12 LABORATORY SAMPLE PREPARATION

12.1 Introduction

On first impression, sample preparation may seem the most routine aspect of an analytical protocol. However, it is critical that analysts realize and remember that a measurement is only as good as the sample preparation that has preceded it. If an aliquant taken for analysis does not represent the original sample accurately, the results of this analysis are questionable. As a general rule, the error in sampling and the sample preparation portion of an analytical procedure is considerably higher than that in the methodology itself, as illustrated in Figure 12.1.

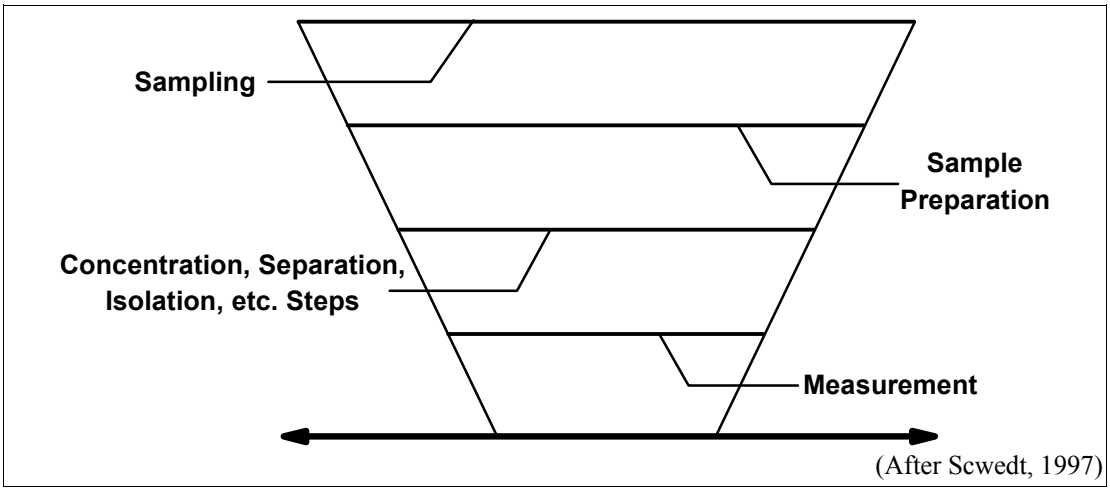

FIGURE 12.1—Degree of error in laboratory sample preparation relative to other activities

One goal of laboratory sample preparation is to provide, without sample loss, representative aliquants that are free of laboratory contamination that will be used in the next steps of the protocol. Samples are prepared in accordance with applicable standard operating procedures (SOPs) and laboratory SOPs using information provided by field sample preparation (Chapter 10, *Field and Sampling Issues that Affect Laboratory Measurements*), sample screening activities, and objectives given in the appropriate planning documents. The laboratory sample preparation techniques presented in this chapter include the physical manipulation of the sample (heating, screening, grinding, mixing, etc.) up to the point of dissolution. Steps such as adding carriers and tracers, followed by wet ashing or fusion, are discussed in Chapter 13 (*Sample Dissolution*) and Chapter 14 (*Separation Techniques*).

This chapter presents some general guidance

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for sample preparation to avoid sample loss and sample contamination. Due to the physical nature of the matrix, sample preparation for solids requires the most attention, and therefore is discussed at great length (Section 12.3). General procedures for preparing solid samples (such as drying, obtaining a constant weight, grinding, sieving, mixing, and subsampling) are discussed. Some sample preparation procedures then are presented for typical types of solid samples (e.g., soil and sediment, biota, food, etc.). This chapter concludes with specific guidance for preparing samples of filters (Section 12.4), wipes (Section 12.5), liquids (Section 12.6), gases (Section 12.7), and bioassay (Section 12.8).

12.2 General Guidance for Sample Preparation

Some general considerations during sample preparation are to minimize sample losses and to prevent contamination. Possible mechanisms for sample loss during preparation steps are discussed in Section 12.2.1, and the contamination of samples from sources in the laboratory is discussed in Section 12.2.2. Control of contamination through cleaning labware is important and described in Section 12.2.3, and laboratory contamination control is discussed in Section 12.2.4.

12.2.1 Potential Sample Losses During Preparation

Materials may be lost from a sample during laboratory preparation. The following sections discuss the potential types of losses and the methods used to control them. The addition of tracers or carriers (Section 14.9) is encouraged at the earliest possible point and prior to any sample preparation step where there might be a loss of analyte. Such preparation steps may include homogenization or sample heating. The addition of tracers or carriers prior to these steps helps to account for any analyte loss during sample preparation.

12.2.1.1 Losses as Dust or Particulates

When a sample is dry ashed, a fine residue (ash) is often formed. The small particles in the residue are resuspended readily by any air flow over the sample. Air flows are generated by changes in temperature (e.g., opening the furnace while it is hot) or by passing a stream of gas over the sample during heating to assist in combustion. These losses are minimized by ashing samples at as low a temperature as possible, gradually increasing and decreasing the temperature during the ashing process, using a slow gas-flow rate, and never opening the door of a hot furnace (Section 12.3.1). If single samples are heated in a tube furnace with a flow of gas over the sample, a plug of glass or quartz wool can be used to collect particulates or an absorption vessel can be used to collect volatile materials. At a minimum, all ash or finely ground samples should be covered before they are moved.

Solid samples are often ground to a fine particle size before they are fused or wet ashed to increase the surface area and speed up the reaction between the sample and the fluxing agent or

acid (see Chapters 13 and 14 on dissolution and separation). Since solid samples are frequently heterogeneous, a source of error arises from the difference in hardness among the sample components. The softer materials are converted to smaller particles more rapidly than the harder ones, and therefore, any loss in the form of dust during the grinding process will alter the composition of the sample. The finely ground particles are also susceptible to resuspension. Samples may be moistened carefully with a small amount of water before adding other reagents. Reagents should be added slowly to prevent losses as spray due to reactions between the sample and the reagents.

12.2.1.2 Losses Through Volatilization

Some radionuclides are volatile under specific conditions (e.g., heat, grinding, strong oxidizers), and care should be taken to identify samples requiring analysis for these radionuclides. Special preparation procedures should be used to prevent the volatilization of the radionuclide of interest.

The loss of volatile elements during heating is minimized by heating without exceeding the boiling point of the volatile compound. Ashing aids can reduce losses by converting the sample into less volatile compounds. These reduce losses but can contaminate samples. During the wet ashing process, losses of volatile elements can be minimized by using a reflux condenser. If the solution needs to be evaporated, the reflux solution can be collected separately. Volatilization losses can be prevented when reactions are carried out in a properly constructed sealed vessel. Table 12.1 lists some commonly analyzed radioisotopes, their volatile chemical form, and the boiling point of that species at standard pressure. Note that the boiling point may vary depending upon solution, matrix, etc.

Often the moisture content, and thus, the chemical composition of a solid is altered during grinding and crushing (Dean, 1995). Decreases in water content are sometimes observed while grinding solids containing essential water in the form of hydrates, likely as a result of localized heating. (See Section 12.3.1.2 for a discussion of the types of moisture present in solid samples.) Moisture loss is also observed when samples containing occluded water are ground and crushed. The process ruptures some of the cavities, and exposes the water to evaporation. More commonly, the grinding process results in an increase in moisture content due to an increase in surface area available for absorption of atmospheric water. Both of these conditions will affect the analysis of ^{3}H since ^{3}H is normally present in environmental samples as ^{3}HOH. Analysis for tritium in soils should avoid these types of sample preparation prior to analysis. Instead, total water content should be determined separately. Tritium analysis then could be performed by adding tritium-free ("dead") water to an original sample aliquant followed by filtration or distillation.

TABLE 12.1 — Examples of volatile radionuclides

Isotope	Chemical Form	Boiling Point (°C) *
Tritium — ^{3}H	H_2O	100°
Carbon — ^{14}C	CO_2 (produced from CO_3^{-2} or oxidation of organic material)	-78.5°
	Magnesium, calcium, and sodium carbonates	Natural ores of these metals decompose between 825° and 1,330° to yield the respective metal oxides
Iodine — ^{131}I, ^{129}I	I_2	185.2° (sublimes readily)
Cesium — ^{134}Cs, ^{135}Cs, ^{136}Cs, ^{137}Cs	Cs^0 (as metal) Cs_2O (as metallic oxide) (nitrates decompose to oxides) CsCl (as metallic chloride)	678.4° (melts at 28) ~400° 1290°
Technetium — ^{99}Tc	Tc_2O_7 $TcCl_4$ TcO_2	310.6° Sublimes above 300° Sublimes above 900°
	[Most Tc compounds sublime above 300°. Tc(VII) is an oxidant that reacts with organic solvents forming Tc(IV)]	
Polonium — ^{208}Po, ^{209}Po, ^{210}Po	Po^0 $PoCl_4$ $Po(NO_3)_4$ [as a solid] PoO_2	962° 390° Decomposes to PoO_2 above ~150° Decomposes to Po metal above 500°
Lead — ^{210}Pb, ^{212}Pb, ^{205}Pb	Pb^0 $PbCl_2$ $Pb(NO_3)_2$ PbO	1744° 950° Decomposes to oxide above 470° 888°

***** The closer the sample preparation temperature is to the boiling point of the compound, the more significant will be the loss of the material. However, if the objective is to distill the analyte compound from other nonvolatile materials, then boiling temperature is needed. Sample preparation near the decomposition temperature should be avoided for those compounds that have a decomposition temperature listed in the table.
Sources: Greenwood and Earnshaw (1984); Windholz (1976); Schwochau (2000); Sneed and Brasted (1958).

Additional elements that volatilize under specific conditions include arsenic, antimony, tin, polonium, lead, selenium, mercury, germanium, and boron. Chromium can be volatilized in oxidizing chloride media. Carbon, phosphorus, and silicon may be volatilized as hydrides, and chromium is volatilized under oxidizing conditions in the presence of chloride. The elements in Table 12.1 are susceptible to changing oxidation states during sample preparation. Thus, the pretreatment should be suited to the analyte. The volatility of radionuclides of tritium, carbon, phosphorus, and sulfur contained in organic or bio-molecules is based on the chemical properties of those compounds. If such compounds are present, special precautions will be necessary during sample preparation to avoid the formation of volatile compounds or to capture the volatilized materials.

