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## Wet Digestion

R M Twyman, University of York, York, UK

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### Introduction

Wet digestion methods for elemental analysis involve the chemical degradation of sample matrices in solution, usually with a combination of acids to increase solubility. The various acid and flux treatments are carried out at high temperatures in specially designed vessels that help to minimize contamination of the sample with substances in the air, the local environment, and from the vessel walls. Losses from the sample may occur due to adsorption onto the vessel walls, volatilization, and coextraction, but these can be reduced by procedural modifications. The use of closed systems, where the digestion reaction is completely isolated from the surroundings, may help to reduce both contamination and sample loss.

### The Nature of the Sample Matrix

Many techniques employed for elemental analysis require the conversion of the sample matrix into a solution form. The selection of an appropriate treatment for sample dissolution depends on the nature of the sample, and different approaches are required for predominantly inorganic and predominantly organic matrices. Geological, geochemical, and soil samples generally contain silicate, metal oxides, carbonates, and, in many cases, organic matter. Such samples must be dried and ground to a fine powder to

facilitate dissolution. Minerals and coal often have a nonuniform distribution of elements, while fly ash is very fine and is composed of metal silicates and oxides. Both these types of sample are difficult to solubilize. Similarly, alloys can be difficult to dissolve because of the strong bonds between metal atoms and their brittle nature. Solid and crystalline samples may possess interstitial water and water of crystallization, so thorough drying of samples is necessary before and after grinding.

Biological samples must be processed with great care, since the dissolution and total decomposition of all organic matter is required for the release of trace elements. However, the use of oxidizing acids to decompose organic matter can produce violent reactions and the alternative procedure of dry ashing may be more suitable in some cases. Environmental and water samples often contain mixtures of organic and inorganic substances, so dissolution techniques need to be modified to take this composition into account. In particular, water samples may contain dissolved and suspended solids, colloids, and microorganisms. Elements embedded in such samples may be present both in dissolved and solid forms. The nature of the sample matrix must be given special attention during wet digestion.

### Extraction of the Analyte

Solid samples generally contain some adsorbed and/or absorbed water. In the case of inorganic materials, drying is carried out in an oven at 105–110°C for a few hours, although lower temperatures need to be used if the sample contains volatile components. On the other hand, higher temperatures may be required to remove water trapped within crystalline matrices.

Frequently, the sample is not soluble in water and must be treated with acids or mixtures of acids to facilitate solubilization. The type of acid treatment must be given careful consideration, since particular acids may or may not oxidize the sample, and may be incompatible with certain elements. For example, sulfuric acid cannot be used to dissolve samples containing barium, while hydrochloric acid cannot be used to dissolve silver or samples containing lead and lead compounds. The choice of acid is also restricted by sample volatilization, e.g., hydrochloric acid should be avoided in samples containing arsenic since this is more volatile as a trichloride.

Naturally occurring inorganic materials, such as ores, must be given special treatments to facilitate solubilization. The two most common methods employed in dissolving samples are treatments with hydrochloric, hydrofluoric, nitric, sulfuric, or perfluoric acids (or various combinations thereof) and fusion with an acidic or basic flux followed by treatment with water or an acid. Organic materials are usually decomposed by wet digestion with a boiling oxidizing acid or acid mixture, ultimately producing carbon dioxide, water, and other volatile compounds that are driven off to leave behind salts or acids of the inorganic constituents of the sample. Wet digestions may be performed in open beakers on hot plates, but Kjeldahl flasks or specially designed containment vessels give results that are more satisfactory.

### Wet Digestion with Single Acids

The solvent action of an acid depends on several factors:

1. The reduction of hydrogen ions by metals that are more active than hydrogen, for example:  $\text{Zn(s)} + 2\text{H}^+ \rightarrow \text{Zn}^{2+} + \text{H}_2(\text{g})$ .
2. The combination of hydrogen ions with anions of a weak acid, for example:  $\text{CaCO}_3(\text{s}) + 2\text{H}^+ \rightarrow \text{Ca}^{2+} + \text{H}_2\text{O} + \text{CO}_2(\text{g})$ .
3. The oxidizing properties of the acid anion, for example:  $3\text{Cu(s)} + 2\text{NO}_3^- + 8\text{H}^+ \rightarrow 3\text{NO(g)} + 4\text{H}_2\text{O}$ .
4. The tendency of the acid anion to form soluble complexes with the sample cation, for example:  $\text{Fe}^{3+} + \text{Cl}^- \rightarrow \text{FeCl}^{2+}$ .

