technique. This improved technique is efficient for the digestion of mafic rocks, ultramafic rocks, and chromites. The stainless-steel high-pressure autoclave is inexpensive and easy to maintain compared with the equipment required for the HPA-S technique.

In summary, the Carius tube and HPA-S techniques have the lowest procedural blanks of all the digestion techniques. This technique permits Re–Os dating and the determination of low concentrations of PGEs in geologic and environmental samples. However, the reproducibility is poor due to the small sample size (1–2 g) and the possible nugget effect in some sample types. Because only aqua regia is used, this technique may cause incomplete dissolution for some samples that contain refractory minerals, such as chromites and olivines. Carius tubes may explode under high temperatures and pressures, and the HPA-S technique requires expensive equipment.

### 15.5.3.9 Direct Fusion of Rock Powder

During the last decades, LA-ICP-MS has developed into an accurate and sensitive microanalytical technique for the analysis of solid samples. Because of its unique advantages (minimal sample preparation and rapid throughput) and the problems associated with wet chemical dissolutions, there is an increasing trend to use LA-ICP-MS for whole rock sample analysis. A homogeneous sample is a prerequisite to obtain reliable bulk analytical results using microanalytical techniques. The direct fusion of rock powder is a rather simple method to obtain a

homogeneous sample for LA-ICP-MS analysis. Sylvester (2001) has reviewed the trace element analysis of fused whole rock glasses using LA-ICP-MS.

#### 15.5.3.9.1 Flux-free fusion glasses

Rucklidge et al. (1970), Nicholls (1974), and Brown (1977) first reported the W-, Ir-, and Mo-strip fusion methods, respectively, for the determination of major element concentrations on glass beads using an electron microprobe. Fedorowich et al. (1993) prepared glass beads by melting small quantities (~25 mg) of rock powders on a tungsten-strip heater under an Ar atmosphere. The optimum melt conditions were achieved for most rock types by maintaining the temperature at 1700–1800 °C for 2 min. Hf and Ta contaminations from the tungsten strip and losses of Li and Pb at high strip temperatures and under longer melting conditions were reported. The Hf and Ta contaminations were avoided by using an iridium-strip heater instead of a tungsten-strip heater (Norman et al., 1996). Reid et al. (1999) used isotope dilution for the measurement of Zr and Hf in fused whole rock glasses. To maximize the homogeneity of the sample and enriched tracers, the resulting glass was ground and re-fused on an iridium-strip heater at 1600 °C for 2 min. Replicate analyses on these glasses resulted in precisions of approximately 1% for Zr and approximately 3.5% for Hf, which suggests a high degree of homogeneity in the samples. Jochum et al. (2000) have prepared large amounts (50–100 g) of silicate glasses (MPI-DING glasses) from rock powders to be used as reference materials in platinum crucibles by direct fusion at temperatures in the range of 1400–1600 °C. The resulting glasses are homogeneous for most elements at the micrometer to millimeter scale. Kurosawa et al. (2006) prepared fused glasses of seven Japanese silicate reference materials for LA-ICP-MS and particle-induced x-ray emission analysis by rapid fusion (2 min at 1200 °C) and subsequent quenching in welded platinum capsules. The fused glasses were found to be homogeneous for major elements and for trace elements with concentrations of more than 1 µg g<sup>-1</sup> within the observed precision (10%) on a 70 µm sampling scale. The values obtained by LA-ICP-MS for almost all the elements (including the relatively volatile elements Zn, Ga, Rb, and Pb) agreed well with the reference values, except for B and Cu. Pack et al. (2007) prepared small meteorite material glasses (~10 mg) by means of a SYNRAD 50 W CO<sub>2</sub> laser fusion system and an aerodynamic levitation device. Switching off the laser and cooling via the gas stream ensured rapid quenching. Although the cooling rates were approximately 520 K s<sup>-1</sup>, crystallization during the quenching of the Fe- and Ni-rich samples could not be avoided. Stoll et al. (2008) developed an automated Ir-strip heater, which enables the accurate control of the melting temperature and the melting time. This control makes it possible to achieve reproducible melting conditions. Elements with condensation temperatures (at a pressure of 10 Pa) higher than approximately 900 K (e.g., Zr, Hf, Ba, Sr, REEs, U, Mo, Ni, Rb, and Ga) were found not depleted at 1600 °C for 10 s.

The direct Ir-strip fusion method is suitable for mafic compositions (<55 wt% SiO<sub>2</sub>) that can easily be fused at 1200 °C. The fusion of siliceous samples is more problematic, because rapid homogenization during melting on the strip is hindered by high melt viscosities (Nehring et al., 2008). High melting

temperatures (1700–1800 °C), long fusion times (60–120 s), and stirring at high temperatures are required to achieve homogeneity in such samples (Nicholls, 1974), but these conditions lead to loss of volatile elements. For example, a high loss (20–90%) of highly volatile elements (e.g., Cs, Ge, Sn, and Pb) was observed at high melting temperatures (≥1600 °C) and long melting times (80 s) (Stoll et al., 2008). The dilution of a high SiO<sub>2</sub> concentration by the addition of MgO is another way to facilitate rapid fusion and homogeneity (Gumann et al., 2003; Nehring et al., 2008). Nehring et al. (2008) evaluated the melting behavior of a wide range of rock compositions (55–80 wt% SiO<sub>2</sub>) and the dependence of trace element concentrations on the sample/MgO mixing ratio, melting time, and melting temperature. The melting conditions of 1600 °C and 20 s for samples are recommended when the SiO<sub>2</sub> content is between 55% and 70 wt%, whereas 1800 °C and 20–30 s are often required for samples with >70 wt% SiO<sub>2</sub> (Nehring et al., 2008). Pb and Cs due to volatilization on the Ir strip are partly lost. Zhu et al. (2011) proposed a modified method using a double iridium-strip heater, which suppresses the volatilization of Pb and Zn to a certain extent, to fuse the rock powder without flux.