12.2.1.3 Losses Due to Reactions Between Sample and Container

Specific elements may be lost from sample materials from interaction with a container. Such losses may be significant, especially for trace analyses used in radioanalytical work. Adsorption reactions are discussed in Chapter 10 for glass and plastic containers. Losses due to adsorption may be minimized by using pretreated glassware with an established hydrated layer. Soaking new glassware overnight in a dilute nitric or hydrochloric acid solution will provide an adequate hydrated layer. Glassware that is used on a regular basis will already have established an adequate hydrated layer. The use of strong acids to maintain a pH less than one also helps minimize losses from adsorption.

Reactions among analytes and other types of containers are described in Table 12.2. Leaving platinum crucibles uncovered during dry ashing to heat samples will minimize reduction of samples to base metals that form alloys with platinum. Porcelain should not be used for analysis of lead, uranium, and thorium because the oxides of these elements react with porcelain glazes. Increasing the amount of sample for dry ashing increases the amount of ash, minimizing the loss of the sample's trace materials to the container surface.

TABLE 12.2 — Properties of sample container materials

Material	Recommended Use	Properties
Borosilicate Glass	General applications	Transparent; good thermal properties; fragile; attacked by HF, H_3PO_4, and alkaline solutions.
Fused Quartz	High temperature applications	Transparent; excellent thermal properties (up to 1,100 °C); fragile; more expensive than glass; attacked by HF, H_3PO_4, and alkaline solutions.
Porcelain	High temperature applications and pyrosulfate fusion	Used at temperatures up to 1,100 °C; less expensive than quartz; attacked by HF, H_3PO_4, and alkaline solutions.
Nickel	Molten alkali metal hydroxide and Na_2O_2 fusions	Suitable for use with strongly alkaline solutions. Do not use with HCl.
Platinum	High temperature or corrosive applications	Virtually unaffected by acids, including HF; dissolves readily in mixtures of HNO_3 and HCl, Cl_2 water or Br_2 water; adequate resistance to H_3PO_4; very expensive; forms alloys with Hg, Pb, Sn, Au, Cu, Si, Zn, Cd, As, Al, Bi, and Fe, which may be formed under reducing conditions; permeable to H_2 at red heat, which serves as a reducing agent; may react with S, Se, Te, P, As, Sb, B, and C to damage container; soft and easily deformed, often alloyed with Ir, Au, or Rh for strength. Do not use with Na_2CO_3 for fusion.
Zirconium	Peroxide fusions	Less expensive alternative to platinum; extremely resistant to HCl; resistant to HNO_3; resistant to 50% H_2SO_4 and 60% H_3PO_4 up to 100 °C; resistant to molten NaOH; attacked by molten nitrate and bisulfate; usually available as Zircaloy—98% Zr, 1.5% Sn, trace Fe, Cr, and Ni. Do not use with KF or HF.

Material	Recommended Use	Properties
Alumina (Al_2O_3)	Acids and alkali melts at low temperatures	Resistant to acids and alkali melts; rapidly attacked by bisulfate melts; brittle, requires thick walled containers.
Polyethylene	Sample and reagent storage	Resistant to many acids; attacked by 16M HNO_3 and glacial acetic acid; begins to soften and lose shape at 60 °C; appreciably porous to Br_2, NH_3, H_2S, H_2O, and HNO_3 (aqueous solutions can lose ~1% volume per year when stored for extended periods of time).
Teflon™	Corrosive applications	Inert to almost all inorganic and organic compounds except F_2; porosity to gases is significantly less than that of polyethylene; safe to use below 250 °C but decomposes at 300 °C; difficulty in shaping containers results in high cost; low thermal conductivity (requires long periods of time to heat samples).
Polystyrene	Sample and reagent storage	Only useful for acid solutions < 0.1 M; brittle

The internal surface area of a container, whether used for sample preparation or storage, may cause loss of analyte. Scratches and abrasions increase the surface area, and their geometry make loss of analyte likely. Thus, it is important to discard containers that are scratched or abraded on their interior surfaces.

12.2.2 Contamination from Sources in the Laboratory

Contamination leads to biased data that misrepresent the concentration or presence of radionuclides in a specific sample. Therefore, laboratory personnel should take appropriate measures to prevent the contamination of samples. Such precautions are most important when multiple samples are processed together. Possible sources of contamination include:

- Airborne;
- Reagents (tracers are discussed in Chapter 14);
- Glassware/equipment;
- Facilities; and
- Cross-contamination between high- and low-activity samples.

The laboratory should use techniques that eliminate air particulates or the introduction of any outside material (such as leaks from aerosols) into samples and that safeguard against using contaminated glassware or laboratory equipment. Contamination of samples can be controlled by adhering to established procedures for equipment preparation and decontamination before and after each sample is prepared. Additionally, the results of blank samples (e.g., sand), which are run as part of the internal quality assurance program, should be closely monitored, particularly following the processing of samples with elevated activity.

"Cross-contamination" is the contamination of one sample by another sample that is being

processed concurrently or that was processed prior to the current sample leaving a residue on the equipment being used. Simply keeping samples covered whenever practical is one technique to minimize cross-contamination. Another technique is to order the processing of samples beginning with the lowest contamination samples first. It is not always possible to know the exact rank of samples, but historical or field screening data may be useful.

Laboratory personnel should be wary of using the same equipment (gloves, tweezers for filters, contamination control mats, etc.) for multiple samples. Countertops and other preparation areas should be routinely monitored for contamination.

12.2.2.1 Airborne Contamination

Airborne contamination is most likely to occur when grinding or pulverizing solid samples. Very small particles (~10 μm) may be produced, suspended in air, and transported in the air before settling onto a surface. Other sources of potential airborne contamination include samples that already consist of very small particles, volatile radionuclides (including tritium), or radionuclides that decay through a gaseous intermediate (i.e., ^{226}Ra decays to ^{222}Rn gas and eventually decays to ^{210}Pb). Therefore, the grinding or pulverizing of solid samples or the handling of samples that could produce airborne contamination should be carried out under a laboratory hood or ventilated enclosure designed to prevent dispersal or deposition in the laboratory of contaminated air particulates. These particles easily can contaminate other samples stored in the area. To prevent such cross-contamination, other samples should be covered or removed from the area while potential sources of airborne contamination are being processed.

If contamination from the ambient progeny of ^{222}Rn is a concern, it can be avoided by refraining from the use of suction filtration in chemical procedures, prefiltering of room air (Lucas, 1967), and use of radon traps (Lucas, 1963; Sedlet, 1966). The laboratory may have background levels of radon progeny from natural sources in soil or possibly in its construction materials.

12.2.2.2 Contamination of Reagents

Contamination from radiochemical impurities in reagents is especially troublesome in low-level work (Wang et al., 1975). Care must be taken in obtaining reagents with the lowest contamination possible. Due to the ubiquitous nature of uranium and thorium, they and their progeny are frequently encountered in analytical reagents. For example, Yamamoto et al. (1989) found significant ^{226}Ra contamination in common barium and calcium reagents. Other problematic reagents include the rare earths (especially cerium salts), cesium salts that may contain ^{40}K or ^{87}Rb, and potassium salts. Precipitating agents such as tetraphenyl borates and chloroplatinates may also suffer from contamination problems. In certain chemical procedures, it is necessary to replace stable carriers of the element of interest with isotopes of another element when it is difficult to obtain the stable carrier in a contamination-free condition. Devoe (1961) has written an extensive review article on the radiochemical contamination of analytical reagents.

12.2.2.3 Contamination of Glassware and Equipment

Other general considerations in sample preparation include the cleaning of glassware and equipment (Section 12.2.3). Criteria established in the planning documents or laboratory SOPs should give guidance on proper care of glassware and equipment (i.e., scratched glassware increases the likelihood of sample contamination and losses due to larger surface area). Glassware should be routinely inspected for scratches, cracks, etc., and discarded if damaged. Blanks and screening should be used to monitor for contamination of glassware.

Whenever possible, the use of new or disposable containers or labware is recommended. For example, disposable weigh boats can be used to prevent contamination of a balance. Disposable plastic centrifuge tubes are often less expensive to use than glass tubes that require cleaning after every use. If non-disposable containers or labware are used, it may be necessary to use new materials for each new project to reduce the potential for contamination. Blanks can be used to detect cross-contamination. Periodic rinsing with a dilute solution of nitric acid can aid in maintaining clean glassware. However, Bernabee et al. (1980) could not easily remove nuclides sorbed onto the walls of plastic containers by washing with strong mineral acids. They report that nuclides can be wiped from the walls, showing the importance of the physical action of a brush to the cleaning process.

12.2.2.4 Contamination of Facilities

In order to avoid contamination of laboratory facilities and possible contamination of samples or personnel, good laboratory practices must be constantly followed, and the laboratory must be kept in clean condition. The laboratory should establish and maintain a Laboratory Contamination Control Program (Section 12.2.4) to avoid contamination of facilities and to deal with it expeditiously if it occurs. Such a program should address possible samples of varying activity or characteristics. This minimizes sample cross-contamination through laboratory processing equipment (e.g. filtering devices, glassware, ovens, etc).

12.2.3 Cleaning of Labware, Glassware, and Equipment

12.2.3.1 Labware and Glassware

Some labware is too expensive to be used only once (e.g., crucibles, Teflon™ beakers, separatory funnels). Labware that will be used for more than one sample should be subjected to thorough cleaning between uses. A typical cleaning protocol includes a detergent wash, an acid soak (HCl, HNO_3, or citric acid), and a rinse with deionized or distilled water. As noted in Chapter 10, scrubbing glassware with a brush aids in removing contaminants.

The *Chemical Technician's Ready Reference Handbook* (Shugar and Ballinger, 1996) offers practical advice on washing and cleaning laboratory glassware:

- Always clean your apparatus immediately after use. It is much easier to clean the glassware before the residues become dry and hard. If dirty glassware cannot be washed immediately, it should be left in water to soak.

- Thoroughly rinse all soap or other cleaning agent residue after washing glassware to prevent possible contamination. If the surface is clean, the water will wet the surface uniformly; if the glassware is still soiled, the water will stand in droplets.

- Use brushes carefully and be certain that the brush has no exposed sharp metal points that can scratch the glass. Scratched glassware increases the likelihood of sample contamination and losses due to larger surface areas. Moreover, scratched glassware is more easily broken, especially when heated.

Automatic laboratory dishwashers and ultrasound or ultrasonic cleaners are also used in many radiochemical laboratories. It is important to note that cleaning labware in an automatic laboratory dishwasher alone may not provide adequate decontamination. Contaminated glassware may need to be soaked in acid or detergent to ensure complete decontamination. Ultrasonic cleaning in an immersion tank is an exceptionally thorough process that rapidly and efficiently cleans the external, as well as the internal, surfaces of glassware or equipment. Ultrasonic cleaners generate high-frequency sound waves and work on the principle of cavitation, which is the formation and collapse of submicron bubbles. These bubbles form and collapse about 25,000 times each second with a violent microscopic intensity that produces a scrubbing action (Shugar and Ballinger, 1996). This action effectively treats every surface of the labware because it is immersed in the solution and the sound energy penetrates wherever the solution reaches.