Ideally, the chosen reagent should cause the complete dissolution of the sample. As a general guide it is useful to classify the more common acid treatments according to whether they oxidize the sample or not. The nonoxidizing acids include dilute hydrochloric, hydrofluoric, sulfuric, and perchloric acids, whereas the oxidizing acids include hot, concentrated nitric, sulfuric, and perchloric acids. Dissolution of metals

by nonoxidizing acids is a process of hydrogen replacement.

Hydrochloric acid will dissolve metals above the standard reduction potential of hydrogen, salts of weak acids, and many oxides. Dilute sulfuric and perchloric acids are useful for metals above the standard reduction potential of hydrogen. Hot, concentrated sulfuric acid will often dissolve metals below the standard reduction potential of hydrogen. The most potent oxidizing conditions are obtained using hot concentrated perchloric acid, which will dissolve all common metals. Concentrated hydrochloric acid is an excellent solvent for many metal oxides as well as those metals that are more easily oxidized than hydrogen. In addition, it is often a better solvent for oxides than the oxidizing acids.

Hot, concentrated nitric acid will dissolve all common metals with the exception of aluminum and chromium, which are passive to the reagent as a result of surface oxide formation. Hot nitric acid also readily oxidizes many organic substances. Hot, concentrated sulfuric acid can be used to decompose and dissolve many substances in part because of its high boiling point (340°C), and it is particularly useful for the dehydration and oxidation of organic samples. Most metals and alloys are also attacked by this hot acid.

Perchloric acid is a potent oxidizing agent that leads to the formation of highly soluble perchlorate salts. As with sulfuric acid, perchloric acid dehydrates and oxidizes organic samples very efficiently. It also attacks iron alloys and stainless steel, which are resistant to other mineral acids. Care is required when using perchloric acid because it is explosive in contact with certain organic compounds and easily oxidized inorganic materials. Special chemical hoods are recommended. Perchloric acid, as a 72–74% solution, boils at 203°C.

Hydrofluoric acid is a weak, nonoxidizing acid that is particularly useful for dissolving silicate samples since it removes the silicon quantitatively as volatile  $\text{SiF}_4$ . In many cases, hydrofluoric acid dissolution can be achieved by adding sodium fluoride to samples treated with hydrochloric acid.

### Wet Digestion with Acid Mixtures

Acids in combination are preferred for certain inorganic matrices and are generally more advantageous for the decomposition of organic compounds. Wet digestion procedures using acid mixtures can be divided into four types:

1. Total decomposition, usually with hydrofluoric acid and another mineral acid.
2. Strong attacks, for routine analysis but leaving a residue of certain minerals, particularly

silicates. Carried out with various mixtures of sulfuric, nitric, and perchloric acids.

3. Moderate attacks, using weaker acid mixtures.
4. Partial digestions (acid leaching).

Both (3) and (4) are typically employed for environmental analysis where complete dissolution is either not required or is undesirable and the goal is to determine the presence of certain trace elements.

For geochemical samples containing silicates, the matrix is decomposed by heating with hydrofluoric acid in combination with either nitric or perchloric acid, each of which has a higher boiling point than hydrofluoric acid. The presence of the second acid with a higher boiling point ensures that, once the hydrofluoric acid has been boiled off and the dry sample redissolved, sparingly soluble metal fluorides are converted to salts that are more soluble. As stated above, however, caution should be exercised with the use of perchloric acid if the sample has a significant organic component. Perchloric acid is also more expensive than nitric acid, and can introduce chloride ions as contaminants.