In summary, the flux-free fusion of a rock powder is a simple and rapid method that does not require acid digestion. It needs very small amounts of sample (10–50 mg), which makes it suitable for bulk analyses of valuable samples (e.g., lunar samples). The obtained precision and accuracy by LA-ICP-MS on fused whole rock glasses are comparable with those of other routine bulk analytical techniques. The limitations of this technique include the loss of some highly volatile trace elements (e.g., Pb, Zn, Sn, Ge, In, and Cs) during sample fusion and the requirement for high melting temperatures (>1600 °C), long fusion times, and/or the addition of MgO for samples with higher SiO<sub>2</sub> contents (>55%). Selection of an appropriate melting temperature and time for the sample preparation is an essential prerequisite for the accurate analysis of fused whole rock glasses by LA-ICP-MS.

#### 15.5.3.9.2 Lithium–borate fusion glasses

Another method for bulk rock analysis by LA-ICP-MS is to generate glasses by adding the flux agents LiBO<sub>2</sub> (Perkins et al., 1993; Pickhardt et al., 2000; Sylvester, 2001), Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub> (Günther et al., 2001; Ødegård and Hamester, 1997; Ødegård et al., 1998), or LiBO<sub>2</sub> and Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub> (Beck and Dietze, 1999; Yu et al., 2003) to the rock powders prior to fusion. This technique is commonly used for making fused glass disks for major element analysis using x-ray fluorescence (Norris and Hutton, 1969). A commonly used recipe for making fused disks involves mixing 0.1–1 g of rock powder with a fivefold excess of lithium–borate flux in a platinum/5% gold crucible. This mixture is then heated to 1000–1100 °C for 5–20 min in a furnace (Sylvester, 2001). The addition of the flux agents significantly reduces the temperature required for fusion compared with that needed for the rock powder alone, thereby reducing the possible loss of volatile elements. The flux agents can also sufficiently change the melt composition such that olivine crystals do not form upon melt quenching of komatiites and peridotites and break down the rigid structure of the siliceous melt such that the viscosity is reduced and homogenization is rapidly achieved (Sylvester, 2001). This method is suitable for a wide variety of bulk compositions, including



mafic, intermediate, and silicic rocks (Yu et al., 2003). The analytical precision reported in the studies mentioned earlier typically ranged from 2% to 7% for most trace elements, which suggests that most of the lithium–borate fusion glasses are homogeneous at the scale of laser sampling. The disadvantages of this method include contamination of the rock sample by impurities in the flux agents, a lower detection power because of sample dilution due to flux, and long-term instrumental memory effects from lithium and boron contaminations. For example, for some elements (e.g., Be, Sc, Sr, La, Ti, V, Cr, Ni, Cu, Zn, Y, Zr, Ba, Nd, and Pb), impurities of up to several micrograms per gram have been observed in the lithium–borate flux (Ødegård and Hamester, 1997; Sylvester, 2001). For LA-ICP-MS analyses, these impurities necessitate significant blank subtractions for these elements. Moreover, long-term analyses of the lithium–borate fusion glasses preclude the precise measurement of Li and B isotope ratios and the detection of low concentrations of Li and B on the contaminated instrument. Thus, the lithium–borate fusion techniques are not popularly used for LA-ICP-MS analysis currently.

### 15.5.4 Summary and Overview

Sample digestion is a fundamental and critical stage in the process of sample analysis, particularly with respect to the digestion of most geologic samples (e.g., rocks, minerals, soils, and sediments) that have to be digested into the solution to satisfy the requirements for chemical analyses. Clearly, no single digestion technique will allow the determination of all elements. The performance of analytical instrumentation for chemical analysis has improved dramatically over the past several decades. However, methods of sample digestion have not changed to keep pace and have lagged far behind developments in analytical instrumentation. Future developments in digestion methods need to be focused on aspects of sample throughput, precision and accuracy, analytical cost, simplification of the operating procedure, and as many elements as possible for measurements, minimization of waste generation, and safety considerations. There is little doubt that automation technology will be increasingly used in sample digestion in the near future, which would especially improve sample throughput and analytical reproducibility.

Improved measurement techniques and instruments allow the use of smaller analytical test portions to determine analyte concentrations. However, smaller test portions mean greater difficulty in achieving representativeness of the population. The minimum sampling mass of the sample materials largely depends on the sample particle size. The processing and use of ultrafine samples (<30 µm) will significantly influence the future development of digestion techniques as a consequence of the potential significant reduction in the masses of the test portions (Wang et al., 2004), which will provide the added advantages of enhanced digestion efficiency and speed, lower costs, and lower environmental impacts.

Finally, it is evident that sample digestion methods will remain an important area for development, in order to keep up with the rapidly evolving measurement techniques and instruments (see Chapters 15.10; 15.11; 15.12; 15.13; 15.14; 15.15; 15.16; 15.17; 15.18; 15.19; 15.20; 15.21; 15.22; and 15.23).

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