15 Quantification of Radionuclides

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15.1 Introduction

This chapter presents descriptions of counting techniques, instrument calibration, source preparations, and the instrumentation associated with these techniques, which will help determine what radioanalytical measurement methods best suit a given need. This chapter also describes radioanalytical methods based on nuclear-decay emissions and special techniques specific to the element being analyzed. For example, samples containing a single radionuclide of high purity, sufficient energy, and ample activity may only require a simple detector system. In this case, the associated investigation techniques may offer no complications other than those related to calibration and reproducibility. At the other extreme, samples may require quantitative identification of many radionuclides for which the laboratory may need to prepare unique calibration sources. In the latter case, specialized instruments are available. Typically, a radiochemical laboratory routinely will encounter samples that require a level of information between these two extremes.

A number of methods and techniques employed to separate and purify radionuclides contained in laboratory samples, particularly in environmental samples, are described in Chapter 14 (*Separation Techniques*), and sample dissolution is discussed in Chapter 13 (*Sample Dissolution*). This chapter focuses on the instruments used to detect the radiations from the isolated radionuclides or the atoms from the separations and purification processes.

A typical laboratory may be equipped with the following nuclear counting instrumentation:

- Gas proportional detectors for alpha and beta-particle counting (GP);
- Sodium iodide or high resolution germanium detectors for gamma detection and spectrometry [NaI(Tl) and HPGe];
- Low-energy gamma- or X-ray detectors [HPGe or Si(Li)];
- Solid-state detectors for alpha spectrometry (HPGe); and

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- Liquid scintillation counters suitable for both alpha- or beta-emitting radionuclides (LSC and "Photon Electron Rejecting Alpha Liquid Scintillation"—PERALS®).

It may also have the following equipment, which rely on atom- or ion-counting techniques, molecular methods of analysis, or gamma-ray spectrometry:

- Kinetic Phosphorimeter Analysis (KPA)
- Mass Spectrometric Analyses
  - Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)
  - Thermal Ionization Mass Spectrometry (TIMS)
  - Accelerator Mass Spectrometry (AMS)
- Neutron Activation

15.2 Instrument Calibrations

In this chapter, the term "test source" is used to describe the radioactive material prepared to be introduced into a measurement instrument, and "laboratory sample" is used to identify the material collected for analysis. Thus, a test source is prepared from laboratory sample material for the purpose of determining its radioactive constituents. "Calibration source" means that the prepared source is for calibrating instruments.

The goal of calibration- or test-source preparations is to maximize detection capability while minimizing the introduction of bias and uncertainty into the measurement process. To achieve this goal, calibration sources should be prepared in a manner that provide comparability to test sources with respect to geometry, composition, and distribution of the test-source material within a container or on a source mount. This section will provide an overview of the need for calibration and test-source-correspondence congruence, analyte homogeneity within the source, corrections for self-absorption and scattering of the emitted radiations, and estimation of calibration uncertainty. Specific information and guidance relative to these topics can be found in the subsequent sections of this chapter and in Chapters 13, 14, 19, and 20.

Proper instrument calibrations are essential for the proper identification and quantification of radionuclides in samples. It is important to initially calibrate the instruments with calibration sources that are traceable to a national standards body. Once calibrated, the continuing validity of calibrations should be checked on a periodic basis (Chapter 18, *Laboratory Quality Control*) as specified in a laboratory's quality manual. This is usually done by counting a check source or some secondary calibration source in an instrument and comparing the results to those previously obtained when the instrument was known to be in calibration. The frequency and other aspects of calibrations and verifications may be specified in project planning documents and laboratory quality documents (Chapter 4, *Project Plan Documents*) and in analytical statements of work

(Chapter 5, *Obtaining Laboratory Services*). Section 18.5.6 ("Summary Guidance on Instrument Calibration, Background, and Quality Control") within Chapter18 provide guidance on the frequency of instrument calibration and quality controls checks when requirements are not specified in a statement of work.

15.2.1 Calibration Standards

Instrument calibration should be performed as needed only with sources traceable to a national standards body such as the National Institute of Science and Technology (NIST) in the United States (ANSI N42.23). Calibrations of instruments should be made using certified reference materials of known and documented value and stated uncertainty. These certified reference materials may be supplied by:

- NIST (www.nist.gov) and the New Brunswick Laboratory (www.nbl.doe.gov) directly;
- A calibration-source supplier whose measurement capabilities or manufacturing processes are tested periodically by NIST (complies with ANSI N42.22);
- International Atomic Energy Agency (www.www.iaea.org/programmes/aqcs/main_database.htm);
- Other national standards bodies such as the National Physics Laboratory (NPL) of the United Kingdom (www.npl.co.uk/) and Physikalisch-Technische bundesanstalt (PTB) of Germany (www.ptb.de/); or
- A calibration-source supplier who documents derived materials with stated uncertainty, and whose values has been verified with analytical and measurement systems that have been tested periodically through an unbroken chain of comparisons to the national standards.

The sections on alpha, beta, and gamma-ray detection methods have subsections (15.4, 15.5, and 15.6) that list the nuclides commonly used for instrument calibrations.

15.2.2 Congruence of Calibration and Test-Source Geometry

For nuclear-decay emission analyses, instrument calibrations generally are performed to establish the detector counting efficiency of an instrument. The detector counting efficiency establishes the rate of detected events registered in the detector(s) of a counting system compared to the particle- or photon-emission rate of the source. Counting efficiencies are specific to the radionuclide (emission type or energy), the geometrical relationship between the source and detector, and a number of characteristics of the source material, especially those that affect the absorption and scattering of the radiation. It is common practice to have several different calibrations on a given detector in order to accommodate a number of radionuclides, source-to-detector distances, and counting containers that a laboratory will be required to employ in order to meet project analytical requirements and the variety of media encountered.

Where the efficiency of the detector varies with energy, it may be necessary to perform the calibration at a number of energies and to establish an efficiency curve that covers the range of energies to be encountered. Some radiation detection instruments require other types of calibrations. These are discussed under specific instrument calibrations. Generic issues that govern the conduct of calibrations are discussed below, and specific instrument and test-source considerations are provided in the appropriate sections in this chapter.

To assure that the instrument calibration is unbiased, calibration sources should be prepared and counted in a manner that assures that they are virtually identical to the test sources in all respects that could affect the counting efficiency determination (ANSI N42.23). The geometry, including the size and shape of the calibration source and counting container (beaker, planchet, vial, etc.) and source-to-detector distance and alignment, should be controlled. Backscatter, scattering, and self-absorption present during test-source counting should be duplicated in the calibration process. The density of the calibration source material should be consistent with that of the test sources.

When possible, counting efficiency calibrations should be performed using the radionuclide whose activity is to be determined in test sources. This may not be possible when the radionuclide is not available as a standard reference material or when gross analyses are performed. When the actual radionuclide is not available, an alternate radionuclide may be selected that has the same type of particle or photon emission (α, β, or γ) and approximate energy. When calibrating an instrument in this manner, corrections should be made for any differences between the decay schemes of the two nuclides. Calibrations used in alternate radionuclides should be verified to produce satisfactory results.

If any factor could vary that would significantly affect the counting efficiency determination with respect to measurement quality objectives (MQOs), calibrations should be performed that simulate this variability over the range expected to be encountered during test-source counting. An example is the necessity to develop a self-absorption curve for alpha or beta counting to account for the changing overall counting efficiency because of absorption in the variable source thickness.

The geometry of a test source should be suitable for the counting instrument and—particularly—it should be reproducible. The test-source geometry should remain constant from source to source and with respect to that of the calibration source. This requirement is necessary for performing accurate measurements of all types of radioactivity and for all types of measurement instruments.

15.2.3 Calibration and Test-Source Homogeneity

The calibration and test sources should be prepared in a manner that reduces the nonuniformity of the material. Any deviation from this requirement can lead to biased results and contribute to the overall uncertainty of the laboratory results. Source uniformity is related to the physical nature of the source material. Uniformity of source material relative to its thickness, density (which can be influenced by water content), and homogeneity is important. Nonuniformity can result from a variation in the thickness of the source material over its cross sectional area. If sources are deposited in a nonuniform manner, absorption characteristics will vary from source to source, and acceptable reproducibility may not be achieved.

Variation in source thickness or density can have a particularly large effect in the measurement of alpha-particle activity and, because of their smaller mass and charge, a lesser effect in the measurement of beta-particle activity. Alpha and beta sources that are hygroscopic, once prepared, often are stored in a desiccator to maintain a constant moisture content. Source uniformity is relevant to gamma-ray measurements, not because of the absorption of gamma rays, but because nonuniformity (inhomogeneity) in the distribution of activity throughout a large source changes the effective detection efficiency. For example, if the gamma-ray-emitting radionuclides are concentrated in the portion of the test-source container nearest the detector, the counting efficiency will be greater than if the radionuclides were uniformly distributed throughout the test source. Since measurements of nonuniform sources are not reproducible, radioactive sources of all types should be homogeneous.

Liquid sources are more likely to be homogeneous than are solids, particularly if a reference material has been added to a solid matrix, such as soil. Multiple-phase samples are some of the least homogeneous matrices. Precipitates and multiple-phase liquid samples cannot provide consistent results unless particular measures are taken to ensure their homogeneity (e.g., remove suspended solids, dissolve and recombine, or analyze separately). In order to minimize the overall uncertainty associated with calibration, care should be taken to assure the reference material is thoroughly mixed into the calibration source and distributed uniformly throughout its volume.

15.2.4 Self-Absorption, Attenuation, and Scattering Considerations for Source Preparations

Alpha and beta particles emitted from a source can be scattered by elastic and inelastic collisions with nuclei of the source material, degrading the energy of the particle (self-scatter), or if sufficiently thick, the particle may be absorbed totally by the source (self-absorption). Absorption and scattering within the source material are less pronounced when measuring gamma rays than when analyzing for charged particles.

In order to ensure accurate results, it is important that calibration sources for the determination of counting efficiency and self-absorption corrections are prepared identically in all aspects to the expected test sources. Self-absorption increases with the density of the source material and with the size and charge of the emitted particle. Thus, source thickness is of greater concern for measuring alpha particles than for beta-particle emissions and has even less importance in measuring gamma rays, except for low-energy X- or gamma rays. Thus, sources prepared for alpha-particle measurements should be very thin and uniform for maximum detection capability and reproducibility.

Because of their much smaller mass, beta particles are scattered more readily in the source material than alpha particles. Depending on counter geometry, the measured beta-particle count rate (from sources of equal activity) can increase first as the source thickness increases because of the scattering of electrons out of the source plane and into the detector (Friedlander et al., 1981). At greater thicknesses, self-absorption begins to dominate, and the observed count rate eventually approaches a constant value. When this occurs, the source is said to be "infinitely thick." Counting a source at infinite thickness refers to a measurement made with a source thickness such that further increasing the amount of material added would have no effect on the count rate. The minimum source thickness required for this type of measurement clearly is not more than the maximum range *R* of the particle in the source material, and is often estimated to be 0.75 *R* (Friedlander et al., 1981). A scattering/self-absorption factor can be used, however, to correct the measured count rate (or activity) at a given source mass to that of an infinitely thin source. For beta counting, this factor is proportional to $(1 - e^{-\mu x})/\mu x$, where μ is the linear absorption coefficient for beta particles in the source material, and x is the source thickness (Friedlander et al., 1981).

The moisture content of the source material will affect the density of the source and the absorption characteristics of the source. A change in source moisture content will alter the density and affect the reproducibility of the measurement. Thus, the amount of moisture within the source should be controlled. The following procedures are often followed in order to maintain a low and constant moisture content of sources to be counted.

- Sources prepared by precipitation or coprecipitation may be dried with the filter in the suction-filter apparatus by washing the precipitate with a volatile, nonaqueous solvent. Acetone or ethanol typically is used for this purpose. The filter with source is removed from the filtering apparatus, mounted on a planchet, and stored in a desiccator prior to counting. Alternatively, a wet precipitate on the filter paper may be dried under a heat lamp and mounted on a planchet. In some cases, the wet precipitate is transferred as a slurry to a planchet and dried under a heat lamp.

- Electroplated sources are dried by heating on a hot plate, in an oven, or under a heat lamp.

- Laboratory samples analyzed nondestructively usually are dried prior to measurement in order to control moisture content and help ensure that source characteristics are reproducible.

Laboratory samples, such as soil, biota, and vegetation, usually are dried in an oven. When an even moisture content is important, sources should be maintained in a desiccator.

- Evaporated sources may be flamed and then stored in a desiccator to maintain a constant moisture content.

Another concern in measuring both alpha and beta particles from deposited sources is backscattering: the scattering of particles from the source mount back through the source material and into the sensitive part of the detector. Backscattered beta particles have degraded energies but can have the apparent effect of increasing the counting efficiency. This may seem to have the desired effect of improving the overall counting efficiency, but the percent of backscattered beta particles from the source should remain constant and be consistent with that of the calibration source. The magnitude of backscatter is dependent on the beta-particle energy and the thickness, density, and atomic number of the backing material (Faires and Boswell, 1981). Thus, to reduce the affect of backscatter on beta-particle measurements, the source often is mounted on a thin, low Z (atomic number), low density material, such as aluminum foil or thin organic films (Blanchard et al., 1960). For very precise measurements, a conducting metal film is vaporized onto the organic film so that any electrical charge build up because of the emission of charged particles can be eliminated.