EPA (1992) contains a table of glassware cleaning and drying procedures for the various methods given in the manual (including methods for the analysis of radionuclides in water). The suggested procedure for cleaning glassware for metals analysis is to wash with detergent, rinse with tap water, soak for 4 hours in 20 percent (by volume) HNO_3 or dilute HNO_3 (8 percent)/HCl (17 percent), rinse with reagent water, then air dry. Shugar and Ballinger (1996) suggest treating acid-washed glassware by soaking it in a solution containing 2 percent NaOH and 1 percent disodium ethylenediamine tetraacetate for 2 hours, followed by a number of rinses with distilled water to remove metal contaminants.

More specifically to radionuclides, in their paper discussing the simultaneous determination of alpha-emitting nuclides in soil, Sill et al. (1974) examined the decontamination of certain radionuclides from common labware and glassware:

> By far the most serious source of contamination is the cell, electrode, and "O" ring used in the electrodeposition step. Brief rinsing with a strong solution of hydrochloric acid containing hydrofluoric acid and peroxide at room temperature was totally ineffective in producing adequate decontamination. Boiling anode and cell with concentrated nitric acid

> for 10 to 15 minutes removed virtually all of the activity resulting from the analysis of samples containing less than 500 disintegrations per minute (dpm). When larger quantities of activity such as the 2.5×10^4 counts per minute (cpm) used in the material studies ... had been used, a second boiling with clean acid was generally required. However, boiling nitric acid precipitates polonium and other procedures have to be used in its presence. When such high levels of activity have been used, a blank should be run to ensure that decontamination was adequate before the system is permitted to be used in the analysis of subsequent low-level samples. Prudence suggests that a separate system should be reserved for low-level samples and good management exercised over the level of samples permitted in the low-level system to minimize the number of blanks and full-length counting times required to determine adequate decontamination.
>
> ...Beakers, flasks, and centrifuge tubes in which barium sulfate has been precipitated must be cleaned by some agent known to dissolve barium sulfate, such as boiling perchloric or sulfuric acids or boiling alkaline DTPA [diethylenetriaminepentacetate]. This is a particularly important potential source of contamination, particularly if hot solutions containing freshly-precipitated barium sulfate are allowed to cool without stirring. Some barium sulfate post-precipitates after cooling and adheres to the walls so tenaciously that chemical removal is required. Obviously, the barium sulfate will contain whichever actinide is present, and will not dissolve even in solutions containing hydrofluoric acid. Beakers or flasks in which radionuclides have been evaporated to dryness will invariably contain residual activity which generally requires a pyrosulfate fusion to clean completely and reliably. Separatory funnels can generally be cleaned adequately by rinsing them with ethanol and water to remove the organic solvent, and then with hydrochloric-hydrofluoric acids and water to remove traces of hydrolyzed radionuclides...

However, one should note that current laboratory safety guidelines discourage the use of perchloric acid (Schilt, 1979).

12.2.3.2 Equipment

In order to avoid cross-contamination, grinders, sieves, mixers and other equipment should be cleaned before using them for a new sample. Additional cleaning of equipment prior to use is only necessary if the equipment has not been used for some time. The procedure can be as simple or as complicated as the analytical objectives warrant as illustrated by Obenhauf et al. (2001). In some applications, simply wiping down the equipment with ethanol may suffice. Another practical approach is to brush out the container, and briefly process an expendable portion of the next sample and discard it. For more thorough cleaning, one may process one or more batches of pure quartz sand through the piece of solid processing equipment, and then wash it carefully. The efficacy of the decontamination is determined by monitoring this sand for radionuclide contamination.

An effective cleaning procedure for most grinding containers is to grind pure quartz sand together with hot water and detergent, then to rinse and dry the container. This approach incorporates a safety advantage in that it controls respirable airborne dusts. It is important to note that grinding containers become more difficult to clean with age because of progressive pitting and scratching of the grinding surface. Hardened steel containers can also rust, and therefore should be dried thoroughly after cleaning and stored in a plastic bag containing a desiccating agent. If rust does occur, the iron oxide coating can be removed by a warm dilute oxalic acid solution or by abrasive cleaning.

12.2.4 Laboratory Contamination Control Program

The laboratory should establish a general program to prevent the contamination of samples. Included in the program should be ways to detect contamination from any source during the sample preparation steps if contamination of samples occurs. The laboratory contamination control program should also provide the means to correct procedures to eliminate or reduce any source of contamination. Some general aspects of a control program include:

- Appropriate engineering controls, such as ventilation, shielding, etc., should be in place.
- The laboratory should be kept clean and good laboratory practices should be followed. Personnel should be well-trained in the safe handling of radioactive materials.
- Counter tops and equipment should be cleaned and decontaminated following spills of liquids or dispersal of finely powdered solids. Plastic-backed absorbent benchtop coverings or trays help to contain spills.
- There should be an active health physics program that includes frequent monitoring of facilities and personnel.
- Wastes should be stored properly and not allowed to accumulate in the laboratory working area. Satellite accumulation areas should be monitored.
- Personnel should be mindful of the use of proper personnel protection equipment and practices (e.g., habitual use of lab coats, frequent glove changes, routine hand washing).
- Operations should be segregated according to activity level. Separate equipment and facilities should be used for elevated and low-level samples whenever possible.
- SOPs describing decontamination and monitoring of labware, glassware, and equipment should be available.

- Concentrated standard stock solutions should be kept isolated from the general laboratory working areas.

As an example, Kralian et al. (1990) have published the guidelines for effective low-level contamination control.

12.3 Solid Samples

This section discusses laboratory preparation procedures for solid samples as illustrated in Figure 12.2. General procedures such as exclusion of unwanted material in the sample; drying, charring, and ashing of samples; obtaining a constant weight (if required); and homogenization are discussed first. Examples of preparative procedures for solid samples are then presented.

Solid samples may consist of a wide variety of materials, including:

- Soil and sediment;
- Biota (plants and animals); and
- Other materials (metal, concrete, asphalt, solid waste, etc.).

Before a solid sample is prepared, the specific procedures given in the planning documents should be reviewed. This review should result in a decision that indicates whether materials other than those in the intended matrix should be removed, discarded, or analyzed separately. Any material removed from the sample should be identified, weighed, and documented.

To ensure that a representative aliquant of a sample is analyzed, the sample should first be dried or ashed and then blended or ground thoroughly (Section 12.3.1.4 and Appendix F, *Laboratory Subsampling*). Homogenization should result in a uniform distribution of analytes and particles throughout the sample. The size of the particles that make up the sample will have a bearing on the representativeness of each aliquant.

12.3.1 General Procedures

The following sections discuss the general procedures for exclusion of material, heating solid samples (drying, charring, and ashing), obtaining a constant weight, mechanical manipulation grinding, sieving, and mixing), and subsampling. Not every step is done for all solid sample categories (soil/sediment, biota, and other) but are presented here to illustrate the steps that could be taken during preparation.

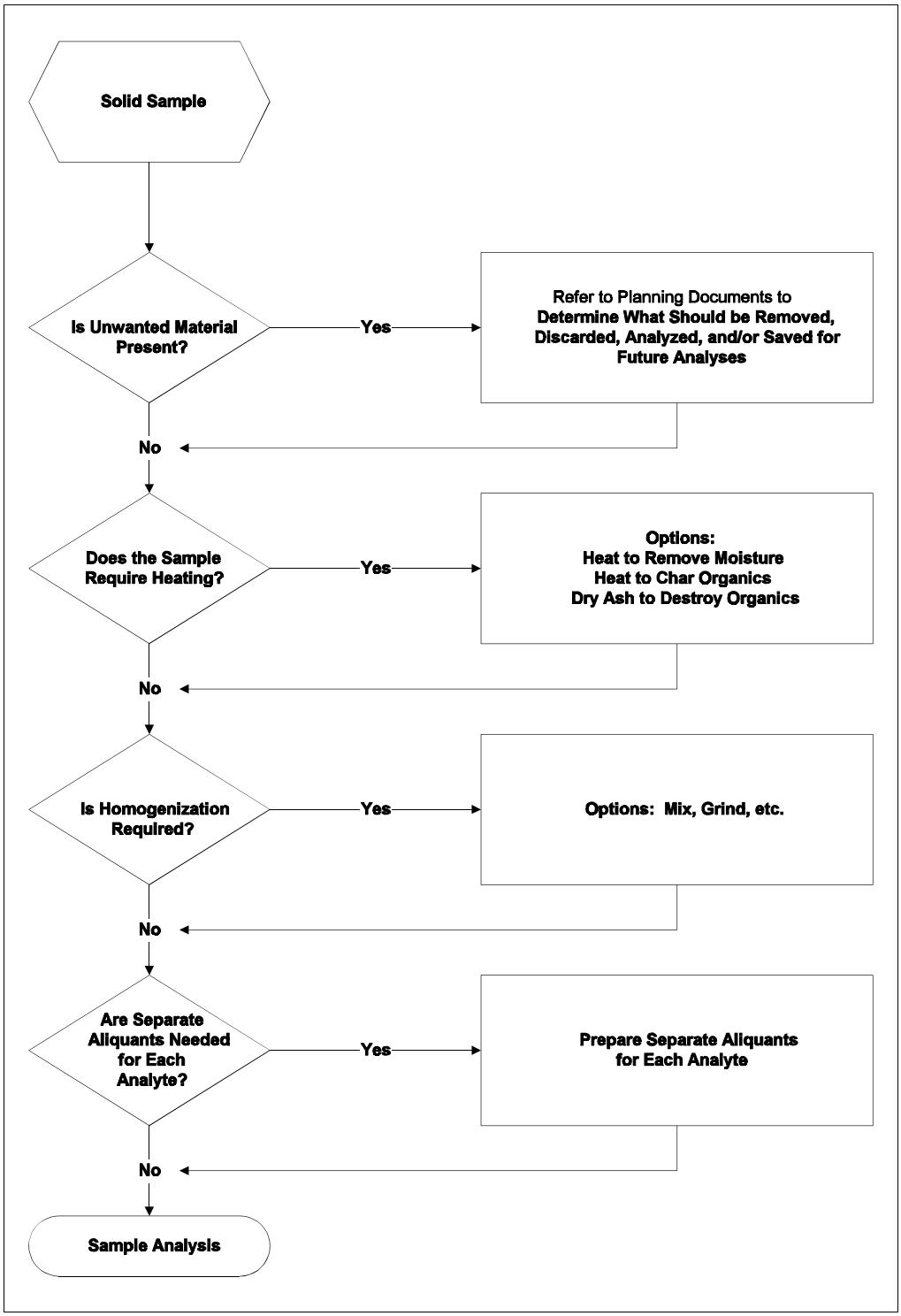

FIGURE 12.2—Laboratory sample preparation flowchart (for solid samples)

12.3.1.1 Exclusion of Material

EXCLUSION OF MATERIAL BY SIZE AND COMPOSITION

During solid preparation, some particles may be identified in the sample that are not a part of the matrix intended for analysis. Examples of such particles are rocks and pebbles or fragments of glass and plastic. Depending on the specific procedures given in the planning documents on the constitution of the sample taken, rocks and pebbles can be removed and analyzed separately if desired. The sample should be weighed before and after any material is removed. Other materials that are not a part of the required matrix can also be removed and analyzed separately. If analysis of the material removed is necessary, applicable SOPs should be used to prepare the material for analysis.