For organic samples, a widely used mixture is aqua regia (1:3 nitric acid–hydrochloric acid). The nitric acid acts as the oxidizing agent, while the hydrochloric acid provides the complexing properties. The addition of bromine or hydrogen peroxide can sometimes increase the solubilizing power of mineral acids. Wet digestion is generally carried out in open flasks, covered loosely to avoid atmospheric contamination. However, it is becoming increasingly common to use closed vessels, such as polytetrafluoroethylene (PTFE)-lined containers or ultrapure quartz vessels, especially for small samples.

A 1:4 mixture of sulfuric and nitric acids is also widely employed for organic samples. The nitric acid decomposes the bulk of the organic matter but does not reach a temperature sufficient to destroy the last traces. However, as the nitric acid boils off, the sulfuric acid is left behind. Dense  $\text{SO}_3$  fumes evolve and begin to reflux in the flask, making the solution very hot and allowing the hot sulfuric acid to decompose the remaining organic matter. Because of the fumes produced in this method, it must be carried out under a fume hood. More nitric acid may be added to prolong the digestion and eliminate any stubborn organic material.

A very efficient acid mixture is nitric, sulfuric, and perchloric acid in a volume ratio of ~3:1:1. For a typical 10 g sample of tissue or blood, 10 ml of this solution is sufficient for complete dissolution. The samples are heated until the nitric acid boils off and perchloric acid fumes begin to appear. Heating continues until the perchloric acid boils off and  $\text{SO}_3$

fumes appear. There is little danger of perchloric acid explosions as long as sufficient nitric acid is present to decompose the bulk of the organic matter, and as long as sulfuric acid remains after the perchloric acid has evaporated to prevent the sample becoming dry. Perchloric acid should never be added directly to an organic sample. A mixture of nitric and perchloric acid may also be used.

The availability of strong hydrogen peroxide solutions allows a combination of sulfuric acid and hydrogen peroxide to be used for the decomposition of organic matter. Hydrogen peroxide is a vigorous oxidizing agent and is particularly useful for the degradation of resistant plastics. There is little danger of explosion if sulfuric acid is present in excess. Most elements can be recovered quantitatively in this procedure, with the exceptions of ruthenium, osmium, germanium, arsenic, and selenium. In the case of germanium and arsenic, loss is attributable to volatilization of chlorides. Additionally, precipitated calcium sulfate may retain lead and silver if not solubilized. After decomposition, the sulfuric acid solution should be diluted and boiled gently for 10 min to destroy any remaining hydrogen peroxide.

The recovery of trace elements after wet digestion using the methods described above is compared in Tables 1 and 2.

**Table 1** Recovery of trace elements after wet digestion of cocoa

Element	Recovery <sup>a</sup> (%)			
	$\text{HNO}_3$ & $\text{HClO}_4$	$\text{HNO}_3$ , $\text{HClO}_4$ & $\text{H}_2\text{SO}_4$	$\text{HNO}_3$ & $\text{H}_2\text{SO}_4$	$\text{HNO}_3$
Ag	91	99	100	95
As	99	99	98	91, 98
Cd	101	102	102	99
Co	98	99	101	100
Cr	100	101	100	101
Cu	100	99	100	100
Fe	99	99	102	97
Hg	79	89	93	—
Mo	97	98	101	98
Pb	100	99, 93	90, 93	100
Sb	99, 94	100	100	97
Se	101	101	79	1
Sr	100	97	98	95
Zn	99	101, 94	100	99

<sup>a</sup>Oxidation mixtures respectively as follows:

15 ml concentrated  $\text{HNO}_3$ , 10 ml 60%  $\text{HClO}_4$ .

15 ml concentrated  $\text{HNO}_3$ , 5 ml conc.  $\text{H}_2\text{SO}_4$ , 10 ml 60%  $\text{HClO}_4$ .

15 ml concentrated  $\text{HNO}_3$ , 10 ml conc.  $\text{H}_2\text{SO}_4$ .

Concentrated and fuming  $\text{HNO}_3$ .

500 ml flask used for 2 g cocoa sample.

Radioactive nuclides were used to determine recovery of 1–10  $\text{mg kg}^{-1}$  level.