As with absorption, backscatter increases with the thickness of the scattering material up to a saturation level, beyond which it remains constant. The saturation level is reached at a thickness that is about one-third the maximum range of the scattered particle (Faires and Boswell, 1981). Therefore, because of the dependency of backscatter on atomic number and thickness, the backing used for the calibration source should be identical to that used for the source mount. For example, if the presence of hydrogen chloride in the source requires changing from an aluminum planchet to platinum, a platinum backing should also be used in counting the calibration source.

15.2.5 Calibration Uncertainty

There are many parameters that may affect the calibration of an instrument and subsequent test-source results. These parameters may include those associated with the calibration source (certified value and source purity), the source matrix/mount (nuclide and matrix homogeneity, self absorption and backscatter), and the measurement process (variability among calibration and test-source geometry/matrix, source-to-detector positioning, and counting uncertainty). Quantifying the uncertainty of each parameter during an instrument calibration is extremely important and a necessity for calculating realistic measurement uncertainties. The uncertainties (standard uncertainty) in the various parameters affecting the instrument calibration should be propagated to give a combined standard uncertainty (CSU). The CSU should be documented on the calibration certificate or report. A detailed discussion on the propagation of uncertainties applicable to calibration and test-source measurements can be found in Chapter 19. An instrument calibration certificate/document should include an estimate of the calibration uncertainty.

The counting uncertainty associated with a calibration can be reduced by the accumulation of as many counts as practical during the calibration process. The two controllable factors for achieving this are the amount of activity in the calibration source and the counting time allocated for the calibration. As a general rule, sufficient counts should be accumulated to obtain a 1 percent (1 standard deviation) or less net counting uncertainty when calibrating a detector system. The activity of calibration sources should be limited to an amount that will not lead to significant dead-time losses and random summing in the instrument being calibrated. Unaccounted for, dead-time losses and random summing could lead to an efficiency determination that is biased and artificially low. In addition, one should be aware of the potential for detector contamination, this is particularly true for semiconductor detectors used for alpha spectrometry.

15.3 Methods of Source Preparation

This section provide an overview of various commonly used methods used to prepare calibration and test sources. Source preparation methods specific to the measurement of nuclear decay emissions (α, β, γ) and atoms or mass also may be found in Sections 15.4, 15.5, and 15.6. The source preparation categories in this section include electrodeposition, precipitation/coprecipitation, evaporation, thermal volatilization/sublimation, and special source matrices.

15.3.1 Electrodeposition

High-resolution alpha spectrometry requires a very thin, uniform, flat, and nearly massless source mount. Ideally, the source plate to determine alpha activity by a spectrometer would be a flat plate coated with a single layer of radioactive atoms and with no foreign material above the layer to attenuate the alpha radiation (Kressin, 1977). The electrodeposition of radionuclides on a suitable metallic surface from an aqueous solution often can produce thin and uniform test sources that approach these ideal conditions. Thus, this technique is very appropriate for preparing sources of alpha emitters, especially the actinides, which include uranium, plutonium, thorium, americium, and neptunium (ASTM, D3865; DOE, 1997; EPA, 1979). For certain long-lived nuclides, such as ^{232}Th, there may be micrograms of the plated nuclide that can affect the alpha spectrometry resolution.

There are a number of electrolytic cell designs used to electrodeposit radionuclides. The cathode on which the radionuclide deposits is often a thin metal foil or disc, such as platinum or stainless steel, or a metal-coated plastic film (Blanchard et al., 1960). The stirring rod, often made of platinum, serves as the anode of the cell. Deposition of actinides for alpha spectrometry also has been performed in disposable cells constructed from 20-30 mL polyethylene scintillation vials and highly polished stainless-steel planchets (Talvite, 1972). Disposal of the plastic cells prevents cross contamination. The composition of the electrolyte and the parameters applied in the electrodeposition process, such as applied voltage, amperage, current density, and deposition time, are dependent upon the chemical properties of the element, especially its reduction potential, and foreign material that might be present. Thus, "each element requires optimization of its own procedure" (Adloff and Guillaumont, 1993). Deposition time varies from 10 minutes to two hours.

Actinides and similar elements are extremely hydrolytic and can deposit on the glass cell wall or anode or precipitate during deposition (Puphal et al., 1983). Electrodeposition typically is performed, therefore, in electrolytic solutions at low pH (~ 2) to prevent hydrolysis or precipitation. The solution may contain complexing agents (such as fluoride) and chelates (such as ethylene diamine tetraacetate, or EDTA) to minimize the effect of interfering ions, commonly encountered in biological and environmental samples (Puphal and Olsen, 1972). The procedure of Kressin (1972), however, illustrates the admonition of Adloff and Guillaumont cited above: citrate and fluoride, a chelate and complexing agent, respectively, which interfere with the electrodeposition of plutonium and americium in his process. Cable et al. (1994) provide guidance on the optimum conditions for the electrodeposition of actinides, U, Th, Pa, Pu, and Am.

Electrodeposition is applicable to more than 30 radionuclides. The main advantage of electrodeposited sources over other methods of preparation is their extremely thin, uniform deposit of a radionuclide on a plate, which permits high resolution spectrometry; however, the yield is often not quantitative (Adloff and Guillaumont, 1993). Thus, the yield should be monitored with the inclusion of a known quantity of another radioisotope of the same element whenever feasible, which is deposited simultaneously with the analyte. Radioactive sources of the following elements have been prepared successfully by electrodeposition (Blanchard et al., 1960; DOE, 1997; Johnston et al., 1991):

Actinium
Americium*
Antimony
Bismuth
Cadmium
Cobalt
Copper
Curium*
Gold
Hafnium
Indium
Iron
Lead
Neptunium*
Nickel
Plutonium*
Promethium
Protactinium*
Radium*
Silver
Rhenium
Ruthenium
Selenium
Thorium*
Strontium
Tellurium
Thallium
Zinc
Tin
Uranium*
Yttrium

* primarily alpha-counting applications

Particularly important to environmental analysis is a procedure by which virtually all alpha-emitting nuclides—radium through californium—can be determined in soil in any combination on a single sample with few interferences using electrodeposition to prepare the source (Sill et al., 1974).

Although sources of radioactive isotopes of these elements have been prepared by electrodeposition, the technique may not be optimal for certain applications. For various reasons, other methods of test-source preparation may be superior. The presence of other metals sometime interferes, the quality of deposition might be poor (flaking), the recovery can be low, the spectral resolution may be poor, and some procedures require rather elaborate equipment, are expensive, and are time consuming, thus labor intensive (Sill and Williams, 1981; Hindman, 1986). Interference will be caused by several factors: (1) "Any element present in the separated fraction that is able to be electrodeposited will be present on the metal disc"; (2) "Incomplete separation of rare earth elements or incomplete wet ashing for the removal of organic material will decrease the efficiency of the electrodeposition and may result in a thick deposit unsuitable for α-spectrometry measurement"; and (3) "Samples containing more than 20 µg of U are unsuitable for measurement by alpha spectrometry because of the thickness of the deposit" (DOE, 1997). When stainless-steel planchets cannot be used, because of the corrosive nature of the electrolyte, and platinum is required, the method can be quite expensive and time consuming, since recycling of the expensive electrode material requires thorough cleaning to prevent cross contamination.

Test sources of actinides are often prepared by electrodeposition with yields of 90 percent and higher (DOE, 1997; EPA, 1979; Sill et al., 1974; Puphal and Olsen, 1972; Kressin, 1977; Talvite, 1972; Mitchell, 1960; Shinohara and Kohno, 1989). In addition, ^{54}Mn sources have been successfully prepared by the electrodeposition from mixed-solvent electrolytes onto stainless steel planchets (Sahoo and Kannan, 1997). ASTM D3865 provides a standard test method employing electrodeposition for the isotopes of plutonium.

If the redox couple between the metal cathode and the radionuclide to be deposited is positive, the radionuclide will deposit spontaneously. (One side of the disk may be covered with tape or acrylic spray so that deposition occurs only on the other.) That is, it will deposit quantitatively without using any applied potential. Generally, a metal planchet (disk) simply is suspended in the solution that is stirred with a glass stirring rod for a few hours (Blanchard, 1966; DOE, 1997). An example of such a spontaneous reaction between polonium and nickel is given below.

$$\mathrm{Po}^{+4} + 2\,\mathrm{Ni} \rightleftharpoons \mathrm{Po} + 2\,\mathrm{Ni}^{+2} \qquad E^{o} = 0.98 \text{ volt}$$

Polonium also will deposit spontaneously on silver planchets. Po-210 is an important naturally occurring radionuclide that is often included in environmental studies. Spontaneous deposition onto nickel, silver, or copper disks is the preferred technique for preparing ^{210}Po sources for measurement.

A similar technique, called internal electrolysis, is preformed by selecting electrodes that have a large difference in potential. No applied voltage is required for these techniques. A conventional electrolytic cell containing an acid solution of the radionuclide to be deposited may be used. A magnesium (E^{o} = +2.37 volts) strip, for example, is inserted into the electrolyte and connected by an external circuit to the inert metal cathode (planchet), usually platinum. A spontaneous current flows and deposition on the cathode will occur. The conditions at the inert cathode are exactly the same as if an external voltage were applied; however, longer electrolysis times are necessary to achieve quantitative recoveries. Very thin and uniform sources of ^{106}Ru, ^{110}Ag, ^{203}Hg, ^{60}Co,

^{114}In, ^{51}Cr, ^{198}Au, and ^{59}Fe were prepared by this technique, with greater than 96 percent recovery in all cases (Blanchard et al., 1957; Van der Eijk et al., 1973).

15.3.2 Precipitation/Coprecipitation

Another attractive technique used to mount sources for alpha spectrometry is microprecipitation. The classical techniques of precipitation utilize milligram to gram quantities of materials in order to make accurate mass measurements. Since such a relatively large mass of material would have a significant impact on sample self absorption and alpha peak shape, the classical method cannot be used. Typically, 0.1 to1.0 µg of a highly insoluble lanthanide (commonly Nd, Ce, or La) is added to the sample being processed just prior to the final separation of the actinide. This is followed by the addition of hydrofluoric acid to the solution, which causes precipitation of the lanthanide and coprecipitation of the actinide (ASTM D3084 and C1163). A quantitative, micro-pore filter (usually 0.45 µm) is used to separate the precipitate from the supernate. This is necessary because the low mass and concentration of materials forms a precipitate of fine-sized particles. The micro-pore filter allows a slower filtration rate yielding a more uniform deposition of the precipitate in a thin film. Some radiochemists prefer this method to electrodeposition, maintaining that "The procedure is faster and more reliable than those involving electrodeposition and gives consistently higher yields" (Sill and Williams, 1981). Hindman (1986) asserts that the method is "...more rapid, more economical, and more efficient... and yields good decontamination factors, high recoveries, and excellent resolution of the alpha spectra for uranium, plutonium, americium, and thorium."

Although sources prepared by coprecipitation are generally thicker than those prepared by electrodeposition, sufficiently thin sources, even for alpha spectrometry, can be prepared by controlling the amount of precipitate formed. Actinide sources thinner than 0.5 $\mu g/mm^2$ can be prepared by coprecipitation (EPA, 1984a). Thicker sources lead to degraded resolution of the spectra (Hindman, 1983) and sources produced by any technique that are greater than 10 $\mu g/mm^2$ lead to attenuation of alpha particles (Adolff and Guiallaumont, 1993). Typical rare-earth carrier masses for microprecipitated sources range between 25 and 100 µg.

After separations are completed, a slurried precipitate is poured quantitatively through a filtering apparatus collecting the precipitate on a small (e.g., 25 mm dia.) filter. Vacuum filtration often is used to speed the operation and is required for efficient source preparation. With suction applied, the precipitate typically is washed with water and then ethyl alcohol (sometimes acetone) to dry the precipitate. The filter is removed from the filtering apparatus and mounted on a metal planchet, commonly with double-stick tape or a glue stick, and stored in a desiccator to await counting. Self adhesive planchets are also used effectively. Any ^{222}Rn progeny that collects on the filter during the filtration process will decay in a short period of time and not affect the measurement. Samples with radionuclides listed in Table 15.1 have been prepared for quantitative analysis by coprecipitation or precipitation.