EXCLUSION OF ORGANIC MATERIAL

Leaves, twigs, and grass can easily be collected inadvertently along with samples of soil or sediment. Because these are not usually intended for analysis, they are often removed and stored for future analysis, if necessary. The material removed should be identified, if possible, and weighed.

12.3.1.2 Principles of Heating Techniques for Sample Pretreatment

Applying elevated temperatures during sample preparation is a widely used technique for the following reasons:

- To remove moisture or evaporate liquids, raise the temperatures to 60 to 110 °C, which will not significantly alter the physical composition of the sample.

- To prepare a sample containing organic material for subsequent wet ashing or fusion, "char" the material by heating to medium temperature of 300 to 350 °C (see page 12-19 on "Charring of Samples").

- To prepare the sample for subsequent determination of nonvolatile constituents, dry ash at high temperature of 450 to 750 °C. This may significantly change the physical and chemical properties of the sample.

Once a decision is made to use elevated temperatures during sample preparation, several questions should be considered:

- What material should be used for the sample container?

- What should serve as the heat source?

- How quickly should the temperature be raised? (Rate of stepwise temperature increase)
- What is the maximum temperature to which the sample should be exposed?
- How long should the sample be heated at the maximum temperature?
- How quickly should the sample be cooled afterward?

The following sections provide information related to these questions.

Note that there are times during sample preparation when samples should not be heated. For example, samples to be prepared for ^{3}H or ^{14}C determination should not be heated. Since ^{3}H is normally present as tritiated water in environmental samples, heating will remove the ^{3}H. Similarly, ^{14}C is usually present in environmental samples as carbonates or $^{14}CO_2$ dissolved in water, and heating will release ^{14}C as a gas. Samples to be analyzed for iodine, mercury, antimony, or other volatile elements should be heated only under conditions specified in the planning documents. If both volatile and nonvolatile elements are determined from the same sample, aliquants of the original sample should be removed for determination of the volatile elements.

Ovens, furnaces, heat lamps, and hot plates are the traditional means to achieve elevated temperatures in the laboratory. However, more recently, microwave ovens have added an additional tool for elevating temperature during sample preparation. Walter et al. (1997) and Kingston and Jassie (1988) give an overview of the diverse field of microwave-assisted sample preparation. A dynamic database of research articles related to this topic can be found at the SamplePrep Web™ at www.sampleprep.duq.edu/index.html. As microwave sample preparation has developed, numerous standard methods with microwave assistance have been approved by the American Society for Testing and Materials (ASTM), Association of Official Analytical Chemists (AOAC), and the U.S. Environmental Protection Agency (EPA). The majority of the microwave-assisted methods are for acid-dissolution (Chapter 13), but several are for drying samples.

Alternatives to heating samples include drying them slowly in a vacuum desiccator, air-drying, or freeze-drying. ASTM D3974 describes three methods of preparing soils, bottom sediments, suspended sediments, and waterborne materials: (1) freeze-drying; (2) air-drying at room temperature; and (3) accelerated air-drying.

DRYING SAMPLES

It must be determined at the start of an analytical procedure if the results are to be reported on an *as-received* or *dry-weight* basis. Most analytical results for solid samples should be reported on a

dry-weight basis, which denotes material dried at a specified temperature to a constant weight or corrected through a "moisture" determination made on an aliquant of the sample taken at the same time as the aliquant taken for sample analysis.

Typically, samples are dried at temperatures of 105 to 110 °C. Sometimes it is difficult to obtain constant weight at these temperatures, then higher temperatures must carefully be used. Alternatively, for samples that are extremely heat sensitive and decompose readily, vacuum desiccation or freeze-drying techniques are applicable.

The presence of water in a sample is a common problem frequently facing the analyst. Water may be present as a contaminant (i.e., from the atmosphere or from the solution in which the substance was formed) or be bonded as a chemical compound (i.e., a hydrate). Regardless of its origin, water plays a role in the composition of the sample. Unfortunately, especially in the case of solids, water content is variable and depends upon such things as humidity, temperature, and the state of subdivision. Therefore, the make-up of a sample may change significantly with the environment and the method of handling.

Traditionally, chemists distinguish several ways in which water is held by a solid (Dean, 1995).

- Essential water is an integral part of the molecular or crystal structure and is present in stoichiometric quantities, for example, $CaC_2O_4 \cdot 2H_2O$.

- Water of constitution is not present as such in the solid, but is formed as a product when the solid undergoes decomposition, usually as a result of heating. For example, $Ca(OH)_2 \rightarrow CaO + H_2O$.

- Nonessential water is retained by physical forces, is non-stoichiometric, and is not necessary for the characterization of the chemical composition of the sample.

- Adsorbed water is retained on the surface of solids in contact with a moist environment, and therefore, is dependent upon the humidity, temperature, and surface area of the solid.

- Sorbed water is encountered with many colloidal substances such as starch, charcoal, zeolite minerals, and silica gel and may amount to as much as 20 percent or more of the solid. Sorbed water is held as a condensed phase in the interstices or capillaries of the colloid and it is greatly dependent upon temperature and humidity.

- Occluded water is entrapped in microscopic pockets spaced irregularly throughout solid crystals. These cavities frequently occur naturally in minerals and rocks.

- Water also may be present as a solid solution in which the water molecules are distributed homogeneously throughout the solid. For example, natural glasses may contain several percent moisture in this form.

Heat Source. There are several choices when heating to dryness. The heat source is often determined by the amount of time available for drying and the potential for the sample to spatter or splash during drying. When time is not a primary concern and there is little or no chance of sample cross-contamination, samples are heated uncovered in a drying oven at the minimum temperature needed to remove moisture. If time is of concern, samples with high moisture content usually can be dried or evaporated faster using a hot plate. Heating on a hot plate significantly increases the chance of cross-contamination by spattering or splashing during boiling. However, ribbed watch glasses, which cover the sample yet still allow for evaporation, can be used to minimize cross-contamination in this approach. Samples may also be placed under a heat lamp. This method reduces the risk of cross-contamination by applying heat to the surface where vaporization occurs, minimizing splashing during boiling. However, the elevated temperature is difficult to measure or control, and spattering still may be a problem when the sample reaches dryness.

Microwave systems may also be used to dry samples. ASTM E1358 and ASTM D4643 use microwave energy to dry either wood or soil to a constant weight. In a similar fashion, AOAC Official Methods 985.14 and 985.26 use microwave energy to dry fat from meat or water from tomato juice. Other examples include Beary (1988), who has compared microwave drying to conventional techniques using solid standards from the National Institute of Standards and Technology (coal, clays, limestone, sediment) and foods and food materials (rice and wheat flour), and Koh (1980) who discusses microwave drying of biological materials.

Container Material. A sample container's composition typically poses no problem. Borosilicate glass is generally recommended because it is inexpensive, transparent, reusable, and has good thermal properties. Platinum, Teflon™ (polytetrafluoroethylene—PTFE), porcelain, or aluminum foil containers are acceptable and may be preferable in certain situations. Polyethylene and other plastics of low melting point are only useful in hot water baths or ovens where the temperature is closely monitored. Polyethylene is affected by heat applied directly to the container. The properties of several common materials used for sample containers are presented in Table 12.2 (on page 12-5). Note that the sample containers commonly received from the field will be those suitable for bulk samples rather than containers used during sample preparation. The plan will identify the type of container material to be used for field activities for samples to be shipped to the laboratory and the type of container material to be used during the various steps of sample preparation.

Heating Rate. The heating rate is generally not considered when removing moisture, because the maximum temperature typically is very low (60 to 110 °C). Samples simply are placed inside the

preset oven. Hot plates may be preheated to the desired temperature before heating the sample or turned on and gradually heated with the sample in place.

Maximum Temperature. The maximum temperature used for drying samples typically is just above the boiling point of water—105 to 110 °C. Higher temperatures will not dry the samples significantly faster and may result in accidents or cross-contamination due to uneven heating. Lower temperatures will not reduce the chance of cross-contamination, but will significantly increase the drying time. One exception to this rule occurs when the physical form of the sample needs to be preserved. Many minerals and chemicals have waters of hydration that affect the structure and may also affect the chemical and physical properties. Samples heated at 60 °C will retain the waters of hydration in most chemicals and minerals and still provide dry samples in a reasonable period of time (e.g., 12 to 15 hrs.).

Time. The duration a sample is heated to remove moisture depends on the size of the sample, the amount of moisture in the sample, the air flow around the sample, and the temperature applied to the sample. If heating the sample is to provide a constant dry weight, it is more difficult to determine how long to heat the sample. One convenient approach, especially when working with numerous samples, is to dry all materials overnight, or occasionally longer. This amount of heating is usually more than sufficient for drying samples for radiochemical analysis. If time is a critical factor or if a quantitative assessment of the uncertainty in the sample weight is required by the planning documents, the sample can be subjected to repeated cycles of drying and weighing until a series of weights meet the specified requirements (Section 12.3.1.3). For example, one such requirement might be to obtain three consecutive weights with a standard deviation less than 5 percent of the mean. While repeated cycles of drying and weighing can provide a quantitative measure of the uncertainty in the sample weight over time, a single weight after an overnight drying cycle typically provides a similar qualitative level of confidence with significantly less working time. Another time-saving step is to use microwave techniques rather than conventional heating sources during sample preparation (ANL/ACL, 1992; Walter et al., 1997).