**Wet Digestion with Fluxes**

Some materials are particularly resistant to acid digestion, e.g., certain rocks, mineral oxides, phosphates, and some iron alloys. For these samples, high-temperature fusion with an acidic or basic flux such as lithium metaborate (LiBO<sub>3</sub>) in the molten state can be used to render such materials soluble in water or dilute acid. Fusion decompositions are the most rigorous methods available and all silicate materials, including refractory substances like zircon and cassiterite, can be dissolved completely when fused with an appropriate flux. However, there are several disadvantages to this method including the introduction of additional salts into the final solution

**Table 2** Recovery of metals from various biomaterials after wet digestion

Element	Recovery (%)				
	Blood	Urine	Leaves	Animal tissue	Reflux condenser
As	93	94	97	92	101
Au	77	100	77	65	100
Fe	98	92	95	85	100
Hg	24	84	45	30	100
Sb	99	95	94	94	100

Ag, Co, Cr, Cu, Mn, Mo, Pb, V, Zn: 98–102% for all samples. Samples: 5 ml horse blood; 250 mg sugar beat leaves; 10 ml urine; 1.5 g animal tissue. Digested for 1.5 h with 5 ml of a mixture of 98% H<sub>2</sub>SO<sub>4</sub>, 70% HClO<sub>4</sub>, and 66% HNO<sub>3</sub> in the volume ratio 1:1:3 in a micro-Kjeldahl flask. Amount of metal present was 0.05–0.3 mg. Urine was digested with concentrated HNO<sub>3</sub> only.

(e.g., lithium metaborate, typically used at a 3:1 flux–sample ratio, introduces lithium and boron), loss of materials by volatilization, and the encouragement of sample contamination from the vessel walls, which also become solubilized. The properties of some useful fluxes are summarized in Table 3.

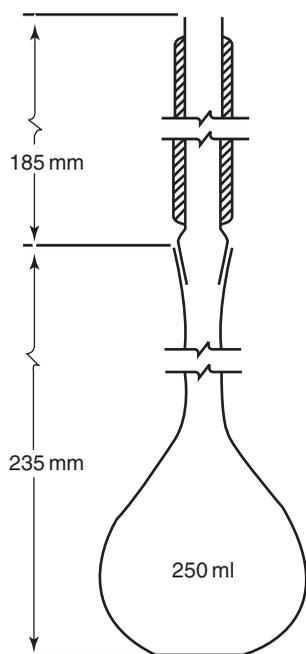
**Dissolution Techniques**

Depending on the nature, origin, sample quantity, elements of interest, and concentration range, a variety of different techniques for sample dissolution can be used. Dissolution assemblies such as the Kjeldahl flask, Parr bomb, crucible, quartz and platinum vessels, PTFE containers, and specially designed apparatus can be used for wet digestion (Figures 1 and 2). Many suitable small vessels and devices for sample heating and filtering are available. In the case of classical milliliter, microliter, and nanoliter methods, solution concentrations are generally >0.01 mol l<sup>-1</sup>. The quantities of the decomposition reagents and the decomposition vessels are adjusted to the smaller sample weights.

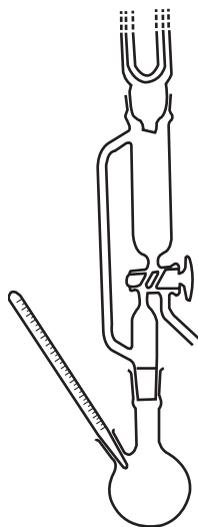
Inorganic materials subjected for trace metal analysis are generally decomposed and solubilized by treatment with mineral acids or by fusion with fluxes. Some inorganic samples, e.g., soils, may also contain considerable amounts of organic material, which can also be solubilized by acid treatment. Faster and more efficient decompositions of both organic and inorganic materials is possible using closed reaction vessels (bombs) that allow higher temperatures and pressures to be applied. For example, bombs have been designed for the decomposition of silicates with