TABLE 15.1 — Radionuclides prepared by coprecipitation or precipitation

Radionuclide	Carrier	References
^{32}P*	$MgNH_4PO_4$	a
^{51}Cr*	$BaCrO_4$	a
$^{89/90}$Sr*	$SrCO_3$	a,b,c
^{90}Y*	$Y_2(C_2O_4)_3$	a,b,c
^{131}I*	PdI_2	a,b,c
^{137}Cs*	Cs_2PtCl_6	b
^{147}Pm	$Nd_2(C_2O_4)_3$	a
^{210}Bi*	BiOCl	a
^{226}Ra	$BaSO_4$	b
Th	$Ce(IO_4)_4$	d
Th	LaF_3	a,b
U	LaF_3 (NdF_3)	a,b,f
Np	LaF_3	b
Pu	LaF_3(NdF_3)	a,b,d,f
Am	LaF_3(NdF_3)	a,b,d,f
Cm	LaF_3	b
Th	$Ce(OH)_2$	e
Np	$Ce(OH)_2$	e
Pu	$Ce(OH)_2$	e
Am	$Ce(OH)_2$	e
Cm	$Ce(OH)_2$	e
U*	UF_3	e

a	EPA (1984a)	c	DOE (1997)	e	Sill (1981)
b	EPA (1980)	d	Hindman (1983)	f	Hindman (1986)

* precipitation

It should be emphasized that precipitated sources should be thoroughly dry before measurement, otherwise, self-absorption and scattering will change with time as water evaporates. Also, sources are often covered with a "thin film," such as Mylar™ or Formvar™, to avoid test-source loss and contamination of counting equipment. A thin film may also be made by preparing a solution of colloidion and isoamyl acetate. When a 1:1 solution of this mixture is dispersed on distilled water, a thin film is created that can be placed over the source to prevent contamination. Care should be taken to avoid excessive handling of the source that can change the physical nature of the co-precipitate, producing an uneven thickness.

15.3.3 Evaporation

When a high degree of uniformity of the deposit is not a requirement for the measurement, sources can be prepared by simple evaporation under a heat lamp (Bleuler and Goldsmith, 1952).

This procedure is easy, fast, and adequate for many types of measurements. Water samples for gross alpha and beta screening measurements are often prepared by this method (EPA, 1980; EPA, 1984a). An aliquant of the water laboratory sample is evaporated on a hot plate until only a few milliliters remain. The concentrated solution that remains is then transferred quantitatively with a pipette to a tared stainless-steel planchet, usually 50 mm in diameter, and evaporated to dryness under a heat lamp or in an oven. The planchet, with the evaporated test source, may then be flamed over a burner until dull red to reduce the amount of solids present and to convert the matrix to an oxide. (Insoluble hydroxides, which are often bulky and gelatinous, are prime candidates for ashing, as the oxide formed is much firmer, more uniform, and better defined.) The test source is cooled, weighed, and counted for alpha and beta particles in a proportional counter. Planchets containing evaporated solids may not be flamed if volatile radionuclides (such as Cs, Po, or I) are to be measured.

A commonly encountered problem occurs when most of the solids in an evaporated source deposit in a ring around the edge. Techniques to improve uniformity include the addition of a wetting agent, such as tetraethylene glycol or a 5 percent insulin solution (Shinohara and Kohno, 1989), freeze-drying the sample, or precipitating and settling the active material prior to evaporation (Friedlander et al., 1981; Van der Eijk and Zehner, 1977). The wetting agent is pipetted onto the spot to be covered by the test source, then removed with the pipette. That remaining can be dried under a heat lamp. A known quantity of the laboratory sample is then pipetted onto the spot and dried under a heat lamp. Additional portions of the sample may be added and evaporated.

Sample spreading on the planchet, as it is heated, can result in depositing test-source material on the planchet walls or in the flow of the liquid over the edge of a flat, lipless planchet. Such spreading can be controlled or restricted by outlining the desired source area with a wax pencil. Metal planchets often are constructed with a small lip around their circumference that retains the test source on the planchet. Source spreading during evaporation has been restricted by electrospraying a silica gel suspension onto a thin film to produce a circular pad. The radioactive source solution is dropped onto the circle and evaporated to dryness (Chen et al., 1989).

EPA's (1980) prescribed Method 900.0 for measuring gross alpha and beta radioactivity in drinking water requires that the sample aliquant be limited to what will produce 5 mg/cm^2 of solids on the planchet. Thus, for a 50.8 mm planchet (~20 cm^2), an aliquant containing 100 mg of nonvolatile dissolved solids is the maximum test-source mass.

APHA (1998) emphasizes that some low-energy alpha particles (< 8 MeV) will be stopped if covered by only 4 mg/cm^2 of sample solids. For gross beta-particle counting, a solids thickness of 10 mg/cm^2 or less is recommended. Mills et al. (1991) successfully used water sample conductivity to estimate the concentration of dissolved matter in a water sample. The maximum water sample volume that could be evaporated to meet the EPA solids limit of 5 mg/cm^2 can be calculated from this conductivity measurement.

After a radionuclide in solution has been purified by chemical techniques, i.e., impurities removed, the solution can be transferred to a planchet and evaporated to dryness, as described above. Evaporation of a laboratory sample after purification is used by the EPA to measure ^{228}Ac in the analysis for ^{228}Ra (EPA, 1984a), and sources of thorium, isolated from marine carbonates, have been prepared by evaporation for measurement by alpha spectrometry (Blanchard et al., 1967). Measured count rates of identified radionuclides, for which absorption curves have been prepared, can be adjusted for self absorption in evaporated test sources.

In the case of all dry sources, steps should be taken to prevent solids from exiting the planchet, which will affect the measurement and may contaminate the detector. Sources consisting of loose, dry material, or with a tendency to flake, may be covered with thin plastic or immobilized by evaporating a few drops of a lucite-acetone solution on the solid deposit (PHS, 1967a).

The use of metal planchets for mounting sources is very common for most alpha, beta and gamma counting techniques. A wide variety of planchets made of platinum, nickel, aluminum, and stainless steel can be obtained in various sizes. It is normally not of great importance which type is used as long as several factors are considered (PHS, 1967a). Some factors that should be considered in selecting a planchet are:

- CHEMICAL REACTIVITY. The metal planchet should be inert to the chemicals in the test source, as corrosion of the planchet surface radically alters test-source absorption and geometry characteristics.

- RADIOACTIVITY. The metal comprising the planchet should contain minimal radioactivity and, although this is generally not a serious problem, the planchet background should be measured and corrections applied as necessary for each batch of planchets used.

- SIZE. Two-inch (5 cm) planchets (assuming the detector is at least that large) are often preferred for gross alpha/beta counting to expedite and simplify the evaporation of liquid samples and provide a greater surface area for solid samples, while 1-inch (2.5 cm) planchets are generally used for alpha spectrometry test sources.

- CONFIGURATION. Planchets can be procured in high-walled and low-walled configurations, each with a flat or ribbed bottom. Flat-bottomed planchets are preferred for swipes, air particulate filter samples, and test-source precipitates (or microprecipitates) on filter papers. Ribbed-bottomed planchets, made with a series of raised (ribbed) concentric rings, are typically used for evaporated and chemical precipitate test sources. Precipitates or evaporated residue test sources prepared in a ribbed-bottom planchet that was rotated under a heat lamp tend to be more uniformly distributed compared to sources prepared in a flat-bottomed planchet. The user normally selects a low-walled (3.2 mm wall height) or a high-walled (6.4 mm) planchet depending on the amount of sample to be placed in the planchet and the possibility of the test source creeping up the side of the planchet.

- COST. Platinum planchets should not be used if stainless-steel ones are adequate for the purpose.

It is usually impractical to reuse planchets, and it is generally not recommended. Except for those made of platinum, planchets are inexpensive, and it is not cost effective to clean the planchets and ensure they are not contaminated from the prior test source. Platinum planchets are quite expensive and usually can be cleaned effectively in acid and recounted prior to reuse to ensure that they are not contaminated.

15.3.4 Thermal Volatilization/Sublimation

Vacuum thermal volatilization or sublimation is often used when very thin and uniform sources are required (Blanchard et al., 1957; Friedlander et al., 1981). The disadvantages of this technique are that it is time consuming and the recoveries are often less than 50 percent (NAS/NRC 1962).

The apparatus used to perform this procedure consists of a demountable vacuum chamber that contains either a ribbon filament, often with a shallow trough, or a crucible. The collector plate is usually mounted less than a couple of centimeters away. The source solution is first evaporated onto the filament. As the required temperature of the filament is reached, the trough in the filament tends to collimate the sublimed material onto the collecting plate, increasing the recovery of the sample.

Pate and Yaffe (1956) designed a system for volatilizing radionuclides from a crucible heated with electrical resistance wire. Their design resulted in nearly 100 percent yields on thin collecting films, and made it possible to prepare thin and uniform sources containing a known aliquant of a stock solution (NAS/NRC, 1962).

For very thin sources, it is necessary either to swing the collector plate away or have it covered during initial heating in order to burn off impurities at low temperatures without volatilizing them onto the source mount. Separation from contaminants can be accomplished at the time of source preparation by considering differences in vapor pressure and carefully controlling the temperature (Coomber, 1975). The temperature at which a radionuclide will volatilize depends on the compound in which it exists, e.g., as a hydride, oxide, or halide. Sources have been prepared by thermal volatilization/sublimation for radioisotopes of manganese, chromium, cobalt, rhodium, arsenic, silver, ruthenium, technetium, and many others (Blanchard et al., 1957; Coomber, 1975). See Section 13.5, "Volatilization and Distillation," for further discussion of this topic with examples.

A technique called vacuum evaporation has been used to prepare thin, uniform radioactive sources (Van der Eijk, 1973). Radioactive substances are volatilized by heating a solution in an oven under reduced pressure. Yields, usually rather low, can be improved by using a collimating oven.

15.3.5 Special Source Matrices

15.3.5.1 Radioactive Gases

Gaseous radionuclides most often measured include tritium, both as a vapor (^{3}HOH) and in the elemental form (^{3}H-H), $^{14}CO_2$, and the noble gases, ^{37}Ar, ^{41}Ar, ^{85}Kr, ^{222}Rn, ^{131m}Xe, and ^{133}Xe.

Tritiated water vapor often is collected by condensation from a known volume of air (EPA, 1984b). The air is drawn first through a filter to remove all particulates and then through a cold trap submerged in a dry-ice/alcohol bath. A measured aliquant of the collected water is analyzed by liquid scintillation spectrometry (EPA, 1984b). Tritiated water vapor is sometimes collected by pulling air through a trap containing materials like silica gel (SC&A, 1994) or through a molecular sieve. After collection, the water is distilled from the silica gel, collected, and counted in a liquid scintillation spectrometer.

Gaseous products of oxidation or combustion can be trapped in a suitable media, such as water for ^{3}H, ethanolamine for ^{14}C, peroxide for ^{35}S, and then analyzed by liquid scintillation spectrometry (NCRP, 1978). For this method, it is very important to de-aerate the liquid prior to introducing the gas, and the temperature should be carefully controlled since gas solubilities are temperature dependent (NCRP, 1978), generally inversely proportional to the temperature.

Although not as common nor convenient as liquid scintillation spectrometry, a gaseous radionuclide can be measured in an internal proportional counter as a component of the counter-filling gaseous mixture, usually argon, methane, or an argon-methane mixture (Friedlander et al., 1981; NAS/NRC, 1962; Bleuler and Goldsmith, 1952). For example, tritiated water can be reduced to hydrogen gas ($^3H_2$) by passing water vapor over a bed of hot zinc, and sodium carbonate can be converted to carbon dioxide ($^{14}CO_2$) with an acid (NCRP, 1978). These gases then can be mixed with a counting gas and introduced into the proportional-counter chamber. The major disadvantage of this technique is that it requires a gas handling system.

Concentrations of radioactive noble gases in the effluents of some nuclear facilities are sufficiently high that source preparation simply involves filling an evacuated vessel with the gaseous sample or flushing the vessel sufficiently to ensure a 100 percent exchange (EPA, 1984b). The counting geometries (efficiencies) of the collection vessels can be determined, allowing the collected test sources to be measured directly in the vessels by gamma-ray spectrometry.

For environmental samples collected downwind of a nuclear facility, concentrating the nuclides in the gaseous sample is nearly always required prior to measurement. One example is the “Penn State Noble Gas Monitor,” which was designed to measure low concentrations of radioactive noble gases (Jabs and Jester, 1976; Jester and Hepburn, 1977). Samples of environmental air are compressed in high-pressure bottles to about 20,800 kPa (~ 3,000 psig), providing a sample volume of 2.3 m^3. The inlet air to the compressor passes through a scrubbing train that contains particulate filters and activated charcoal to remove radioiodine. The noble-gas measurement system consists of a spherical 14.69 L, high-pressure, stainless steel vessel with a reentrant well in its base to permit insertion of a Ge detector connected to a spectrometry system. The vessel is surrounded with 5 cm (2 inches) of lead shielding.

There may be occasions when radioiodine is discharged into the atmosphere in several chemical forms. A molecular species filtering system, described by EPA (1990), collects four primary species of iodine on separate cartridges so that they can be measured individually. Air is pulled first through a particulate filter and then through the cartridges placed in series. The normal order of the four cartridges in the filtering system is: (1) cadmium iodide media (CdI_2) for I_2 retention; (2) 4-iodophenol ($I \cdot C_6H_4 \cdot OH$) on alumina for HOI retention; (3) silver-salt (AgX) loaded zeolite or impregnated charcoal for organic iodine retention; and (4) charcoal for a breakthrough monitor. Air, at a calibrated flow, is passed through the system at a rate of 28 to 56 L/min (1–2 ft^3/min). When the sample-collection period is complete, the cartridges are separated, and the activities of each are measured separately by direct counting of the individual cartridges using gamma-ray spectrometry.

15.3.5.2 Air Filters

Air filters containing particulates may be counted directly by a proportional or scintillation detector. Minimal source preparation is normally required for directly counted filters. Some project plans may require that the mass of the particulates on filters be determined. If so required, the filters are weighed on receipt and the net particulate mass calculated by subtracting the mass of an average filter mass or, if pre-weighed, the beginning filter mass.