Alternatives to Heating. (1) Vacuum-desiccation. A desiccator is a glass or aluminum container that is filled with a substance that absorbs water, a "desiccant." The desiccator provides a dry atmosphere for objects and substances. Dried materials are stored in desiccators while cooling in order to minimize the uptake of ambient moisture. The ground-glass or metal rim of the desiccator should be greased lightly with petroleum jelly or silicone grease to improve performance. Calcium sulfate, sodium hydroxide, potassium hydroxide, and silica gel are a few of the common desiccants. The desiccant must be renewed frequently to keep it effective. Surface caking is a signal to renew or replace the desiccant. Some desiccants contain a dye that changes color upon exhaustion.

Vacuum desiccators are equipped with a side-arm so that they may be connected to a vacuum to aid in drying. The contents of the sealed evacuated desiccator are maintained in a dry, reduced-

pressure atmosphere. Care must be exercised when applying a vacuum as a rapid pressure reduction, for high water content samples can result in "boiling" with subsequent sample loss and potential cross-contamination. The release of vacuum should be accomplished by the slow introduction of dry or ambient-humidity air into the chamber.

(2) Freeze-drying. Certain substances (i.e., biological materials, pharmaceuticals), which are extremely heat sensitive and cannot be dried at atmospheric conditions, can be freeze-dried (Cameron and Murgatroyd, 1996). Freeze-drying, also known as "lyophilization," is the process by which substances are frozen, then subjected to high vacuum. Under these conditions, ice (water) sublimes and other volatile liquids are removed. The non-sublimable material is left behind in a dry state.

To freeze-dry effectively, dilute solutions are used. In order to increase the surface area, the material is spread out on the inner surface of the container as it is frozen. Once the solution or substance to be dried is frozen solid, the primary drying stage begins in which a high vacuum is applied, and the ice sublimes, desorbing the free ice and some of the bound moisture. During secondary drying, a prolonged drying stage, the sorbed water that was bound strongly to the solids is converted to vapor. This can be a slow process, because the remaining bound water has a lower pressure than the free liquid at the same temperature, making it more difficult to remove. Secondary drying actually begins during the primary drying phase, but it must be extended after the total removal of free ice to achieve low levels of residual moisture.

Commercial freeze-drying units are self-contained. Simple units consist of a vacuum pump, adequate vapor traps, and a receptacle for the material to be dried. More sophisticated models include refrigeration units to chill the solutions, instrumentation to designate temperature and pressure, heat and cold controls, and vacuum-release valves. The vacuum pump should be protected from water with a dry-ice trap and from corrosive gases with chemical gas-washing towers.

CHARRING OF SAMPLES TO PARTIALLY OXIDIZE ORGANIC MATERIAL

Heating samples at a moderate temperature (300 to 350 °C) is sometimes used as a method of preparing a sample for subsequent decomposition using wet ashing or fusion techniques. Large amounts of organic material can react violently or even explosively during decomposition. Heating the sample to partially oxidize—or "char"—the organic material may limit reactivity during subsequent preparation.

Heat Source. Heat lamps, muffle furnaces, or hot plates may be used as a heat source for charring samples. Heat lamps are often selected because they can also be used to dry the sample before charring. Once dried, the sample can be moved closer to the lamp to raise the temperature and char the sample (confirmed by visual inspection). Heat lamps also reduce the potential for cross-contamination by minimizing spattering and splashing. Hot plates can be used similarly to heat

lamps. The sample is dried and the temperature is raised to char the sample; however, hot plates increase the probability of spattering and splashing. Muffle furnaces can be used when the charring is performed as part of dry ashing instead of part of the drying process. In this case, the muffle furnace temperature is first raised slowly.

Sample Container. The choice of sample container depends primarily on the next step in the sample preparation process. When dry ashing or fusing, the sample container will usually be a platinum or porcelain crucible. Zirconium or nickel crucibles may also be used. If the sample will be dissolved using wet ashing techniques, the container may be borosilicate glass or a platinum crucible. Care should be taken to prevent ignition of samples in glass containers. Ignited samples may burn at temperatures high enough to cause damage to the container and loss of sample. Polyethylene and Teflon™ generally are not acceptable because of the increased temperature and risk of melting the container.

Heating Rate. Heating rate becomes a concern when charring samples because of the increased temperatures. The general rule is to raise the temperature slowly to heat the sample evenly and prevent large increases in temperature within the sample, which could lead to ignition. Typically, a rate of 50 to 100 °C per hour is considered appropriate. Samples containing large quantities of organic material may require slower heating rates.

Maximum Temperature. One of the primary goals of charring a sample is to oxidize the materials slowly and gently. Gentle oxidation is accomplished by slowly raising the temperature close to the ignition point and letting the sample smolder. Most organic compounds will char and decompose in the range of 300 to 350 °C, so this is usually the range of temperatures where charring takes place. Ignition results in rapid oxidation accompanied by large volumes of released gases and potential sample loss. This reaction can raise the temperature of the sample to several hundred degrees above the desired maximum and result in significant losses during off-gassing. The progress of the reaction can be monitored visually by observing the volume of gas or smoke released. Thin wisps of smoke are usually allowable; clouds of smoke and flames are not. Visual inspection is easily accomplished when hot plates or heat lamps are used as heat sources. Some muffle furnaces are fitted with viewing windows to allow visual inspection. Never open a muffle furnace just to check on the progress of a reaction. This will cause a sudden change in temperature, increase the oxygen level and possibly ignite the sample, and disrupt air currents within the furnace to increase potential sample loss.

Time. The duration required to char a sample depends on the sample size, the amount of organic material in the sample, the ignition point of the organic material, the temperature of the sample, and the oxygen supply. Samples usually are heated until smoke begins to appear and allowed to remain at that temperature until no more smoke is evident. This process is repeated until the temperature is increased and no more smoke appears. Charring samples may require a significant amount of time and effort to complete. The duration may be reduced by improving the flow of air to the sample or mixing HNO_3 or nitrate salts with the sample before drying. However, this

approach is recommended only for well-characterized samples, those previously evaluated for the applicability of this technique, because nitrated organic compounds can oxidize in a violent or explosive manner.

DRY ASHING SAMPLES

The object of dry ashing is to combust all of the organic material and to prepare the sample for subsequent treatment using wet ashing or fusion techniques. This procedure involves heating a sample in an open dish or crucible in air, usually in a muffle furnace to control the temperature and flow of air. Microwave techniques are also available for dry ashing samples.

Dry ashing is used to determine ash weight as well as nonvolatile constituents. The associated chemistry is very complex, with oxidizing and reducing conditions varying throughout the sample and over time. During the combustion process, temperatures in the sample may reach several hundred degrees above the desired temperature, particularly if there is good air flow at the beginning of the ashing process (Bock, 1979). Covering samples during heating is not recommended, especially when using platinum crucibles. The lack of air produces a reducing atmosphere that results in reduction of metals that alloy with the crucible (Table 12.2 on page 12-5). This reaction results in loss of sample and potential for contamination of subsequent samples when using the same crucible.

Heat Source. The traditional heat sources for dry ashing are muffle furnaces or burner flames. Electronic muffle furnaces are recommended for all heating of platinum crucibles because burners produce significant levels of hydrogen gas during combustion, and platinum is permeable to hydrogen gas at elevated temperatures. Hydrogen gas acts as a reducing agent that can result in trace metals becoming alloyed to the platinum.

Microwave ovens have also proved to be quick and efficient when dry ashing plant tissue samples, with results comparable to conventional resistance muffle furnaces (Zhang and Dotson, 1998). The microwave units are fitted with ashing blocks (a ceramic insert) that absorb microwave energy and quickly heats to high temperatures. This, in combination with the microwave energy absorbed directly by the sample, allows for rapid dry ashing of most materials. The units are designed for increased air flow that further accelerates combustion of the samples.

Sample Container. Platinum, zirconium, or porcelain are usually used to form crucibles for dry ashing. Nickel may also be appropriate for some applications (Table 12.2). Platinum generally is recommended when available and is essentially inert and virtually unaffected by most acids. Zirconium and porcelain crucibles are resistant to most acids, are more resistant to HCl, and are significantly less expensive than platinum. Glass and plastic containers should not be used for dry ashing because the elevated temperatures exceed the melting point of these materials.

Crucibles fabricated from ceramic, graphite, and platinum can be used in microwave applications. Quartz fiber crucibles can accelerate the ashing process since this material rapidly cools and allows many sample types to be reweighed in 60 seconds or less after removal from the microwave unit.

Heating Rate. Samples should be dried before dry ashing and placed in an unheated furnace; then, the furnace temperature is gradually increased. The sample should be spread as thinly and evenly as possible on the bottom of the container to allow for its equal heating. To ensure even heating of the sample and to minimize the chance of ignition, the temperature of the furnace is raised slowly. If the sample was previously charred, a rate of approximately 100 °C per hour is typical. This rate is slow enough that small amounts of organic material or water can be removed from the sample without violent reactions. If the sample is not charred and contains a significant amount of organic material, a slower rate may be necessary to control the oxidation of organic material.

Maximum Temperature. The maximum temperature is determined by the sample matrix and the volatility of the elements to be analyzed. Generally, the temperature should be as low as possible to reduce the loss of volatile compounds, but high enough to ensure complete combustion of the sample. A minimum temperature of 450 °C is often used to ensure complete combustion (Bock, 1979). The upper limit for dry ashing is usually determined by the sample container and the elements being analyzed and is generally considered to be 750 °C, but sample-specific conditions may use temperatures up to 1,100 °C. However, in practice, some components that are normally considered to be nonvolatile may be lost at temperatures above 650 °C (Bock, 1979). Ashing aids may be added to samples to accelerate oxidation, prevent volatilization of specific elements, and prevent reaction between the sample and the container. Examples include adding nitrate before drying to assist oxidation and loosen the ash during combustion, adding sulfate to prevent volatilization of chlorides (e.g., $PbCl_2$, $CdCl_2$, NaCl) by converting them to the higher boiling sulfates, and adding alkaline earth hydroxides or carbonates to prevent losses of anions (e.g., Cl^-, As^{-3}, P^{-3}, B). Table 12.3 lists dry ashing procedures using a platinum container material for several elements commonly determined by radiochemical techniques.

Time. The duration required to completely combust a sample depends on the size of the sample, the chemical and physical form of the sample before and after ashing, and the maximum temperature required to ash the sample. In many cases, it is convenient to place the sample in an unheated furnace and gradually raise the temperature during the day until the maximum temperature is achieved. The furnace is then left at the maximum temperature overnight (12 hours). The furnace is allowed to cool during the next day, and samples are removed from a cold oven. This procedure helps prevent sudden changes in temperature that could cause air currents that may potentially disturb the ash. An alternative is to leave the sample at maximum temperature for 24 hours and let the sample cool in the oven the second night to ensure complete combustion of the sample.