**Table 3** Common fluxes

Flux	Melting point (°C)	Type of crucible/dish for fusion	Type of substance decomposed
Na <sub>2</sub> CO <sub>3</sub>	851	Pt	For silicates and silica containing samples; alumina-containing samples; sparingly soluble phosphates and sulfates
Na <sub>2</sub> CO <sub>3</sub> + an oxidizing agent such as KNO <sub>3</sub> , KClO <sub>3</sub> , or Na <sub>2</sub> O <sub>2</sub>	318	Pt (not with Na <sub>2</sub> O <sub>2</sub> ), Ni	For samples requiring an oxidizing environment; that is, samples containing S, As, Sb, Cr, etc.
NaOH or KOH	380	Au, Ag, Ni	Powerful basic fluxes for silicates, silicon carbide, and certain minerals; main limitation: purity of reagents
Na <sub>2</sub> O <sub>2</sub>	Decomposes	Fe, Ni	Powerful basic oxidizing flux for sulphides; acid insoluble alloys of Fe, Ni, Cr, Mo, W and Li; platinum alloys, Cr, Sn, Zr minerals
K <sub>2</sub> S <sub>2</sub> O <sub>7</sub>	300	Pt, porcelain	Acid flux for slightly soluble oxides and oxide-containing samples
B <sub>2</sub> O <sub>3</sub>	577	Pt	Acid flux for decomposition of silicates and oxides where alkali metals are to be determined
CaCO <sub>3</sub> + NH <sub>4</sub> Cl		Ni	Upon heating the flux, a mixture of CaO and CaCl <sub>2</sub> produced; used to decompose silicates for the determination of the alkali metals



**Figure 1** Reaction flask with asbestos-jacketed air condenser. The flask is a 250 ml borosilicate volumetric flask. A condenser is made from ST 19/38 ground glass joint, with a jacket of woven asbestos tubing held in place by wrapping with PTFE sealing tape. (Reproduced with permission from Feldman C (1974) *Analytical Chemistry* 46: 1607; © American Chemical Society.)



**Figure 2** Apparatus for wet oxidation of organic material. Stopcock, having three positions, allows (1) refluxing, (2) distillation, (3) removal of distillate. (Taken from Bethge PO (1954) *Analytica Chimica Acta* 10: 317; and Gorsuch TT (1959) *Analyst* 84: 147. Copyright by the Chemical Society.)

hydrofluoric acid at temperatures up to 150°C and pressures in excess of 8000 kPa. In the milligram range, the Parr bomb using metallic sodium or the Wurzschnitt bomb using sodium peroxide can be used to decompose refractory substances.

## Contamination and Loss of Analyte

### Contamination

The introduction of foreign substances during wet digestion and sample processing may have serious consequences in elemental analysis, and sources of contamination and their likely impact should be anticipated in order to minimize the resulting errors.

Airborne contaminants, in the form of dust, corrosion products, and residues from paints, etc., can introduce many different elements into a sample, e.g., sodium, potassium, calcium, magnesium, and aluminum. This is a significant threat where open reaction vessels are used, and can be avoided by simple precautionary measures such as covering the dissolution vessel with a dish or beaker equipped with a side arm through which a stream of filtered air or gas is passed. More stringent measures include the use of a clean air room kept under positive pressure, with the reaction itself carried out under a laminar flow hood. Gaseous contaminants can be eliminated from the reaction vessel's air supply using appropriate adsorption filters.

Another significant source of contamination is the vessels used for reagent storage and decomposition. There is no such thing as a completely inert vessel, although the choice of an appropriate vessel that is the least reactive under the chosen storage or decomposition conditions is recommended. Table 4 shows the elemental composition of four materials commonly used in decomposition and storage vessels, therefore revealing likely contaminants and the proportions in which they would be found. Dissolution vessels of Pyrex and quartz can introduce contamination from many elements, but ultrapure quartz can reduce the level of contamination from trace elements by up to 1000-fold as long as the surfaces are scrupulously cleaned before use. Polypropylene bottles, which are often used for the storage of acids, become brown after some time indicating the dissolution of the vessel's organic material. Even platinum vessels, which are required for fusions, contain small amounts of contaminating iron that can dissolve in contact with an acidic solution.