Actual preparation may be limited to a reduction of the size of the filter and placing it in the appropriate counting container, e.g., a planchet. If the filter is of the correct size and shape to fit directly in a counting container, no preparation may be required. Since particulate matter is deposited on the surface of the filter medium, care should be exercised in handling, particularly during size reduction, so that particulate material is not removed.

Because potentially contaminated material is relatively easily removed from a filter surface, caution is necessary to avoid contamination of detectors. If a filter is to be gamma counted it can remain in the envelope or plastic bag in which it is received for counting. The filter may be placed in such an enclosure if not received in that manner. The size of the filter may be reduced by simply folding the filter to a standard size for gamma counting.

When specific alpha- and beta-emitting nuclide analyses are required (e.g., Pu, U, Th, Am, Sr), the filter media along with the particulate material are usually ashed or dissolved and processed as any digestate by the procedure used in the laboratory.

15.3.5.3 Swipes

Swipes (also called “smears”) are collected to determine the level of removable surface contamination. They are normally taken on a filter or fabric pad by rubbing it over a predetermined surface area, nominally 100 cm^2. Swipes are routinely counted directly in a proportional counter or liquid scintillation counter for alpha and beta activity determination. The size of the swipe is selected to allow it to be placed in a standard-size planchet for counting. If elevated beta radioactivity is identified, a swipe may be gamma counted to determine the contributing radionuclide. Elevated alpha activity may require isotopic analyses for identification.

The precaution given in the previous section concerning contamination for air filters applies as well to swipes. All swipes should be treated as if they are contaminated until proven otherwise. In some cases swipes may be wetted with water or alcohol prior to collection of the sample. When counted in a gas proportional counter, wet swipes should be allowed to air dry prior to counting in order to avoid self-absorption of the alpha and beta particles by the liquid remaining on the swipe (see Section 10.6.1 for further information on swipes). Ensuring that the swipes are dry before counting is important for gross alpha counting measurements. Wet swipes, especially those used to detect removable tritium contamination, normally can be counted using a liquid scintillation without sample preparation. In this instance, it is important that the swipe material be translucent to the radiation emitted by the fluor.

15.4 Alpha Detection Methods

15.4.1 Introduction

When compared to other radioactive particle emissions (such as beta particles), alpha (α) particles are relatively massive. As a result, alpha particles expend their energy over short distances and typically exhibit limited penetration into materials. Alpha particles are also characterized by an intense, high rate of energy loss while passing through matter (see ICRU, 1992, for a discussion of dose equivalents and linear energy transfer). The high rate of energy loss produces dense ionization or intense scintillation which is used to differentiate alpha radioactivity from other types of radiations (beta and photon emissions). Practically, this high rate of loss of energy when passing through matter, requires more stringent sample processing and final sample mounting for alpha counting than is necessary for other types of radioactive counting sources. Examples of direct alpha counting to determine total alpha activity are given in ASTM C799, D1943, and D3084.

Alpha radioactivity normally can be measured by several types of detectors in combination with suitable electronic components. The alpha detection devices most widely used are ionization chambers, proportional counters, solid-state (silicon) semiconductor detectors/spectrometers, and scintillation counters (plastic, ZnS phosphor-photomultiplier tube combination, or a liquid cocktail). The associated electronic components in all cases include high-voltage power supplies, preamplifiers, amplifiers, pulse discrimination, scalers, and recording devices. For spectrometry systems, an analog-to-digital converter (ADC) and a multichannel analyzer (MCA) would be included in the list of components.

Accurate alpha particle measurements will depend on a number of parameters. The most important of these parameters are:

- Test-source geometry;
- Self absorption;
- Absorption in air and detector window;
- Coincidence losses; and
- Backscatter.

These parameters are discussed in detail in the literature (Blanchard et al., 1960; Hallden and Fisenne, 1963) and can be measured or corrected for in many cases by holding conditions constant during the counting of test and calibration sources. In addition, many of these parameters are discussed in Sections 15.2 and 15.3 on the preparation of sources.

Alpha-particle counters typically have low backgrounds and, in many cases, high efficiencies (10 to 100 percent). Because of their short range (about 20 µm) in common materials, only alpha particles from radionuclides in materials very near the sensitive volume of the detector will be detected. Alpha particles from radionuclides in materials farther away from the sensitive volume of the detector, e.g., detector shields, vacuum chambers, source mounts, structural materials, etc., will not be detected. However, some counters are easily contaminated internally and care should be taken to avoid contamination. These include internal gas flow proportional counters and solid-state detectors. Controls should be put in place that minimize the potential for, and detect the presence of, contamination. Solid-state detectors operated in a vacuum may become contaminated because of recoil from sources (Merritt et al., 1956, Sill and Olson, 1970). Some alpha detectors are sensitive to beta radiation (Blanchard et al., 1960; Hallden and Fisenne, 1963). In these cases, electronic discrimination is often used to eliminate or reduce the effect of the smaller resulting voltage pulses because of beta particles. A discussion of alpha-particle attenuation can be found in Sections 15.2 and 15.3.

Alpha calibration standards are available from NIST or a commercial vendor (complying with ANSI N42.22) that supplies NIST-traceable sources. Among the radionuclides available are ^{230}Th, ^{241}Am, ^{235}U, ^{239}Pu, ^{228}Th, ^{238}U, and ^{226}Ra (Table 15.2). Other radionuclides are also available. It is critical that calibration sources be prepared in the same precise geometry and manner as the test sources. The calibration source may be procured as a solution and then prepared in the appropriate counting geometry, or the source may be procured directly in the appropriate geometry, such as an electroplated standard.

TABLE 15.2 — Nuclides for alpha calibration

Purpose	Nuclide	Reference
Specific Nuclide and Gross Alpha	^{239}Pu, ^{241}Am, ^{210}Po, ^{228}Th, ^{230}Th, ^{226}Ra, ^{233}U, ^{235}U, and U_{nat}	ASTM D3648 40 CFR 141.25(a)
Gross Alpha	^{241}Am	EPA ,1980
Gross Alpha	^{241}Am, ^{237}Np, and U_{nat}	ASTM D1943
Gross Alpha	^{241}Am, ^{239}Pu, ^{230}Th, and U_{nat}	APHA (1998), Method 7110

15.4.2 Gas Proportional Counting

The gas proportional (GP) counter is one of the most widely used alpha-particle detection systems. GP counting methods are often referred to as “gross alpha” detection methods because the detector does not differentiate nuclides based on alpha particle energy. GP counters are available in both “windowed” and “internal” (or “windowless”) configurations. Both types of GP counters use a special counting gas during operation. Internal GP counters have the detector configured so that there is no window between the test source and the counting chamber. Although windowless GP counters previously have been considered impractical for routine operations, modern windowless counters have been engineered to optimize detector geometry/efficiency while minimizing contamination. Because the efficiency of these systems can be greater compared to the windowed GP detectors, their use should be considered when determining the appropriate system for alpha particle measurements. Windowed GP counters have a thin membrane (Mylar™ or other special materials) window between the test source and the counting chamber. Windowed GP counters are available commercially with window thicknesses between 0.08 and 0.50 mg/cm^2.

There are several types of commercially available GP counters. These include sequential multiple sample (test source) GP counters and multiple detector single sample (test source) GP counters. Each type of counter can be operated to detect alpha and beta emissions, either separately or simultaneously. Normally, between 50 and 100 prepared test sources can be loaded into a sequential multiple sample (test source) GP counter and counted sequentially for a standard counting interval. A multiple detector unit, also referred to as a “shelf” unit, typically has provisions for four detectors per shelf. These multi-detector units can be “networked” together in groups up to 64 counting chambers.

15.4.2.1 Detector Requirements and Characteristics

As an incident alpha particle enters the sensitive volume of the GP detector, primary ionization occurs through the interaction of the particle with the fill gas. The secondary electrons produced through these interactions are accelerated toward the anode as a result of the bias (volts DC) applied to the system. In proportional counters, the free electrons gain sufficient kinetic energy during acceleration to produce secondary ionization as they migrate toward the positive anode. This effect, known as "gas multiplication," is used to amplify (about 1,000 times) the number of gas ions initially produced and the electrical charge (electrons from ionization process) collected at the anode. As with ionization chambers, the charge collected at the anode (through a resistor-capacitor [RC] circuit) results in a change in the voltage potential and the generation of a voltage pulse. As a result of gas multiplication, the voltage pulse produced is considerably larger than the pulse produced in an ionization chamber. When operated at the correct detector high voltage bias, the magnitude of the voltage pulse produced is proportional to the original number of ion pairs formed by the incident particle.

The most common counting gas used in commercial units is a purified 90 percent argon and 10 percent methane gas mixture referred to as " P-10." However, a mixture of 4 percent isobutane and 96 percent methane, and pure methane, also have been used with success. The operating voltage of a detector using pure methane is nearly twice the operating voltage for P-10 gas. Commercial manufacturers of gas proportional counters recommend a P-10 gas purity specification that limits the concentrations of hydrogen, nitrogen, oxygen, carbon monoxide, carbon dioxide, moisture, ethane and methane. Windowed-type detectors may be a sealed type that has a finite amount of the counting gas in the sensitive volume of the detector or a gas flow type wherein the gas flows continuously through the sensitive volume of the detector. Commercial units typically use a gas flow type detector operating with a flow rate of approximately 50 mL per minute.

Gas proportional detectors generally are constructed of stainless steel, oxygen free/high conductivity (OFHC) copper, or aluminum. Commercial GP counters have detectors with diameters between 25.4 mm and 133 mm. Most commercially available automated GP counters have a detector size of 57.2 mm (2.25 inches). Test-source mounts, normally stainless steel planchets, accommodate test sources of similar diameters and heights up to 9 mm. The manufacturer's specifications for a GP counter of either type should include performance estimates of a background count rate, length and slope of the voltage plateau, and efficiency of counting a specified electrodeposited calibration source, along with the type of gas used in the tests. For a windowed GP counter, the window thickness is important and the user may want to compromise on the thickness for both alpha and beta counting applications. A thin window is needed for counting nuclides having alpha and low-energy beta emissions. Common window thicknesses offered by the manufacturers include 0.08 and 0.50 milligrams per square centimeter. For GP alpha-particle counting, typical values for the important operational parameters are provided in Table 15.3.

One instrument manufacturer has engineered a windowless GP counter available as a sequential multiple sample (test source) or a multiple detector single sample (test source) GP counter. The units available typically have lower alpha background and higher detector efficiency specifications compared to windowed GP counters.

TABLE 15.3 — Typical gas operational parameters for gas proportional alpha counting

Background count rate (57 mm diameter detector)	3–10 counts/hour or 0.83 to 2.8×10^{-3} cps
Length of voltage plateau	300–800 V DC using P-10 gas
Slope of voltage plateau for well-designed detector	1–2.5%/100 V for an electroplated source
Windowless detector efficiency – $\frac{100\times\text{count rate}}{\alpha\ \text{emission rate}}$	49–51% for an electroplated source including backscatter
Windowed efficiency (0.8 – 0.5 mg/cm^2 thickness) – $\frac{100\times\text{count rate}}{\alpha\ \text{emission rate}}$	30–40% for an electroplated source

SHIELDING

The purpose of shielding is to reduce the background count rate of a measurement system. Shielding reduces the background count rate by absorbing some of the components of cosmic radiation and radiations emitted from materials in the surroundings of the measurement system. Ideally, the material used for shielding should itself be free of any radioactive material that might contribute to the background. In practice, this is difficult to achieve as most construction materials contain at least some naturally radioactive species (such as ^{40}K, members of the uranium and thorium series, etc.). However, most alpha detectors are quite insensitive to the electromagnetic components of cosmic and other environmental radiations. In addition, when properly operated, the alpha particle detector or detection system will be insensitive to, or will electronically discriminate against, beta particles. Because of their short range, alpha particles from outside sources will not penetrate the active area of the alpha detector. Therefore, a minimum amount of shielding is necessary for alpha particle GP counting of test sources. However, most low-background GP systems are used for beta-particle measurements as well and, as such, shielding is needed to reduce the beta background count rate.

BACKGROUND

Most of the commercial GP counting systems have passive detector shielding and active cosmic guard (anti-coincidence counting detectors/circuits) systems to reduce a detector's background. However, these background reduction methods are more applicable to beta-particle measurements than to alpha-particle measurements. This is because the short range of alpha particles in common materials (about 20 μm) allows only alpha particles from radionuclides in materials near the sensitive volume of the detector to be detected. To reduce the alpha (and beta) background, the detector manufacturers purposely construct detectors from materials that have a minimum amount of naturally occurring radioactivity, e.g., trace amounts of uranium and thorium.

The alpha particle background for gas proportional counters will depend upon detector size. For some commercial units with a 57.2 mm diameter detector with a 0.08 mg/cm^2 window thickness using P-10 gas, the alpha background count rate is typically under 6 counts per hour (0.1 counts per minute [cpm]). Alpha background count rates of 3 counts per hour (0.05 cpm) may be obtained for commercial GP counters with different detector specifications.