The elapsed time for dry ashing samples can be significant (greater than 36 hours), but the actual time required by laboratory personnel is minimal.

TABLE 12.3 — Examples of dry-ashing temperatures (platinum container)

Element	Temperature/Matrix
Cobalt	450–600 °C for biological material; some losses reported due to reactions with crucible; increased volume of sample increases volume of ash and limits loss of sample.
Cesium	400–450 °C for food and biological material; CsCl and $CsNO_3$ begin to volatilize when held at temperatures above 500 °C for any length of time.
Iodine	450–500 °C with an alkaline ashing aid to prevent volatilization; losses reported for temperatures as low as 450 °C even with alkaline ashing aids added; total volatilization >600 °C.
Lead	450–500 °C acceptable for most samples; bone or coal (lead phosphate) may be ashed as high as 900 °C without significant losses; PbO_2 reacts with silica in porcelain glaze at low temperatures; $PbCl_2$ is relatively volatile and nitrate or sulfate ashing aids have been used to good effect.
Plutonium	450 °C with nitric acid ashing aid for biological material, 550 °C for dust on air filters, 700 °C for soil; high temperature leads to adsorption onto carbon particles and incomplete dissolution of ash.
Strontium	450–550 °C for plants, 600 °C for meat, 700 °C for milk and bone.
Technetium	725–750 °C for plants treated with ammonia.
Thorium	750 °C for bone.
Uranium	600 °C for coal, 750 °C for biological material; uranium reacts with porcelain glaze resulting in sample losses.

Source: Bock (1979).
(Note that reducing conditions for platinum containers are given in Table 12.2)

12.3.1.3 Obtaining a Constant Weight

If required, constant weight is obtained by subjecting a sample to repetitive cycles of drying and weighing until a series of weights meets specified requirements. Project-specific planning documents or laboratory SOPs should define the acceptance criteria. For example, in Greenberg et al. (1992), solids are repetitively heated for an hour, then weighed until successive weighings agree within 4 percent of the mass or within 0.5 mg. In the ASTM guidelines for the preparation of biological samples (ASTM D4638), an accurately weighed sample (1 to 2 g ± 0.1 mg, 5 to 10 g ± 1 mg, >10 g ± 10 mg) is heated for 2 hours, cooled in a desiccator, and weighed. Drying is repeated at hourly intervals to attain a constant weight within the same accuracy. The consistent drying of materials from a large sample set may require a qualitative evaluation of change in the sample composition. If a qualitative change occurs the drying method may need to be checked for completeness. One way to do this would be to perform routine dry-to-constant-weight evaluations on separate samples.

Laboratory conditions and handling of the samples by the analyst during sample weight determinations can increase the uncertainty of the final sample mass.

12.3.1.4 Subsampling

Laboratories routinely receive larger samples than required for analysis. The challenge then becomes to prepare a sample that is representative and large enough for analysis, but not so large as to cause needless work in its final preparation. Generally, a raw sample first is crushed to a reasonable particle size and a portion of the crushed material is taken for analysis. This step may be repeated with intermittent sieving of the material until an appropriate sample size is obtained. Then, this final portion is crushed to a size that minimizes sampling error and is fine enough for the dissolution method (Dean 1995; Pitard, 1993).

French geologist Pierre Gy (1992) has developed a theory of particulate sampling that is applicable to subsampling in the laboratory. Appendix F summarizes important aspects of the theory and includes applications to radiochemistry. Some of the important points to remember include the following:

- For most practical purposes, a subsample is guaranteed to be unbiased only if every particle in the sample has the same probability of being selected for the subsample.
- The weight of the subsample should be many times greater than the weight of the largest particle in the sample.
- The variance associated with subsampling may be reduced either by increasing the size of the subsample or by reducing the particle sizes before subsampling.
- Grouping and segregation of particles tends to increase the subsampling variance.
- Grouping and segregation can be reduced by increment sampling, splitting, or mixing.

Increment sampling is a technique in which the subsample is formed from a number of smaller portions selected from the sample. A subsample formed from many small increments will generally be more representative than a subsample formed from only one increment. The more increments the better. An example of increment sampling is the one-dimensional "Japanese slab-cake" method (Appendix F, *Laboratory Subsampling*).

Splitting is a technique in which the sample is divided into a large number of equal-sized portions and several portions are then recombined to form the subsample. Splitting may be performed by a manual procedure, such as fractional shoveling, or by a mechanical device, such as a riffle splitter. A riffle splitter consists of a series of chutes directed alternately to opposite sides. The alternating chutes divide the sample into many portions, which are then recombined into two. The riffle may be used repeatedly until the desired sample size is obtained. Riffle splitters are normally used with free-flowing materials such as screened soils.

Another traditional method for splitting is coning and quartering (Appendix F). Gy (1992) and Pitard (1993) do not recommend coning and quartering because with similar tools and effort, one can do fractional shoveling, which is a more reliable method.

If proper techniques and tools are used and adequate care is taken, samples of the sizes typically encountered in the laboratory can be mixed effectively. However, the effects of mixing tend to be short-lived because of the constant influence of gravity. Heterogeneous material may begin to segregate immediately after mixing.

The method and duration needed to mix a sample adequately depends on the volume and type of material to be mixed. Small volumes can be mixed by shaking for a relatively short time. Large volumes may require hours. Pitard (1993) describes dynamic and discontinuous processes for mixing samples including:

- Mechanical mixing of test tube samples is useful for small sample size and can be performed on many samples at once. Some examples are a pipette shaker with a motor-activated, rocking controlled motion; a nutator mixer with the test tubes fixed to an oscillating plate; and a tube rotator where tubes are attached to a rotating plate mounted at an angle.

- Mechanical mixing of closed containers by rotating about a tumbling axis. A turbula mechanical mixer is an example.

- Magnetic stirrers are commonly used to homogenize the contents of an open beaker.

- V-blenders are used to homogenize samples from several hundred grams to kilogram size.

- Stirrers coupled with propellers or paddles are used to mix large volumes of slurries or pulp.

- Sheet mixing or rolling technique, in which the sample is placed on a sheet of paper, cloth, or other material, and the opposite corners are held while rolling the sample (see ASTM C702 for aggregates).

- Ball and rod mills homogenize as well as grind the sample (see ASTM C999 for soils).

When dealing with solid samples, it is often necessary to grind the sample to reduce the particle size in order to ensure homogeneity and to facilitate attack by reagents. Obenauf et al. (2001) is an excellent resource for information regarding grinding and blending.

For hand grinding, boron carbide mortars and pestles are recommended. For samples that can be pulverized by impact at room temperature, a shatterbox, a mixer-mill, or a Wig-L-Bug™ is appropriate, depending on the sample size. For brittle materials—such as wool, paper, dried plants, wood, and soft rocks—which require shearing as well as impact, a hammer-cutter mill is

warranted. For flexible or heat-sensitive samples such as polymers, cereal grains, and biological materials, cryogenic grinding is necessary. Methods are described below:

- A shatterbox spins the sample, a puck, and a ring inside a dish-shaped grinding container in a tight, high-speed horizontal circle. Within two to five minutes, approximately 100 grams of brittle material can be reduced to less than 200 mesh. Shatterboxes are used typically to grind soils, cement mix, rocks, slags, ceramics, and ores. They have also been used for hundreds of other materials including dried marsh-grass, pharmaceuticals, fertilizers, and pesticides. When used in a cryogenic atmosphere, this approach can be used to grind rubber, polymers, bone, hair, and tissue.

- A mixer-mill grinds samples by placing them in a container along with one or more grinding elements and imparting motion to the container. The containers are usually cylindrical, and the grinding elements are ordinarily balls, but may be rods, cylinders or other shapes. As the container is rolled, swung, vibrated or shaken, the inertia of the grinding elements causes them to move independently into each other and against the container wall, thus, grinding the sample. Mixer-mills are available for a wide-range of sample sizes. The length of time necessary to grind a sample depends on the hardness of the material and the fineness desired in the final product.

- The Wig-L-Bug™ is an example of a laboratory mill for pulverizing and blending very small samples, typically in the range of 0.1 to 1 mL.

- A hammer-cutter mill uses high-speed revolving hammers and a serrated grinding chamber lining to combine both shearing and impact. A slide at the bottom of the hopper feeds small portions of the sample (up to 100 mL) into the grinding chamber. After the sample is adequately pulverized, it passes through a perforated-steel screen at the bottom of the grinding chamber and is then collected. With this approach, dried plants and roots, soils, coal and peat, chemicals, and soft rocks all grind quickly with little sample loss.

- Many analytical samples—such as polymers, rubber, and tissues that are too flexible or susceptible to degradation to be impact-ground at room temperature—can be embrittled by chilling and then pulverized. Samples can be frozen and placed in a traditional grinder, or alternatively, a freezer mill can be used. In a freezer mill, the grinding vial is immersed in liquid nitrogen, and an alternating magnetic field shuttles a steel impactor against the ends of the vial to pulverize the brittle material. Researchers at Los Alamos National Laboratory developed a method of cryogenic grinding of samples to homogenize them and allow the acquisition of a representative aliquant of the materials (LANL, 1996).

When samples agglomerate or "cake" during grinding, further particle size reduction is suppressed. Caking can be caused from moisture, heat, static charge accumulation, the fusing of

particles under pressure, etc. When it occurs, caking is a serious challenge. There are two main approaches to this problem, slurry grinding and dry grinding.

- In slurry grinding, particles are suspended in solution during grinding. Water, alcohol, or other liquids are added to the sample before grinding, and have to be removed afterwards. Slurry grinding is a fairly reliable way of grinding a sample to micron-sized particles, but it is sloppy and time-consuming.

- Dry grinding is often simpler and quicker, but requires careful matching of the technique to the sample. If caking is due to moisture, as in many soils or cements, the sample should be dried before grinding. Grinding aids such as lubricants, antistatic agents, abrasives, and binding agents can also be used. Examples of grinding aids include dry soap or detergent (a lubricant), graphite (an antistatic agent as well as a lubricant), polyvinyl alcohol, phenyl acetate, propylene glycol, and aspirin. For example, propylene glycol (one drop for up to ten grams of sample) is used for laboratory fine grinding of Portland cement and many minerals.

Grinding efficiency can be improved through intermittent screening of the material. The ground sample is placed upon a wire or cloth sieve that passes particles of the desired size. The residual particles are reground and this process is repeated until the entire sample passes through the screen. Sieves with large openings can be used in the initial stages of sample preparation to remove unwanted large rocks, sticks, etc.