As well as the reaction and storage vessels, contamination may also arise from other stages of sample processing. Filter paper can contaminate samples with aluminum, barium, calcium, chromium, copper, iron, germanium, potassium, manganese, magnesium, sodium, antimony, gold, titanium, vanadium, zinc, zirconium, and rare earth metals. It is best to use filter media other than paper and carry out extensive preliminary washing with the operating solutions. Ultrapure water should be used as distilled water contains trace amounts of several

**Table 4** Average content (in  $\mu\text{g kg}^{-1}$ ) of current elements in the materials most commonly used for decomposition and storage vessels

Element	PTFE <sup>a</sup>	Ultrapure quartz	Quartz	Pyrex glass
Al		100	30 000	Main constituent
As		0.1	50	500–20 000
B		10	100	Main constituent
Ca		100	500–3000	1 000 000
Cd		0.1	10	1000
Co	1	1	1	100
Cr	20	2	5	3000
Cu	10	10	50	1000
Fe	10	100	1000	100 000
Hg	10 <sup>b</sup>	1	1	10–100
Mg		10	10	500 000
Mn		10	10	5000
Na	25 000	10	1000	Main constituent
Ni				2000
Sb	0.5	1	2	10 000
Si		Main constituent	Main constituent	Main constituent
Ti		100	1000	3000
Zn		50	50	3000

<sup>a</sup>Isostatic molded polytetrafluoroethylene.

<sup>b</sup>Strongly dependent on cleaning conditions.

From Buldini PL, Ricci L, and Sharma JL (2002) Recent applications of sample preparation techniques in food analysis. *Journal of Chromatography A* 975: 47–70.

**Table 5** Illustrative contents of some trace elements in reagent grade and extra purity acids

Element	Content ( $\mu\text{g l}^{-1}$ )									
	HCl		HClO <sub>4</sub>		HF		HNO <sub>3</sub>		H <sub>2</sub> SO <sub>4</sub>	
	A <sub>max</sub>	B	A <sub>max</sub>	B	A <sub>max</sub>	B	A <sub>max</sub>	B	A <sub>max</sub>	B
Al		8		5	700		400	5	10	8
As	10	<1	50	5	50		10	1	500	<1
Ca		20		1000				7		10
Cd	10									
Co		<1		5				<1		<1
Cr		2								
Cu	500, 50	2	200	5	100	10	100	3, 10	500	3
Fe	100	7	500	100	1000	500	200	5	200	10, 3
Hg		<10						<10	<10	<10
Mg		4								
Mn		1	500	5		1		1, 5	1, 5	1
Ni	500	<1		2		20	100	<1	500	1, 7
Pb	50	<1	100	5		20		2		5
Zn	100	<1		40				<1		<1

A = analytical reagent, B = extra purity reagent ('electronic grade'), maximum content indicated by max; otherwise actual analysis.

inorganic compounds, resulting in contamination with copper, zinc, iron, nickel, aluminum, lead, and others.

Contaminants originating in the mineral acids used for digestion are also a significant source of error. **Table 5** shows the contaminants present in reagent grade and extra-pure mineral acids available from standard laboratory suppliers. Extra-pure acids have low levels of contaminants but are very expensive. It may be possible to eliminate many of the trace contaminants from reagent grade acids, or at

least reduce them to undetectable levels, by several rounds of distillation.

### Losses

During wet digestion, certain components of the sample can be lost, leading to the underestimation of particular elemental contents. Trace elements can be lost by adsorption to the vessel walls, volatilization, coprecipitation, and coextraction. Although the exact nature of adsorption losses is unclear, it may

be due to molecular and ionic interactions. Metal cations exchange with alkali or alkaline earth ions at the glass-solution interface and are replaced by  $H^+$  ions. Anion exchange may also occur, e.g.,  $AuCl_4^-$  for  $\equiv SiOH$  groups on the glass surface. Vigorous shaking of the solution may bring some of the adsorbed species back into solution. Polyethylene and polypropylene also adsorb inorganic and molecular species but to a lesser extent and a mature acid strength of 10% is recommended in stored solutions. Solutions of  $0.1\text{ mol l}^{-1}$  or stronger in mineral acid stored in polyethylene, Pyrex, or similar borosilicate glass bottles remain stable for weeks. Plastic bottles may be preferred because of reduced leaching of trace elements. Sample solutions of water should be acidified to prevent or minimize the adsorption of metals. Mercury concentrations in  $1\text{ mol l}^{-1}$  nitric acid in borosilicate glass do not show any loss over a period of months. Loss of analyte also occurs when filtered through paper, sintered glass, or glass wool due to adsorption. Centrifugation is therefore preferable to filtration.