OPERATING VOLTAGE

The operating voltage of a gas proportional counter used in the alpha-particle counting mode depends on the counting gas used, the amplifier and voltage discriminator settings and the mode of alpha particle discrimination—voltage pulse height discrimination or simultaneous alpha and beta particle counting. The configuration of the ionization collection wires within the detector chamber also affects the operating voltage. However, most commercial manufacturers have standardized on a particular configuration. Currently, the most common counting gas used in commercial windowed type GP units is P-10.

Prior to the operation of a gas proportional counter, the operating voltage of the detector must be determined in conjunction with the other operating parameters. Normally, the manufacturer of the unit recommends the voltage discriminator and amplifier gains settings. The user typically places an electroplated alpha source into the counting position and increases the detector bias voltage in discrete 25 or 50 V DC increments while recording the observed source count rate at each voltage setting. Figure 15.1 illustrates a typical voltage response curve for a commercial windowed type gas proportional counter detector using P-10 counting gas and a massless ^{210}Po source (Canberra, 2002). Notice that the count rate levels off after about 500 V DC to form a plateau that extends to about 900 V DC. For most commercial GP units, the slope of this plateau should be 2.5 percent (or less) per 100 volts. For Figure 15.1, the detector operating voltage for alpha counting would be approximately 550 to 600 V DC. Note that on the beta (beta plus alpha) plateau region of approximately 1200 $V_{DC,}$ there is a 35 percent increase in the ^{210}Po count rate. When using the separate alpha plateau then beta (plus alpha) plateau-counting modes, the increase in the alpha-particle count rate on the beta plateau must be determined at the alpha and beta plateau voltages selected during calibration (i.e., determining the ratio of the alpha-particle count rate on the beta plateau to the alpha-particle count rate on the alpha plateau). For test-source measurements, the observed beta-particle count rate must be adjusted for the alpha-particle count rate on the beta plateau by applying a correction factor using this ratio. The observed increase in the alpha count rate on the beta plateau varies

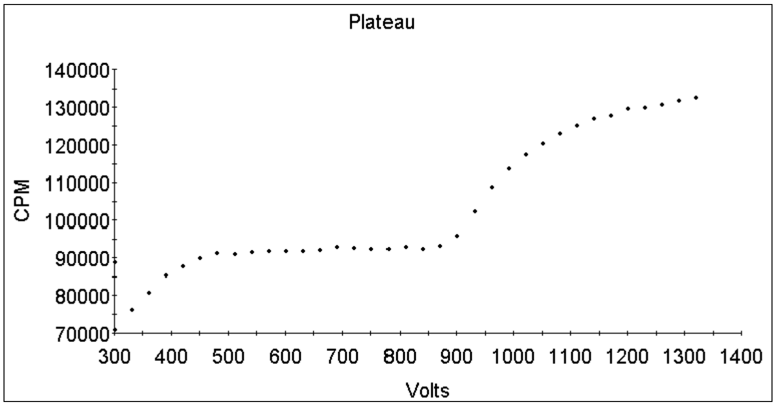

FIGURE 15.1 — Alpha plateau generated by a ^{210}Po source on a GP counter using P-10 gas

according to the alpha emitting nuclide. The difference between the count rates on the two plateaus will be accentuated for nuclides that have both alpha and photon emissions, e.g., ^{241}Am.

For the simultaneous alpha and beta counting mode, the detector operating voltage is located on the beta-particle plateau (Section 15.5.2.1). For this counting mode, the voltage discriminator setting for alpha detection is set so that only a small fraction (less than 1 percent) of the beta detection events will be registered as alpha detection events.

CROSSTALK — REGISTRATION OF BETA PULSES AS ALPHA PULSES

Modern proportional counters are capable of differentiating between alpha and beta interactions in the detector. This is accomplished by identifying the two types of particles based on the resultant voltage pulse heights from their interactive events in the detector. As discussed previously, the interaction of an alpha particle with the counting gas generates substantially more primary ionization events and, thus, a higher resultant voltage pulse compared to a beta particle. Those voltage pulses whose heights exceed an experimentally established alpha voltage discriminator level are registered as alpha counts and those falling below this level are recorded as beta counts. The dynamic range of the voltage separation between the alpha and beta voltage pulses varies by detector design and manufacturer. For some GP counters, depending on the beta particle energy and voltage (pulse) discriminator setting, some small fraction—usually less than 1 percent for a ^{90}Sr/Y ($E_{\beta\max}$ = 2.28 MeV) massless point source counted in the simultaneous counting mode—of the detected beta particles may be recorded as alpha particles. This misclassification of alpha and beta measurement events (counts) is referred to as "crosstalk" or "spillover." The degree of spillover varies according to detector design and GP counter manufacturer.

For some commercial GP counters, crosstalk may occur for both modes of GP counting, i.e., alpha then beta plateau counting and simultaneous alpha and beta counting. For electroplated beta particle sources, the crosstalk is minimum for both counting modes when the voltage (pulse) discriminator is properly set. The beta-to-alpha crosstalk should be evaluated for all applications (i.e., test sources that are massless and not massless).

For both types of counting modes (plateau counting or simultaneous alpha/beta counting), corrections should be made to the alpha-particle count rate to remove the portion contributed by beta particles when significant beta activity is present (greater than 1 percent of the alpha activity). Since the fraction of the beta counts occurring in the alpha channel depends on the beta particle energy and source mass, a crosstalk curve should be developed. The same beta emitting radionuclide selected for the beta particle self-absorption curve should be used for the crosstalk determination. The crosstalk curve would relate the fraction of beta particles counted as alpha particles as a function of source mass. A crosstalk response curve is generated by recording the alpha counts from the beta self-absorption determination at all source masses and plotting the crosstalk fraction (beta count rate in the alpha channel/beta count rate beta channel) as a function of source mass (Section16.4, "Data Reduction on Non-Spectrometry Systems"). Alpha count rates then can be corrected for the influence of the beta particles at all source thicknesses.

15.4.2.2 Calibration and Test Source Preparation

Calibration and test sources for proportional counters are usually prepared by electrodeposition, coprecipitation, or evaporation, as described in Section 15.3. For internal counters, since the source is placed within the detector, care should be exercised in source preparation to avoid the inclusion of chemicals that may react with the detector materials. Likewise, any spillage of source material can result in contamination of the detector.

The absorption of alpha particles in the source material (self-absorption) should be addressed when preparing a test source for counting. Self-absorption is primarily a function of source thickness (t_s) and the range (R_s) of the alpha particles in the source material. For a uniformly thick source, the fraction of alpha particles absorbed by the source increases proportionately to $t_s/2R_s$, when $t_s < R_s$ (NCRP, 1985). Thus, to approach absolute counting in either 2π or 4π counting geometries, test sources should be prepared as thinly and uniformly as possible. Electrodeposited sources provide the most uniform sources for evaluating these parameters.

Another method sometimes used for alpha-emitting test sources in ionization and GP counters is to perform the count at infinite thickness (Sections 15.2 and 15.3). The count rate of a test source at infinite thickness usually is related to the count rate of a calibration source prepared and measured in the exactly the same manner. However, this application is best used when the calibration is for a well known single nuclide source or a source term wherein the multiple nuclide concentration ratios do not vary substantially. The method is less accurate when applied to a mixture of nuclides having different alpha energies and varying concentrations.

Backscatter from alpha sources increases with the atomic number of the backing or source material and with decreasing alpha energy (NAS/NRC, 1962). Scattering of alpha particles from the source material itself is not a significant problem, and scattering from the source backing has only a small affect for very thin sources (NCRP, 1978). When stainless-steel planchets are used, the increase in a count rate because of alpha backscatter is only about 2 percent (PHS, 1967a).

15.4.2.3 Detector Calibration

Gas proportional counters should be calibrated according to their intended use (i.e., nuclide specific or gross alpha measurement applications). Gross alpha measurements, as the name implies, are nonspecific to a given alpha-emitting nuclide or the isotopes of an element (uranium or radium) and typically require no chemical separations or purification steps. The most common applications for gross alpha measures are health physics swipes for contamination surveys, air particulate filter papers from air monitoring programs and evaporated surface or ground waters onto a metal planchet. For gross alpha measurements, the instrument's calibration is related to a reference nuclide, typically one that is specified by a laboratory client, measurement quality objectives or by regulatory requirements. Typical alpha-emitting reference nuclides include ^{241}Am, ^{237}Np, ^{210}Po, ^{239}Pu, ^{228}Th, ^{230}Th, and U_{nat}.

Calibrations for alpha particle measurements can be accomplished for either the alpha plateau counting mode or the simultaneous alpha and beta counting mode. However, for both modes of operation, calibration sources should be prepared in a manner identical to the method used for test-source mounting. This may include massless or electroplated sources, microprecipitated (< 200 µg) sources and low mass (1–125 mg) sources. For accurate results for both counting modes, alpha-particle self-absorption curves and crosstalk corrections should be developed during calibration of the GP counter.

Calibration sources prepared for calibrating counters for a specific nuclide measurement should contain a radionuclide of similar alpha energy and be measured under identical conditions as the test sources to be measured (ASTM D3648). Alpha calibration standards are available from a national standards body such as NIST or as NIST-traceable sources from a commercial vendor that complies with ANSI N42.22. The source may be procured as a solution and then prepared in the appropriate counting geometry, or the source may be procured directly in the appropriate geometry, such as an electroplated standard. See Table 15.2 (Section 15.4.1) for a list of available for alpha-emitting nuclide calibration sources.

The counting efficiency (ε) is determined by counting a calibration source to accumulate sufficient net counts (approximately 10,000) to provide a relative (1σ) counting uncertainty of about 1 percent and dividing the resultant net count rate (cps) by the alpha emission rate of the source (α/s). The alpha emission rate is determined by the source activity (Bq) times the alpha abundance per disintegration:

$$\varepsilon = \frac{\text{Measured Net Count Rate (cps)}}{\text{Bq} \times \text{fractional } \alpha \text{ abundance}}$$

For a nuclide-specific or reference-nuclide counting efficiency, the same equation is used but without the alpha abundance factor. The uncertainty of the detector efficiency factor can be calculated using the methods described in Chapter 19 (*Measurement Uncertainty*).

For health physics swipes and air particulate filter samples (test sources), a calibration source is prepared by spiking an unused filter with the appropriate calibration solution. For health physics swipes, the entire surface of the filter paper may be spiked. However, only the active area of an air filter paper is spiked with the calibration solution. The retainer ring and gasket holding down the filter determines the active area to be spiked. Depending on the filter composition (e.g., glass fiber filter), the filter matrix may cause some wicking of the solution away from the surface. In order to prevent the wicking effect, the surface of the filter may be sprayed with an acrylic lacquer and dried prior to spiking the surface.

Attenuation or self-absorption corrections may be necessary for alpha counting. Attenuation corrections should be made whenever the test-source matrix differs from that of the calibration source. For example, when a gross-alpha analysis is performed on an evaporated water sample of some thickness and an electroplated standard was used for the calibration, attenuation corrections will have to be made. Alpha-particle attenuation corrections generally will be necessary with a test-source density thickness greater than about 1 mg/cm^2.

In cases where finite test-source thicknesses are unavoidable, alpha-source measurements can be adjusted to account for self-absorption (PHS, 1967a). In order to determine the change in counting efficiency as a function of source thickness or mass, a self-absorption curve must be developed. Calibration sources containing a known amount of the radionuclide of interest are prepared in varying thicknesses (masses) and counted. Absorption curves for gross alpha-particle measurements most often are constructed using reference material containing one of the nuclides listed above. The absorption curve is constructed by counting planchets containing varying mass of material but with a known amount (sometimes constant) of added radioactivity. A curve is generated by plotting the efficiency at a given source thickness divided by the efficiency at "zero" thickness versus source mass (mg) or density thickness in µg/cm^2 or mg/cm^2 (NCRP, 1978). Thus, the efficiency relative to the "zero thickness" efficiency can be read directly from this curve for any measured test-source thickness. Test sources prepared for gross measurement are counted in the exact geometry as those used to prepare the absorption curve. The material forming the matrix for the self-absorption calibration source should, when possible, be identical to that expected in the test sources to be analyzed. Based on the test-source mass or density thickness in units of µg/cm^2 or mg/cm^2, the correction factor determined from the absorption curve is applied to the test-source count, yielding the count rate equivalent to an infinitely thin source.

Most radioanalytical laboratories use a more simplified method to generate a self-absorption curve. A self-absorption curve typically is generated by determining the counting efficiency as a function of source mass in milligrams or mg/cm^2 without normalization to the "zero thickness" efficiency. Figure 15.2 illustrates a typical self-absorption curve for ^{230}Th in a dry residue generated from evaporated tap water.