The analysis of solid samples from the environment contaminated with radioactivity represents a special challenge. In most cases, the radioactive materials will be from different sources than the solid sample. Thus the contamination of solid samples with anthropogenic sources of radionuclides will result in a non-uniform particle mix as well as a non-uniform size distribution. This further emphasizes the need for unbiased subsampling procedures.

12.3.2 Soil/Sediment Samples

For many studies, the majority of the solid samples will be soil/sediment samples or samples that contain some soil. The definition of soil is given in Chapter 10 (*Field and Sampling Issues that Affect Laboratory Measurements*). Size is used to distinguish between soils (consisting of sands, silts, and clays) and gravels.

The procedures to be followed to process a raw soil sample to obtain a representative subsample for analysis depend, to some extent, upon the size of the sample, the amount of processing already undertaken in the field, and more importantly, the radionuclide of interest and the nature of the contamination. Global fallout is relatively homogeneous in particle size and distribution in the sample, and therefore, standard preparation procedures should be adequate for this application. However, when sampling accidental or operational releases, the standard procedures may be inadequate. Transuranic elements, especially plutonium, are notorious for being present

as "hot-spots" ions (Eberhardt and Gilbert, 1980; Sill, 1975) and great care must be employed so that the subsample taken for analysis accurately represents the total sample. This will depend on the size and the degree of homogeneity. Multiple subsampling, larger aliquants, and multiple analysis may be the only techniques available to adequately define the content of radionuclides in heterogeneous samples. Therefore, it is imperative that the analyst choose a preparation approach appropriate to the nature of the sample.

12.3.2.1 Soils

ASTM C999 provides guidance on the preparation of a homogenous soil sample from composited core samples. The soil samples are dried at 110 °C until at constant weight, ground and mixed in a ball mill, and processed through a U.S. Series No. 35 (500-µm or 32-mesh) sieve. This method is intended to produce a homogeneous sample from which a relatively small aliquant (10 g) may be drawn for radiochemical analyses.

A similar procedure for homogenizing soil samples is given in HASL-300 (DOE, 1997). Unwanted material (e.g, vegetation, large rocks) is removed as warranted, and the sample is dried. If the sample contains small rocks or pebbles, the entire soil sample is crushed to 6.35 mm, or the entire sample is sieved through a 12.7-mm screen. The sample is blended, then reduced in size by quartering. This subsample of soil is processed through a grinder, ball mill, sieve, or pulverizer until the soil is reduced to <1.3 mm (15 mesh equivalent).

Sill et al. (1974) describe a procedure where they dried raw soil samples for two to three hours at 120 °C and then ground the cooled sample lightly in a mortar and pestle. All rocks larger than ¼ inch (6.25 mm) were removed. The sample was charred at 400 °C for two to three hours, cooled and passed though a No. 35 U.S. standard sieve, and then blended prior to aliquanting (10.0 g are taken for the analysis).

12.3.2.2 Sediments

ASTM D3976 is a standard practice for the preparation of sediment samples for chemical analysis. It describes the preparation of test samples collected from streams, rivers, ponds, lakes, and oceans. The procedures are applicable to the determination of volatile, semivolatile, and nonvolatile constituents of sediments. Samples are first screened to remove foreign objects and then mixed by stirring. The solids are allowed to settle and the supernatant liquid is decanted. To minimize stratification effects due to differential rates of settling, the sample is mixed again before aliquanting for drying and analysis.

12.3.3 Biota Samples

ASTM D4638 is a standard guide for the preparation of biological samples for inorganic chemical analysis. It gives procedures for the preparation of test samples of plankton, mollusks,

fish, and plants. The preparation techniques are applicable for the determination of volatile, semivolatile, and nonvolatile inorganic compounds in biological materials. However, different preparation steps are involved for the three classes of inorganic compounds. In the case of nonvolatile compounds, the first step is to remove foreign objects and most of the occluded water. For large samples such as fish, samples are homogenized using a tissue disrupter, blender, or equivalent, and a moisture determination is performed on a one to two gram aliquant. The samples then are dried by heating in an oven, by dessication, by air drying, by freeze drying, or by low-temperature drying using an infrared lamp, hot plate, or a low setting on a muffle furnace. Finally, the samples are dry ashed.

12.3.3.1 Food

The International Atomic Energy Agency offers a guidebook for the measurement of radionuclides in food and the environment, which includes guidance on sample preparation (IAEA, 1989). Additionally, methods are presented in HASL-300 (DOE, 1997) for the preparation of milk, vegetables, composite diets, etc. (Table 12.4). These methods involve dry ashing samples containing non-volatile radionuclides. Initially the samples are completely dried at 125 °C, and then the temperature is raised slowly over an eight-hour period to 500 °C. As the samples are heated, they will reach ignition temperature. It is important to pass through this ignition temperature range slowly without sample ignition. With careful adjustment of the ashing temperature in a stepwise fashion over this eight-hour interval, sample ignition can be avoided. Table 12.4 lists the ignition temperature ranges for various foods. Once through the ignition temperature range, the temperature can be raised more rapidly to 500 °C. The samples can then be ashed at 500 °C for 16 hours. Ignition sometimes cannot be avoided if the sample type contains large amounts of fat. In addition, glowing of carbonaceous material due to oxidation of carbon will be evident during the ashing process. If only a portion of ash is to be used for analysis, it is ground and sieved prior to aliquanting.

TABLE 12.4 — Preliminary ashing temperature for food samples
(Method Sr-02-RC, HASL-300 [DOE, 1997])

Material	Temp (°C)
Eggs	150-250
Meat	Burning
Fish	Burning
Fruit (fresh)	175-325
Fruit (canned)	175-325
Milk (dry)	—
Milk (wet)	175-325
Buttermilk (dry)	—
Vegetables (fresh)	175-225
Vegetables (canned)	175-250
Root vegetables	200-325
Grass	225-250
Flour	Burning
Dry beans	175-250
Fruit juices	175-225
Grains	225-325
Macaroni	225-325
Bread	225-325

12.3.3.2 Vegetation

There are several DOE site references that contain examples of sample preparation for vegetation. Los Alamos National Laboratory (LANL, 1997) recently grew pinto beans, sweet corn, and zucchini squash in a field experiment at a site that contained observable

levels of surface gross gamma radioactivity within Los Alamos Canyon. Washed edible and nonedible crop tissues (as well as the soil) were prepared for analysis for various radionuclides. Brookhaven National Laboratory has also evaluated the effect of its operation on the local environment. Their site environmental report (DOE, 1995) gives sample preparation steps for radionuclide analysis of vegetation and fauna (along with ambient air, soil, sewage effluent, surface water, and groundwater). HASL-300 (DOE, 1997) also describes sample preparation techniques for vegetation samples for a variety of radionuclides.

12.3.3.3 Bone and Tissue

Bone and tissue samples can be dry ashed in a muffle furnace (DOE, 1997; Fisenne, 1994; Fisenne et al.,1980), wet ashed with nitric acid and peroxide (Fisenne and Perry, 1978) or alternately dry ashed and wet ashed with nitric acid until all visible signs of carbonaceous material has disappeared (McInroy et al., 1985).

12.3.4 Other Samples

The category "other" includes such matrices as concrete, asphalt, coal, plastic, etc. The sample preparation procedures applied to soils are generally applicable for the "other" category, except for more aggressive grinding and blending in the initial step. For example, items such as plastic or rubber that are too flexible to be impact-ground at room temperature must be ground cryogenically. They are embrittled by chilling and then pulverized. ASTM C114 describes the sample preparation steps for the chemical analysis of hydraulic cement, whereas ASTM C702 describes the sample preparation of aggregate samples, and is also applicable to lime and limestone products as noted in ASTM C50. Additionally, ASTM D2013 describes the preparation of coal samples for analysis.

12.4 Filters

Filters are used to collect analytes of interest from large volumes of liquids or gases. The exact form of the filter depends on the media (e.g., air, aqueous liquid, nonaqueous liquid), the analyte matrix (e.g., sediment, suspended particulates, radon gas), and the objectives of the project (e.g., volume of sample passing through the filter, flow rate through the filter, detection limits, etc. (see Section 10.3.2, "Filtration").

Filter samples from liquids usually consist of the filter with the associated solid material. For samples with a large amount of sediment, the solid material may be removed from the filter and analyzed as a solid. When there is a relatively small amount of solid material, the filter may be considered as part of the sample for analytical purposes. When large volumes of liquid are processed at high flow rates, filter cartridges often are used. Typically, the cartridge case is not considered part of the sample, and laboratory sample preparation includes removing the filter

material and sample from the cartridge case. Any special handling instructions should be included as SOPs in the planning documents.

Air filters may be particulate filters, which are prepared in the same manner as liquid filters, or they may be cartridges of absorbent material. Filters that absorb materials are typically designed for a specific analysis. For example, activated charcoal cartridges are often used to collect samples of iodine or radon. Silver zeolite cartridges generally are used for sampling iodine isotopes. These cartridges are often designed to be analyzed intact, so no special sample preparation is needed. If the cartridges need to be disassembled for analysis, a special SOP for preparing these samples is usually required.

Homogenization is rarely an issue when preparing filter samples. Typically, the entire filter is digested and analyzed. However, obtaining a representative sample of a filter does become an issue when the entire filter is not analyzed. The planning document should give the details of sample preparation for portions of a filter (e.g., sample size reduction through quartering). Steps such as using tweezers for holding filters and using individual sample bags should be taken to prevent the loss of material collected on the filter during handling and processing.

12.5 Wipe Samples

Wipe samples (also referred to as "swipes" or "smears") are collected to indicate the presence of removable surface contamination. The removable contamination is transferred from the surface to the wipe material. The type of filter (paper, membrane, glass fiber, adhesive backing, etc.) and counting method influence the preparation requirements (Section 10.6, "Wipe Sampling for Assessing Surface Contamination").

Wipes are usually counted directly without additional sample preparation. Wipe samples can be counted directly with a gas flow proportional counter for alpha or beta radioactivity. For gamma-emitting radionuclides, the wipe also can be counted directly. For very low-energy emissions, wipe samples are commonly counted by liquid scintillation (see Chapter 15, *Quantification of Radionuclides*).

When destructive analysis is required, the techniques in Chapter 13, *Sample Dissolution*, and Chapter 14 *Separation Techniques*, should be followed. Some wipes have adhesive backing that can complicate digestion and require more aggressive treatment with acid to dissolve. When counting with liquid scintillation, the compatibility of the processed wipe with the cocktail is an important consideration.

12.6 Liquid Samples

Liquid samples are commonly classified as aqueous, nonaqueous, and mixtures. Aqueous liquids are most often surface water, groundwater, drinking water, precipitation, effluent, or runoff. Nonaqueous liquids may include solvents, oils, or other organic liquids. Mixtures may be combinations of aqueous and nonaqueous liquids, but may include solid material mixed with aqueous or nonaqueous liquids or both.