Volatile metals are less likely to be lost from basic solutions than from acidic ones. Metals with higher oxidation states tend to form volatile oxides and halides, e.g.,  $OsO_4$ ,  $RuO_4$ ,  $Re_2O_7$ ,  $GeCl_4$ ,  $AsCl_3$ ,  $SbCl_3$ ,  $CrOCl_2$ ,  $SnCl_4$ , and  $TiF_4$ . A few metals can be lost from solutions by volatilization at room temperature, particularly  $OsO_4$  and  $RuO_4$ . Losses associated with the reaction of samples with silica glass, porcelain, and platinum at higher temperatures may also take place.

### Matrix Effects and Modifiers

Many samples with inorganic or organic matrices pose serious problems in elemental analysis due to their composition and nature. It may therefore be necessary to add certain modifiers to the mixture to facilitate dissolution. In addition, dissolution assemblies may need to be modified. The use of hydrogen peroxide, a nonacidic modifier, has already been described. This can be used in conjunction with suitable acids for effective oxidation, and decomposition of organic matter usually proceeds without the danger of an explosion in a mixture of nitric and sulfuric acids at atmospheric pressure. One common modification of dissolution assemblies is the fitting of a condenser, to prevent the loss of volatile mercury, osmium, and ruthenium species. If excessive frothing occurs during wet digestion, a small amount of 2-octanol may be added or the preliminary treatment may be carried out in a beaker with glass beads to prevent bumping. With some organic materials, e.g., rubbers, coated fibers, and polymers, wet digestion in

sulfuric acid should not be carried out if the aim is to determine levels of arsenic. The ammonium salt of ethylenediaminetetraacetic acid is often used as a matrix modifier for the dissolution of sediments and other geological samples with hydrofluoric, sulfuric, and perchloric acids.

Digestion with a mixture of nitric, sulfuric, and perchloric acids is more efficient when a small amount of molybdenum(IV) catalyst is added. As soon as water and nitric acid have evaporated, oxidation proceeds vigorously with foaming and is completed in a few seconds. To avoid the loss of mercury from a digestion, volatile mercury compounds can be reduced to the metal with copper(I) and hydroxylammonium chloride at room temperature, while organic matter is degraded by potassium permanganate. The mercury can then be dissolved and the analysis completed. Nitrogen-containing compounds are commonly digested with sulfuric acid and potassium sulfate to increase the boiling point of the acid and thus the efficiency of the reaction. Proteins can be removed from organic samples by precipitation using trichloroacetic acid, tungstic acid with barium hydroxide, or zinc sulfate.

For the decomposition of inorganic samples by soda ash in platinum crucibles, the resistance of platinum is increased in an atmosphere of carbon dioxide. In a nitrogen atmosphere, platinum is corroded less by alkali metals. Peroxide bombs are good for wet ashing to destroy the organic matter in samples like coal. The PTFE acid digestion bomb prevents contamination and insures no losses by volatilization. Samples like coal can be analyzed in quantities of 50 mg or less.

In the fusion methods, cesium iodide is often added to the fusion mixture as a nonwetting agent to prevent the molten flux from adhering to the walls of the vessel, as well as to prevent incomplete transfer of the bead to the acid solution. In wet digestion of coal and fly ash using the Parr bomb, boric acid is added after digestion and the sample is heated for a further time on a water bath allowing the removal of unburned carbon.

No method of wet digestion is ideal, and both contamination and losses will occur to a greater or lesser degree whichever method is used. The task of the analytical chemist is to choose a procedure that will minimize interference from contaminants, reduce losses as much as possible, and therefore bring errors within acceptable limits. At all times, blank reagents and spiked recovery experiments are required to establish the degree of analyte contamination and loss from the dissolution process.