15.4.2.4 Troubleshooting

Various problems may arise when counting calibration or test sources on a GP counter. These may include instrumentation or test-source preparation related issues. Instrumentation related problems should be identified through the instrument's operational quality control checks that include periodic detector response and background measurements. Section 18.5.6 ("Summary Guidance on Instrument Calibration, Background, and Quality Control") within Chapter18 provides the recommended frequencies for these types of quality control (QC) measurements for a GP counter. Instrumentation problems may arise from electronic component failure or changes, a low flow rate of counting gas delivered to the detector, impure or wrong gas mixture,

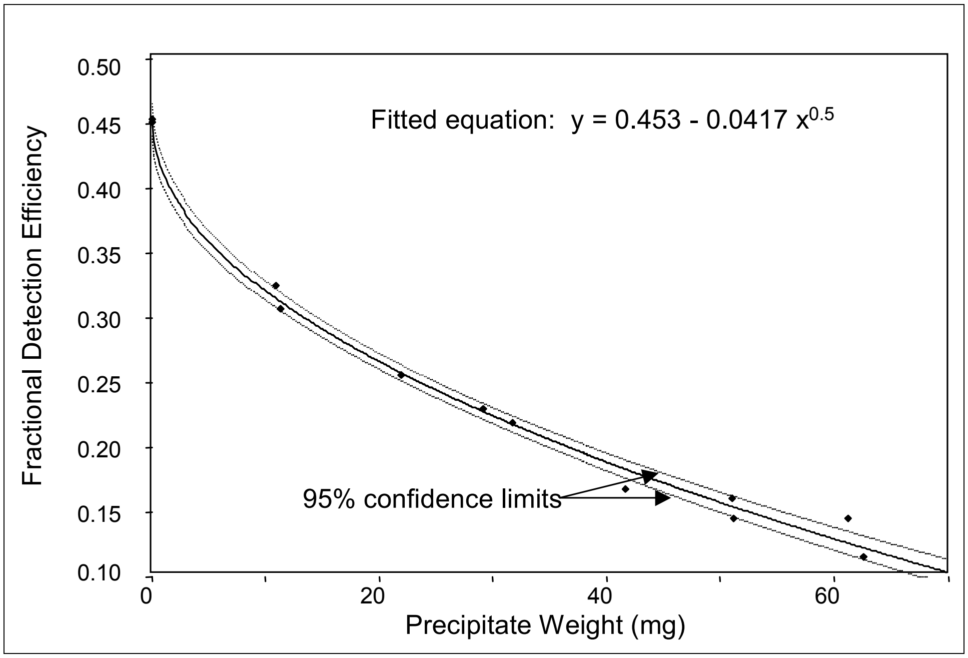

FIGURE 15.2 — Gas proportional counter self-absorption curve for ^{230}Th

malfunction of guard ring, harsh operating environment such excessive temperature and humidity, poor electrical power with excessive noise or radio frequency interference and grounding effects. Identification of an intermittent problem, such as electrical noise, is generally more difficult than identifying a consistent problem such as an instrument component failure. Detector contamination from highly radioactive samples or loose material on a test source (air particulate filters or swipes) may lead to inaccurate results if an increased detector background is not quantified and subtracted from subsequent test-source measurements.

Inaccurate results can occur from the misuse of a specific nuclide detector calibration or if the test sources are prepared differently than the calibration sources. For example, using an alpha self-absorption curve based on a nuclide(s) having a low-energy alpha(s) (e.g., natural uranium) to calculate the activity in test sources containing nuclides of higher alpha energies (e.g., ^{226}Ra plus progeny) may produce inaccurate results. It is important that a laboratory and its client decide cooperatively on the reference nuclide for gross alpha measurements as well as the chemical composition of the calibration sources to generate the self-absorption curve. Some clients may want the laboratory to use the gross alpha reference nuclide that the nationally recognized performance evaluation programs incorporate into their gross alpha test samples.

Inaccurate results also may occur when an alpha detector efficiency factor for a massless calibration source is applied to air particulate and swipe test sources. The magnitude of the inaccuracy depends on many factors affecting alpha self absorption, including the depth of filter penetration by particles, which is a function of flow rate and the type of filter material (e.g., membrane, glass fiber, Teflon®, cotton), and dust or material loading. Dust loading of air filters is a function of the airborne dust concentration, air flow, and sampling duration. For most environmental surveillance programs monitoring airborne contaminants, the air flow and sampling duration are limited to prevent significant and undesired dust loading. When there is minimal dust loading on a filter, such as from short-duration sampling at relatively low flow rates, only a small reduction in the counting efficiency because of alpha self-absorption may be observed. Loysen (1969) indicated alpha self-absorption losses to be about 6 percent for glass and membrane (5 µm pose size) filters used to collect radon progeny, typically in a 20 L sample collected over a 10-minute interval. McFarland (1998) found that air filter and swipe sample results could be "under reported" by applying a detector efficiency factor for electroplated sources to these sample matrices. In the study, the GP detector efficiency for an electroplated ^{241}Am source was 0.485, while the detector efficiency for clean and slightly dirty (5-6 mg) swipe samples was 0.292 and 0.243, respectively. For Mylar®-covered simulated air filters, detector efficiencies of 0.229 and 0.199 were observed for Mylar coatings of 0.5 and 0.85 mg/cm^2, respectively. A discussion and recommendations on the analysis of health physics smear samples by GP counting can be found in ANSI N25.25, Annex B.5.

15.4.3 Solid-State Detectors

Semiconductor detectors used for charged particle spectrometric applications provide many advantages compared with the other alpha detectors. These include good energy resolution, stability or minimal drift in energy response, excellent signal timing characteristics, very thin entrance window to minimize particle energy losses, and simplicity of operation (Knoll, 1979). Solid-state or semiconductor detectors used for alpha counting are essentially solid-state ionization chambers. The ionization of the gas in an ionization chamber by alpha particles produces electron-ion pairs, while in a semiconductor detector electron-hole pairs are produced. The liberated charge is collected by an electric field and amplified by a charge-sensitive amplifier.

There are three technologies used by manufacturers for the production of solid-state alpha detectors made of silicon: diffused junction, surface barrier, and ion-implanted. The detectors can be made partially depleted or totally depleted. These detectors are mostly made of n-type base material. Currently, the majority of semiconductor detectors in use for alpha spectrometric applications are the ion-implanted detector. The semiconductor material must have a high enough resistivity to give the required depletion depth. The depletion depth is the sensitive depth of a detector where charged particles interact with the semiconductor material particle to produce electron-hole pairs and must be thick enough to absorb all of the energy of an alpha particle. The interaction of photons with this thin depletion layer is normally negligible. Since the detector shows a linear response with particle energy, any interactions of beta particles with the detector can be eliminated by electronic discrimination.

When a reverse bias voltage is applied to a semiconductor detector, a leakage current is generated. The leakage current of silicon diodes doubles for every 5.5–7.5 °C rise in ambient temperature. Because the preamplifier high voltage bias resistor adds noise, it is necessarily of high value, typically 100 megaohm. Since a surface barrier detector can have a leakage current in the tenths of microampere, the voltage drop across the bias resistor can be substantial. A couple of degrees rise in the temperature will significantly increase this voltage drop, thereby reducing the voltage at the detector. This bias change can be enough to affect the overall gain of the detector-preamplifier by a substantial amount. The ion-implanted detector, on the other hand, has leakage currents in the nanoampere range and thus does not produce a substantial voltage drop across the bias resistor. The system is therefore not as strongly dependent on temperature.

The semiconductor is of special interest in alpha counting where spectrometric measurements may be made since the average energy required to produce an electron-hole pair in silicon is 3.6 eV and in germanium is 2.96 eV (Gilmore and Hemingway, 1995) compared to the 25 to 30 eV needed to produce an ion pair in a gridded ionization chamber. Consequently, silicon detectors provide much improved resolution and also normally have lower background count rates. In addition, the rise time of a voltage pulse is very fast (~10 ns) and the voltage pulse height does not vary with count rate. (Mann et al., 1991)

15.4.3.1 Detector Requirements and Characteristics

An alpha-particle spectrometry system typically consists of a solid-state detector in a vacuum chamber, high voltage detector bias supply, charge-sensitive preamplifier, amplifier, ADC, and a digital memory storage device. In older systems, the ADC and the digital memory storage device were combined into a multichannel analyzer unit. More recent systems use a computer for the memory storage device. In some multiple detector spectrometry units, the ADC contains a multiplexer to acquire each detector's spectrum and to control the operational aspects of each detector. Alpha-spectrometry systems normally are operated to cover the energy range between 3 and 8 MeV for most long-lived nuclides. However, typical systems can be operated from 0 to 10 MeV. For example, the upper energy range can be extended to10 MeV for quantifying short-lived nuclides such as ^{212}Po and ^{214}Po. An alpha spectrometry system's gain can be selected according to the application and system components but a gain of about 10 keV per channel is common. There are several commercial manufacturers of alpha spectrometry systems, alpha detectors and electronic components.

Four parameters normally are specified when selecting a detector for charged-particle spectrometry. These include resolution, active area, depletion depth, and background. Commercial manufacturers (ORTEC, 2002; Canberra, 2002) have produced a selection of detectors that vary in these four parameters. For most alpha spectrometric applications, a depletion depth in silicon of approximately 100 μm is sufficient. If the detector is used for other charged particle applications (beta or proton), detectors having a depletion depth of 500 μm and greater are available. For alpha particle spectrometry applications, the resolution of a detector increases in a nonlinear fashion as the active detector area increases. Although commercially available detectors are available with an active area between 25 and 3,000 mm^2, a typical alpha-spectrometry detector has a 450 mm^2 active area.

The full-width-half-maximum (FWHM) resolution of an alpha spectrometry system using commercially available detectors depends on several parameters that include; inherent energy resolution of the detector, charge carrier statistics, incomplete charge collection and variations in the energy loss in the dead layer, i.e., entry window thickness. The noise contributions from the nondetector system components to the energy spectrum is minimal for most alpha spectrometry systems.

The quoted resolution specification by a manufacturer is based on an ultra-thin source measured in a vacuum at a source-to-detector distance of 1.5 times the detector's active diameter. Typical detector resolutions, as measured for the 5,486 keV alpha line of ^{241}Am, vary from 15–50 keV for detector areas between 50–2,000 mm^2. For a nominal detector size of 450 mm^2 with a 100 µm depletion depth, a typical detector resolution is about18 to 20 keV. Manufacturers have also produced "ruggedized" ion-implanted contact detectors whose detector surface characteristics permit cleaning in case of contamination. The resolution of these ruggedized detectors is similar to the other detector types or about 20 keV. Some general characteristics and requirements for the detector operation are described below.

OPERATING VOLTAGE

Silicon semiconductor alpha detectors operate at a low reverse bias voltage condition, normally between 50–100 volts DC. The voltage bias supply should be highly regulated to prevent noise and loss of resolution. The polarity of the bias depends on the type of detector, e.g., surface barrier, etc. To avoid possible damage, a voltage bias should not be applied to the detector while exposed to light. Many commercially available multiple detector units have an interlock system for each vacuum chamber that removes the detector bias if the chamber is opened to the atmosphere.

BACKGROUND AND SHIELDING CONSIDERATIONS

Because of their insensitivity to beta and photon radiations, semiconductor alpha detectors with thin depletion depths are not shielded against external background radiations. The depletion depth of an alpha detector is too thin to develop significant pulses from the interactions from cosmic or gamma rays. Without a shielding requirement, multiple alpha detectors can be mounted in close proximity. Multiple detector units typically have eight detectors, each enclosed in separate vacuum chambers

Following manufacture, the background of an alpha semiconductor detector is nearly negligible. Several factors contribute to the low background characteristic. First, the inherent naturally occurring radioactivity in the ultra-pure semiconductor silicon material of the detector is extremely low. Since the surface area of the detector is small and the contact electrodes are extremely thin, there is only a small amount of material that is available to contribute to the detector background. However, only alpha particles from radionuclides in materials near the sensitive volume of the detector will be detected. The detector manufacturers purposely construct detectors from materials that have a minimum amount of naturally occurring radioactivity, such as trace amounts of uranium and thorium. A nominal background specification (ORTEC, 2002) for energies above 3 MeV is less than 1.2 counts per day per cm^2 of active detector area, or less than 24 counts per day for a 450 mm^2 surface area detector. Typical observed backgrounds may range from 8–13 counts per day for an energy window between 3–8.2 MeV. Burnett (1994) has reported a typical background for new Planar Implanted Passivated Silicon (PIPS) detectors of the order of 6 counts per day (0.004 cpm) for a 3 to 8 MeV energy region and about 1 count per day (0.001 cpm) under individual regions of interest of about 300 keV.

VACUUM

In order to obtain the best alpha peak resolution, a solid-state detector is operated in a near vacuum condition to eliminate the alpha-particle energy degradation from interactions with air molecules prior to striking the detector face. In addition, surface barrier detectors are operated (with bias voltage applied) in a near vacuum to prevent damage of the surface layer. (Mann et al., 1991) There are several different vacuum chamber designs manufactured for alpha spectrometry applications. However, all units are light tight and have some type of gasket seal to prevent vacuum degradation. Because of the very thin entry window, the detector is very light sensitive and the bias voltage should not be applied when the detector is exposed to light. (Knoll, 1979). Older single detector chamber units were essentially large stainless steel vacuum bells with provisions for the high voltage bias and signal connectors. More recent vacuum chambers are of a smaller configuration and have several shelves to position the test-source mount at different distances from the detector face. Many commercially available multiple detector units have an interlock system for each vacuum chamber that removes the detector bias if the chamber is opened to the atmosphere.