Preliminary sample measurements (e.g., conductivity, turbidity) may be performed to provide information about the sample and to confirm field processing (see measurement of pH to confirm field preservation in Chapter 11). These measurements are especially useful when there is no prior historical information available from the sample collection site. In addition, this information can also be helpful in the performance of certain radiochemical analyses. In many cases, the results of preliminary measurements can be used to determine the quantity of sample to be used for a specific analysis.

These preliminary measurements typically require little or no sample preparation. However, they should be performed on a separate portion of the sample. This avoids any unexpected degradation of the sample parameters during transport and storage, and allows laboratory analysts to focus on radiochemical analyses. Using a separate aliquant also helps to prevent cross-contamination of samples sent to the laboratory or loss of radionuclides through interaction with field-measuring equipment.

12.6.1 Conductivity

In radiochemistry, conductivity measurements typically are used as a surrogate to estimate dissolved solids content for gross-alpha and gross-beta measurements. Because the preservation of samples with acid prevents the measurement of conductivity, the recommendation is to perform the QC checks for conductivity in the field when the original measurements are performed. If the sample is not preserved in the field, the measurement can be done in the laboratory.

ASTM D1125 is the standard test method for determining the electrical conductivity of water. The method is used for the measurement of ionic constituents, including dissolved electrolytes in natural and treated water.

12.6.2 Turbidity

The presence of dissolved or suspended solids, liquids, or gases causes turbidity in water. Measurement of turbidity provides a means to determine if removal of suspended matter is necessary in order to meet the specifications for liquid samples as given in the plan document.

ASTM D1889 is the standard test method for the determination of turbidity of water and wastewater in the range from 0.05 to 40 nephelometric turbidity units (NTU). In the ASTM method, a photoelectric nephelometer is used to measure the amount of light that a sample scatters when the light is transmitted through the sample. Project planning documents should specify the acceptable turbidity limit for of aqueous samples for direct sample processing without removing solids.

12.6.3 Filtration

The filtration of samples is based on the appropriate plan document that should also give the selection of the filter material to be used. If samples have not been filtered in the field, the laboratory can perform the filtration. Guidance on filtration of liquid samples is provided in Section 10.3.2. However, preservatives should not be added until sample filtration has been performed (if stipulated in the project DQOs). This ensures that insoluble materials in the sample that might be entrained during sample collection do not affect the analytical results.

12.6.4 Aqueous Liquids

Aqueous liquids are a common matrix analyzed by laboratories, and are often referred to as *water samples*. Examples of possible aqueous liquids requiring radionuclide analysis include the following:

- Drinking water;
- Surface water;
- Ground water;
- Soil pore water;
- Storage tank water;
- Oil production water or brine;
- Trench or landfill leachate; and
- Water from vegetation.

For certain samples that are not filtered, inversion is a form of homogenization. Typically, the sample is homogenized by inverting the container several times to mix the sample thoroughly. If there is some air in the container, the passage of air bubbles through the sample will create sufficient turbulence to mix the sample thoroughly with three or four inversions of the sample container. If the sample contains zero headspace (so there is no air in the sample container), the sample should be inverted and allowed to stay inverted for several seconds before the next inversion. Ten to twenty inversions of the sample container may be required to ensure that the sample is mixed thoroughly under zero headspace conditions. Simply shaking the container will not mix the contents as thoroughly as inverting the sample container. Mechanical shakers, mixers, or rotators may be used to homogenize aqueous samples thoroughly.

Filtration and acidification performed in the field is typically the only preparation required for aqueous liquids (Chapter 10). A general discussion concerning preparation of water samples for the measurement of radioactivity is presented in NCRP (1976). PNL/ACL (1992) gives a number of sample preparation methods for various materials, including water samples.

ASTM gives standard test methods for the preparation of water samples for the determination of alpha and beta radioactivity (ASTM D1943 and D1890, respectively). After collecting the water sample in accordance with ASTM D3370, the sample is made radioactively homogeneous by adding a reagent in which the radionuclides present in the sample are soluble in large concentrations. Acids, complexing agents, or chemically similar stable carriers may be used to obtain homogeneity. The chemical nature of the radionuclides and compounds present and the subsequent steps in the method will indicate the action to be taken. Different radiochemical preparation techniques for freshwater and seawater samples are illustrated in EPA (1979) and for drinking water in EPA (1980).

12.6.5 Nonaqueous Liquids

Nonaqueous liquids can be substances other than water such as organic solvents, oil, or grease. Many organic solvents are widely used to clean oil, grease, and residual material from electrical and mechanical equipment. The resulting waste liquid may contain a significant amount of solid material. It may be necessary to filter such liquids to determine (1) if the analyte is contained in the filtrate and is soluble, or (2) if the analyte is contained in the solids and therefore is insoluble. The appropriate plan document should be reviewed to determine if filtration is necessary. ASTM C1234 describes the preparation of homogeneous samples from nuclear processing facilities.

Homogenization of nonaqueous samples is accomplished in a manner similar to that for aqueous samples. Visual inspection is typically used as a qualitative measure of homogeneity in non-aqueous samples. If a quantitative measure of mixing is desired, turbidity measurements can be performed after a predetermined amount of mixing (e.g., every 10 inversions, every 2 minutes, etc.) until a steady level of turbidity is achieved (e.g., 1 to 10 percent variance, depending on the project objectives—see ASTM D1889, *Standard Test Method for Turbidity of Water*).

DOE (ANL/ACL, 1995) evaluated sample preparation techniques used for the analysis of oils. In evaluating the performance of a sample preparation technique, DOE considered the following qualities to be important:

- Thorough sample decomposition;
- Retention of volatile analytes;
- Acceptable analyte recovery;
- Minimal contamination from the environment or the digestion vessel;
- Low reagent blanks; and
- Speed.

One of the preparation methods involved combustion of oil under oxygen at 25 atm pressure (ASTM E926) and another used nitric acid decomposition of the oil in a sealed vessel heated with a microwave (EPA, 1990).

Many nonaqueous liquids present a health hazard (e.g., carcinogenicity) or require special safety considerations (e.g., flammability). Any special handling requirements based on health and safety considerations should be documented in the planning documents.

12.6.6 Mixtures

Some common examples of mixtures that may be encountered by the laboratory are water with lots of total dissolved solids and undissolved solids or water and oil in separate layers. The following sections discuss preparation procedures for these types of mixtures.

12.6.6.1 Liquid-Liquid Mixtures

When aqueous and nonaqueous liquids are combined, they usually form an immiscible mixture, such as oil and water.[1] In most cases, a separatory funnel helps in separating the liquids into two samples. Each sample then is analyzed separately. If, in the rare case, both liquids must be processed together, there is greater difficulty in preparing the combined liquids for analysis. Obtaining a homogenous aliquant is a key consideration in this case. Often times, the entire sample should be analyzed. This approach avoids processing problems and yields the desired result.

12.6.6.2 Liquid-Solid Mixtures

Mixtures of liquids and solids are usually separated by filtering, centrifuging, or decanting, and the two phases are analyzed separately. If the mixture is an aqueous liquid and a solid, and will be analyzed as a single sample, the sample is often treated as a solid. Completely drying the sample followed by dry ashing before any attempt at wet ashing is recommended to reduce the chance of organic solids reacting with strong oxidizing acids (e.g., H_2SO_4, HNO_3, etc.). If the mixture includes a nonaqueous liquid and a solid, it is suggested that the phases be separated by

[1] It is often necessary to determine which liquid is aqueous and which liquid is nonaqueous. Never assume that the top layer is always nonaqueous, or the bottom layer is always aqueous. The density of the bottom layer is always greater than the density of the top layer. Halogenated solvents (e.g., carbon tetrachloride, CCl_4) tend to have densities greater than about 1 g/mL, so they typically represent the bottom layer. Other organic liquids (e.g., diethyl ether, oil, etc.) tend to have densities less than 1g/mL, so they typically represent the top layer. Mixtures of organic liquids may have almost any density. To test the liquids, add a drop of water to the top layer. If the drop dissolves in the top layer, the top layer is aqueous. If the drop settles through the top layer and dissolves in the bottom layer, the bottom layer is aqueous.

filtration and the solid rinsed thoroughly with a volatile solvent such as ethanol or methanol before continuing with the sample preparation process.

In rare cases where a sample contains a mixture of aqueous liquid, nonaqueous liquid, and solid material, the sample can be separated into three different phases before analysis. The sample should be allowed to settle overnight and the liquids decanted. The liquids can then be separated in a separatory funnel without the solid material clogging the funnel. Each liquid should be filtered to remove any remaining solid material. The solid should be filtered to remove any remaining liquid and rinsed with a volatile solvent. This rinse removes any traces of organic liquids to reduce problems during subsequent dissolution activities. The three phases are then analyzed separately. If necessary, the results can be added together to obtain a single result for the mixture after the separate analyses are completed.

12.7 Gases

Sample preparation steps are usually not required for gas samples. Lodge (1988) gives general techniques, including any necessary sample preparation, for the sampling and storage of gases and vapors. The determination of the tritium content of water vapor in the atmosphere is one of the example procedures. ASTM D3442 is a standard test method for the measurement of total tritium activity in the atmosphere. Sample preparation is covered in this test method.

EPA (1989) may be used to demonstrate compliance with the radionuclide National Emission Standards for Hazardous Air Pollutants (NESHAP). This document includes references to air sampling and sample preparation. Table 3-1 of EPA (1989) lists numerous references to radionuclide air sampling and preparation, including Cehn (1979), Eichling (1983), Allied Chemical (1982), and Browning et al. (1978).

12.8 Bioassay

Analyses of bioassay samples are necessary to monitor the health of employees involved in radiological assessment work. Normally these types of samples include urine and fecal specimens.

Urine samples are typically wet ashed with nitric acid (DOE, 1997) or with nitric acid and peroxide (RESL, 1982). Alternatively, there are procedures that co-precipitate the target analytes in urine by phosphate precipitation (Horwitz et al., 1990; Stradling and Popplewell, 1974; Elias, 1997). Fecal samples are normally dry ashed in a muffle furnace (DOE, 1997), or prepared by lyophilization, “freeze drying” (Dugan and McKibbin, 1993).

It is important to note that although ANSI N13.30 indicates that aliquanting a homogeneous sample to determine the activity present in the total sample is acceptable, this standard dictates

that the entire sample should be prepared for analysis and the aliquant taken after the sample preparation has been completed.

12.9 References

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