Traditional silicon surface barrier (SSB) alpha detectors typically are operated under a near vacuum that is less than 500 µm Hg. These systems have bias voltage “cut- outs” to protect the detector if the pressure exceeds this value. The balance of air pressure to protect the detector from recoil contamination and loss of spectral resolution limits the range of pressures under which these detector systems have worked. Vacuum pumps are available to permit detector chambers to reach less than 6.7 Pa (50 µm Hg) and, by continuously running the pump, maintain that level indefinitely. In some vacuum systems, an electronic air pressure sensing device is used to monitor the internal pressure in a chamber and to control the operation of the vacuum pump. The PIPS style alpha detectors can be operated at pressures from 1 to 20,000 µm. Higher pressures prevent recoil contamination. Where recoil is not a concern, the operator can lower pressure to achieve the desired spectral resolution. Burnett (1994) has provided detailed information on the optimum air pressure needed to maintain good spectral resolution and to maintain low detector backgrounds for alpha spectrometry systems.

15.4.3.2 Calibration- and Test-Source Preparation

For best results, the calibration and test sources should be isotopically pure and nearly massless. Some radiochemists prefer test sources that have been electroplated to make a lower mass (Puphal and Olson, 1972), while others prefer preparing test sources using a microprecipitation technique. Microprecipitation as fluorides has been reported with only slight loss of resolution (Sill and Williams, 1981; Hindman, 1983).

Alpha-energy spectra of very high resolution are attainable with semiconductor detectors if the prepared test source is essentially massless, ≤ 1 µg/mm^2 (Herpers, 1986). As the thickness of the test source increases, the spectral energy is degraded because of self-absorption, which broadens the peak and forms a tail on the lower-energy side (Section 16.3.2, "Alpha Spectrometry"). The alpha-energy spectral degradation will increase as the source thickness increases, raising the possibility of overlapping peaks with a loss of spectrum integrity. Thus, it is of utmost importance to prepare very thin and uniform alpha test sources for spectrometry. This may be accomplished by electrodeposition or coprecipitation (ASTM D3084), if reagents are controlled so that only small (microgram) quantities of precipitate are recovered. ASTM D3865 provides a standard method for the electrodeposition of the plutonium isotopes with subsequent counting by semiconductor detectors. For example, in the coprecipitation of actinide test sources for spectral analysis, source thicknesses of 0.4–1 µg/mm^2 (0.04–0.1 mg/cm^2) are achieved routinely, which is quite adequate for producing well-defined alpha spectral peaks (EPA, 1984a). From a practical point-of-view, FWHM resolutions of 53 keV can be achieved with microprecipitates of about100 µg (0.20 µg/mm^2) for nuclides having well-defined and separated alpha peaks. Sill and Williams (1981) have prepared actinides, with the exception of uranium, on a 25 mm membrane filter (0.1µm porosity) with 50 µg of a strongly alkaline solution of EDTA. Resolutions near 70 keV were typical for this microprecitate mass.

15.4.3.3 Detector Calibration

Calibration sources may be prepared by either electrodeposition or coprecipitation. These sources can be prepared by the laboratory or purchased from commercial sources. Because of their durability and stability, electrodeposited calibration sources are often chosen. However, more recent radioanlytical methods are preparing calibration and test sources using coprecipitation that involves microgram quantities of $BaSO_4$, NdF_3, CeF_3, etc. Refer to Chapter 14 for electrodeposition and coprecipitation methods. It is important that the area of deposition be consistent with that of test sources to be counted and that there are no significant impurities present (ASTM D3084). See additional discussion on alpha spectrometer calibrations in Section 16.3.2.

Semiconductor detectors used for alpha spectrometry require both efficiency and energy calibrations. Calibration sources, traceable to NIST, often are prepared with multiple radionuclides so they may be used for both types of calibration (ASTM D3084). Sources containing ^{234}U, ^{238}U,

^{239}Pu, and ^{241}Am have been used for this purpose. When mixed-nuclide calibration sources are used, the average counting efficiency is often calculated using the efficiencies of the individual radionuclides. Some alpha spectrometry analysis programs calculate an average efficiency where the individual radionuclide efficiency is weighted by the uncertainty in its determination. Other radionuclide combinations may be used, but in addition to the requirement for traceability for the disintegration value, the energies of the radionuclides should be known with a high degree of certainty. In selecting an appropriate mixture of radionuclides, one should consider energy range, peak overlap, unresolved secondary alpha peaks, alpha emission abundance, ingrowth of decay progeny, useful life of the source (decay), potential for detector contamination (^{210}Po volatility), nuclide availability, and practicality of preparing the multi-nuclide source.

Calibration or QC sources having volatile radionuclides or extremely high activities should be avoided or their use minimized to prevent contamination.

15.4.3.4 Troubleshooting

A number of factors can influence alpha spectrometry results or cause a detector to malfunction. These include a poor detector chamber vacuum, attenuation or self absorption, detector contamination, and other radionuclide interferences. Attenuation or self-absorption corrections need not be made if constant massless test sources are used for test and calibration source counting. If constant mass cannot be maintained, then spectral degradation adjustments (increase or decrease region-of interest window size) and/or corrections (subtraction of counts from interfering peak) may have to be made in order to produce accurate results. When there is a single peak, or when peaks are well-separated, the region-of interest window size may be increased in order to integrate the entire peak. When peaks begin to overlap because of the degradation in resolution, the region-of interest window for the upper energy peak may be decreased, but the detector efficiency factor must be adjusted accordingly. The spectral interference in the lower energy peak from the widened upper peak must be estimated and removed. These actions generally will increase the relative uncertainty of the analysis.

Some commercially available alpha spectrometry systems have detailed troubleshooting protocols that cover resolution and vacuum leakage problems based on monitoring the leakage current and vacuum during operation. A resolution problem generated by excessive electronic noise can be evaluated by comparing a newly acquired resolution of a pulser peak to the manufacturer's detector specification. A sudden increase in the leakage current of a detector also indicates a problem. An increase in the air pressure in the detector chamber from a defective gasket seal may be sufficient to degrade a spectrum.

Microprecipitation of CeF_3 and NdF_3 require the precipitation in an excess of hydrofluoric acid (HF). In order to prevent damage to a solid-state detector, it is important that all traces of HF be neutralized or removed from the test source before the test source is inserted into the alpha detector chamber. Removal of residual HF involves multiple washes of the microprecipitate after filtration. In addition, a NH_4OH chamber has been used to neutralize residual HF on test sources. If left unchecked, the HF damage is typically progressive over time.

Individual electrical line conditioners or uninterruptible power supplies as well as supplemental air conditioning can be provided in the counting rooms to maintain electrical and environmental stability. Additionally, humidity control is recommended by the detector manufacturers and can be provided easily in most environments. Temperature and humidity may be recorded with a chart recorder.

Detector contamination can also be a problem in some cases and, therefore, detector backgrounds should be checked periodically. Contaminated detectors will have higher background counts. Even when test-source spectra are corrected for the presence of contamination, the higher background results in higher minimum detectable amounts (MDAs). The next section covers detector contamination in detail.

15.4.3.5 Detector or Detector Chamber Contamination

Detector contamination can be a problem, so detector backgrounds should be checked after receipt of the detector from the manufacturer and periodically thereafter (see Section 18.5.6, "Summary Guidance on Instrument Calibration, Background, and Quality Control). Detector contamination may occur quickly or may be a gradual process related to the number of sources analyzed. Even when source spectra are corrected for the presence of contamination, the higher peak background results in a higher minimum detectable activity.

After manufacture, the background for semiconductor alpha detectors is very low, typically ranging from 8 to 17 counts per day (1×10^{-4} to 2×10^{-4} cps) over a 3 to 8 MeV energy range. The detector background may increase after use because of contamination principally from two mechanisms: atom recoil or volatilization of atoms on the test or calibration sources counted in a near vacuum. Recoil contamination takes place when fragments from the test or calibration source travels to the detector and are implanted in the detector surface by the recoil energy imparted to the nucleus of an alpha-emitting atom. The energy of the fragments may be sufficient to implant them in the detector so that they cannot be removed nondestructively. The recoil fragment of the primary alpha-emitting nuclide may be a single decay product or a string of progeny decay products. Since the specific activity is inversely proportional to the half-life for a fixed number of atoms, recoil will produce the most background activity when relatively short-lived progenies are produced. However, if the half-lives in question are very short (up to a few hours), they will decay away quickly enough to be of little concern in alpha spectrometry. Particularly serious are those cases that involve transfer of recoil progeny with half-lives from days to weeks, short enough that a reasonable amount of parent activity will produce a significant amount of recoil contamination and long enough that decay back to normal background levels will require an inappropriately long time. In addition, the effect is chronic: similar recoil-producing test sources counted in the same chamber will produce a long-term build-up of detector background which could eventually become serious.

Some common examples of decay-chains that produce recoil contamination include ^{228}Th, ^{229}Th, and ^{226}Ra. It is important to realize that even beta-emitting nuclides ejected by alpha recoil can contribute to alpha background if they subsequently decay to alpha emitters. For example, the direct progeny of ^{229}Th is ^{225}Ra which decays by beta emission to the alpha producing progeny ^{225}Ac.

The degree and rate of contamination from recoil atoms will vary according to the activity of the source, source-to-detector distance and the frequency of source measurement. The closer the source is to the detector, the more likely contamination will occur. It is strongly recommended that energy and efficiency calibration sources have nuclides that are different from the nuclides measured in the test sources. If this is unavoidable, limit the frequency of usage and the counting time to reduce detector contamination from the calibration sources.

Sill and Olson (1970) minimized the contamination caused by recoil by operating a chamber at a lower pressure equivalent to a 12 μg/cm^2 absorber between the test source and detector and applying a low differential voltage (6 V DC) between the test-source mount and the detector. The authors reported a 1,000-fold reduction in contamination with only a decrease in resolution of 1–2 keV. Burnett (1994) has provided detailed information on maintaining low detector backgrounds for alpha spectrometry systems, including the optimum air pressure needed to maintain a 12 or 16 μg/cm^2 absorber for various source-to-detector distances. Manufacturers have incorporated these concepts into commercially available detector chamber systems.

Contamination of detectors by polonium isotopes, such as ^{210}Po ($t_{½} \approx 138.4$ d), may occur by some other process than alpha recoil. Note that ^{210}Po, the last radioactive member of the ^{238}U decay series, is the daughter of ^{210}Bi, a beta-emitter. The transfer of polonium from a source to a silicon detector has been attributed to "aggregate" recoil and inherent "volatilization" of polonium at low pressure. Whatever the actual mechanism, it is clear that polonium activity is indeed transferred to detectors. Detector contamination by volatilization is a very serious problem with long-lived ^{210}Po and even worse when working with ^{209}Po ($t_{½} \approx 102$ y) as a yield tracer. In order to reduce detector contamination, calibration or QC sources having volatile radionuclides should be avoided or their use minimized when possible.

Manufacturers warn that nonruggedized surface-barrier detectors cannot be cleaned to remove contamination. However, manufacturers have produced certain types of detectors that may be decontaminated. These include the ruggedized detectors and detectors that have ion-implanted contact immediately under the silicon surface. Swabbing the surface with a cotton swab wetted with a chemical cleaning agent followed by blow drying with clean nitrogen gas is the recommended cleaning process for these detectors. A detector chamber may be cleaned by the same process.

15.4.3.6 Degraded Spectrum

A spectrum is considered degraded when the peak resolution has deteriorated from the ideal or desired resolution to the extent that nuclide qualification or quantification difficulties arise. For most analytical methods, a peak resolution of 20 to 70 keV is attainable for electrodeposited sources and microprecipitated mounts. A degraded spectrum may be related to several causes that include: a detector or electronic component problem, accumulation of dirt or film on the detector surface, a poor or degraded calibration- or test-source mount, an excess amount of material on the test or calibration source or a degraded vacuum from a detector chamber leak.

Electronic noise in a spectrometry system, depending on its severity, may lead to poorer resolution and a broadening of alpha peaks. The noisy component (preamplifier, amplifier, bias supply, etc.) of a system may be identified using a pulser, an oscilloscope, or a component replacement process. Detector manufacturers recommend the identification of a noise generated resolution problem by comparing a newly acquired resolution of a pulser peak to the manufacturer's detector specification.

Contamination of a detector surface from dirt or oils from the hand, etc., can lead to the degradation of a spectrum. The severity of the degradation will depend on the extent of the areal contamination and depth of the material.

An air leak from a defective detector chamber gasket seal can increase the detector air pressure sufficiently to degrade a spectrum. However, the air pressure in the chamber usually has to exceed 1 mm Hg before spectral degradation occurs.

Probably the most prevalent cause of a degraded spectrum is from an undesired excess of material that has been electroplated or microprecitated on a calibration- or test-source mount. As the thickness of the test source increases, the alpha spectral energy is degraded because of a self-absorption, which broadens the peak and forms a tail on the lower-energy side. This broadening results in poor resolution and difficulties in resolving peaks in a spectrum. The resolution needed for a given analysis depends on the number and closeness of the alpha peaks expected in the spectrum. In most cases, multiple alpha emitting isotopes or nuclides are electroplated or coprecipitated on the same counting mount. For these cases, a better resolution is needed compared to a simple one peak spectrum. For most microprecipitate/coprecipitate mounting methods, a final mass less than 130 µg is typical. An additional 60–100 µg of material on a mount can degrade an alpha spectrum to the point where peak interference corrections may be necessary depending on the closeness of the peaks. Most laboratories will develop test-source spectrum resolution cutoff values above which a test-source mount will be reprocessed or the sample re-analyzed. It should be remembered that the observed resolution for a spectrum may vary according to the nuclide's alpha emission decay scheme (e.g., the uranium isotopes have multiple alpha emissions that are very close in energies).

Some improvement in the peak resolution will be observed if the source-to-detector distance is increased. However, this results in a lower counting efficiency and, thus, longer counting times to meet a desired detection level.

15.4.4 Fluorescent Detectors

In a scintillation counter, the alpha particle transfers its energy to a scintillator such as zinc sulfide (silver activated). The energy transfer to the scintillator results in the production of light at a wavelength characteristic to the scintillator, and with an intensity proportional to the energy imparted from the alpha particle. In the alpha counter, the scintillator medium is placed in close proximity to the cathode of a photomultiplier tube (PMT) where light photons from the scintillator strike its photocathode, and electrons are emitted. The photoelectrons are passed through a series of dynodes resulting in the multiplication of electrons at each stage of the PMT. After amplification, a typical scintillation event will give rise to 10^7 to 10^{10} electrons, which is sufficient to serve as a signal charge for the scintillation event. The electrons are collected across an RC circuit, which results in a change in potential across a capacitor, thus giving rise to a pulse used as the electronic signal of the initial scintillation event.

The alpha counter size is typically limited by the PMT size, with the most common having a diameter of 51 mm. Two types of systems may be employed. In the first, the phosphor is optically coupled to the PMT and is either covered with a thin (<1 mg/cm^2) opaque window or enclosed in a light-proof sample changer. With the test source placed as close as possible to the scintillator, efficiencies approaching 40 percent may be obtained. The second system employs a bare PMT housed in a light-proof assembly. The test source is mounted in contact with a disposable zinc sulfide disk and placed on the PMT for counting. This system gives efficiencies approaching 50 percent, is associated with a slightly lower background, and less chance of counter contamination.

Other than for analyzing ^{226}Ra, alpha-scintillator detectors have a limited application and are not used routinely in most radioanalytical laboratories. However, a major advantage of alpha scintillation counting is that the test source or mount need not be conducting. However, they are used extensively in remote laboratory locations for health physics applications that involve the measurement of alpha activity on air particulate filters and swipes. Commercially manufactured portable survey detector counting systems are available for these applications.

15.4.4.1 Zinc Sulfide

Silver-activated zinc sulphide is the most commonly used inorganic scintillator for alpha-particle counting. ZnS(Ag) has a wavelength of the maximum photon emission of 450 nm and a decay constant of 0.25 µs (Knoll, 1979). For practical purposes, the preamplifier/amplifier time constants should expect a pulse duration of 10 µs (Watt and Ramsden, 1964). Compared to other inorganic scintillators such as NaI(Tl), ZnS(Ag) has a very high scintillation efficiency.

ZnS is available only as a polycrystalline powder, which limits its application to various detector configurations. In addition, light transmission through thicknesses of 25 mg/cm^2 thickness becomes limited because of the opacity of the multicrystalline layer to its own luminescence (Knoll, 1979).

DETECTOR REQUIREMENTS AND CHARACTERISTICS

An alpha counting system consists of a ZnS(Ag)-phosphor transparent screen and a PMT housed in a light-tight housing coupled to a preamplifier/amplifier/scaler counter. As a precaution, the housing for the PMT should be made with a voltage cutoff switch to remove the high voltage from the PMT when the housing is opened. It is desirable to have a separate screen coated with the ZnS(Ag) rather than coating the PMT with the phosphor. The glass on the PMT has inherent naturally occurring nuclides that may increase the background by as much as a factor of two. Laboratories can fabricate their own detector screens by spraying the ZnS(Ag) phosphor as a pigment onto one side of a Mylar™ film (HASL 300, DOE 1997). ZnS(Ag) may be obtained as a Sylvania Type 130® or Dupont 1101® phosphor. Different batches of ZnS(Ag) may vary in characteristics and inherent background. As such, it is recommended that each batch be tested before use. A thin (clear) Persex® sheet material has been used in addition to the Mylar™. Other techniques for fabricating ZnS(Ag) phosphor screen have been reported by Watt and Ramsden (Watt and Ramsden, 1964).

Previously, phosphor screens were commercially available as discs (24, 49, or 51 mm diameter) or 305 mm wide strips. However, because of the recent low demand for their use, the commercially available source supply for the phosphor screens is limited (vendors can be found by conducting an the Internet search for "ZnS scintillator screens"). ZnS(Ag) screens are commercially available in 216×279 mm sheets and two sizes of discs (47 to 50.8 mm diameter and 38 to 44 mm diameter).

The ZnS(Ag) thickness on the phosphor screen is typically between 8–16 mg/cm^2. Thicknesses greater than 10 mg/cm^2 do not enhance the detection efficiency of the phosphor screen since the alpha particles from most naturally occurring nuclides are absorbed in this thickness (Watt and Ramsden, 1964). In addition, it is most desirable to limit the thickness of the phosphor screen in order to reduce any inherent background from the ZnS(Ag).

In one application for alpha-gamma coincidence counting of the radium isotopes, a small amount of ZnS(Ag) powder was added to a solution of suspended Ba(Ra)SO$_4$, filtered (0.4 μm pore size), and dried. The filter paper was mounted on a 25.4 mm diameter plastic mount, covered with a thin clear Mylar™ sheet, and counted on a PMT. Maximum alpha particle detection efficiency was obtained when the ZnS(Ag) to BaSO$_4$ mass ratio was about 2.4 for a typical final counting mass of about 64 mg, or about 13 mg/cm^2 (McCurdy and Mellor, 1981). This phosphor/test-source configuration has the advantage of a nearly 4π geometry efficiency and a low background.

OPERATING VOLTAGE

The operating high voltage of the ZnS counting system varies according to the size and characteristics of the PMT employed and the voltage discriminator setting of the scaler unit. The operating voltage is determined by developing a voltage versus count rate curve for a calibrated source. Similar to a gas proportional counter, a voltage plateau will be observed after a certain applied voltage. A system having a 89 mm (3.5 inch) diameter PM tube and a plateau length of 200 V DC was reported having a 2–3 percent slope per 100 V DC (PHS, 1967b). The operating voltage is selected at stable point above the knee of the voltage plateau. The voltage plateau will vary according to the PMT size. However, most PMTs for this application will be operated below 2,000 V DC.

SHIELDING

A ZnS(Ag) alpha detection system is normally constructed and operated without shielding from cosmic or terrestrial radiations. The lack of a shielding requirement simplifies the fabrication of a light-tight PMT housing and the cost of the system.

BACKGROUND

In general, the background of an unshielded ZnS(Ag) detector counting system is quite low. For an unshielded thin layer of ZnS(Ag) on a thin plastic disc responding to an energy range of 0.1 to 6 MeV, the background is between one and a few counts per minute. For a 51 mm PMT with the phosphor coupled to the tube, typical background values of 0.006 cps may be obtained. With a disposable phosphor mounted on the test source, a background count rate of 0.003 cps can be obtained.

15.4.4.2 Calibration- and Test-Source Preparation

A source mount shaped like a washer, with one side enclosed with a transparent ZnS(Ag) screen, is an arrangement often used. The test source to be counted is placed in the hole of the “washer,” in contact with the ZnS(Ag) screen. The other side of the test-source mount is sealed, generally with wide transparent tape, securing the test source within the source mount. The test source is then placed on an appropriately sized PMT and counted. Because of the availability of large PMTs, sources up to 5 inches (12.5 cm) in diameter can be prepared for measurement (PHS, 1967a). Thin and thick test sources may be analyzed with a phosphor screen scintillation counter. Infinitely thick test sources have been analyzed for ^{226}Ra and decay products by a scintillation counter (NCRP, 1978). A filter or planchet mount may be used for radiochemical methods that use coprecipitation or precipitation as the final product, e.g., radium isotopes with $BaSO_4$. Because the alpha particle emitted from a source interacts with the phosphor screen, as it does with an internal proportional counter, the description concerning self-absorption and scatter of alpha particles during analysis in a proportional counter (see Section 15.4.2.2 on page 15-25) may be applied to counting source mounts with a ZnS(Ag) scintillation counter. Additional advantages of this counting arrangement are the very low backgrounds that are achievable and the small potential for permanently contaminating the counter, because the zinc sulfide screens can be replaced.

A test source may be prepared by mixing ZnS(Ag) with a precipitate containing the alpha-emitting nuclide. In an application for isotopic radium analysis (McCurdy and Mellor, 1981), a test-source mount was prepared by sandwiching a mixture of $Ba(Ra)SO_4$ precipitate and ZnS(Ag) on a filter paper between two Mylar™ sheets on a Spex™ counting mount. The counting mount was placed on a small PMT and count for alpha activity. This phosphor-test-source configuration can result in almost 100 percent counting efficiency if the precipitate and phosphor mass ratio is properly maintained, and the total test-source mass kept below about 15 mg/cm^2.

15.4.4.3 Detector Calibration

A ZnS(Ag) alpha detection system may have an efficiency for an electrodeposited calibration source of 45 to 50 percent. The considerations related to calibrations discussed for proportional counters (Section 15.4.2.3) apply equally to a scintillation counter calibration. A basic difference between alpha particle scintillation counting and GP counting is the final calibration/test-source mounting scheme. In order to take advantage of the high efficiency of detection, the source mount should be placed against the ZnS(Ag) screen and coupled to the PMT. Only certain mounting schemes permit such source mount configurations. A source/phosphor screen adhered to or inserted into metal planchet typically used for GP counting can be also be used.

15.4.4.4 Troubleshooting

Since the alpha scintillation counting system is relatively simple, problems related to the electronic components are easily evaluated with an oscilloscope. Lack of signal may be from a PM tube failure, loss of detector bias voltage, or a malfunction of a preamplifier or amplifier. Care should be taken to ensure that the PM tube is protected from physical abuse or exposure to the light while operating. Most scintillation counting systems will have an electrical interlock on the detector bias supply that will be activated (removes bias from the detector) when the light-tight PMT housing is opened or removed.

Problems encountered with the preparation of calibration and test sources for alpha particle scintillation counting are similar to those for gross alpha counting by gas proportional counters. Nonuniformity of the phosphor on a scintillation screen as well as the possible variability in the counting efficiency of the individual scintillator screens within a production batch may cause variability in the test-source results.

15.4.5 Photon Electron Rejecting Alpha Liquid Scintillation (PERALS®)

The PERALS spectrometry system combines liquid scintillation counting with pulse shape discrimination to significantly reduce background counts from photo-electrons produced by ambient background gamma rays and to eliminate interferences from beta emitters in the test-source/scintillation cocktail. PERALS® is unique because of its specifically fabricated test-source/detector geometry configuration that uses a silicone oil light-coupling fluid between the PMT face and a test source (10 × 75 mm borosilicate glass culture tubes). McDowell (1992) provides a complete description and some radioanalytical applications of the PERALS system. A 0.5 MeV beta particle and a 5 MeV alpha particle will produce approximately the same amount of light in the scintillator and thus the same voltage pulse height. However, the alpha generated voltage pulses decay much slower than a beta produced voltage pulse. This is because the alpha particle energy deposition takes the fluor to a triplet excited state. Typically, beta particles deposit energy such that the fluor only is excited to the singlet state, which undergoes rapid decay. The de-excitation from triplet state takes about 35 ns. Thus, the beta and alpha pulses can be differentiated. Once the PMT voltage pulses are amplified and shaped, the decay of the light-generated voltage pulse is evaluated, and an analog output pulse is generated that is proportional to the decay of the light produced by the particle. Rejection of the beta–gamma spectrum is accomplished by setting a 10-turn-potentiometer pulse-shape discriminator (PSD) below the alpha spectrum as acquired from the "pulse shape" spectra. In order to reject exceeding large output voltage pulses, a voltage pileup rejection potentiometer is set. The output pulse is fed to a MCA or an ADC/computer combination.

Many laboratories have had success using the PERALS counting system in conjunction with the use of extractive scintillators cocktails that are readily available. Dacheux and Aupiais (1997) presented an evaluation of the PERALS counting system in comparison to typical alpha spectrometry for ^{232}Th, $^{234/238}$U, ^{237}Np, $^{238/239}$Pu, $^{241/243}$Am and $^{244/248}$Cm in aqueous solutions. The authors found that the PERALS extractive scintillator method equaled or bettered detection limits for the nuclides evaluated compared to alpha spectrometric methods.

15.4.5.1 Detector Requirements and Characteristics

PERALS can be a stand-alone unit or mounted into a triple width standard nuclear instrumentation module (NIM). The unit requires an external or optional internal DC power supply (~ mA) for operation with a photomultiplier tube. PERALS also requires an external multichannel analyzer (MCA) or an ADC with computer combination. The PERALS output is connected to the MCA or ADC for spectrometry applications. The unipolor output pulse is less than + 10 V (adjustable) and has a dwell time of 1.5 µs. Typical alpha peak resolution typically is less than 300 keV (FWHM) or about 5 percent when used in conjunction with extractive scintillators formulated for a number of radionuclides of interest. Dewberry (1997) has reported a PERALS system FWHM resolution of 130 keV for uranium analyses using URAEX® extractive scintillator.

OPERATING VOLTAGE

The PERALS NIM module has an optional internal high-voltage power supply that provides bias to the detector. The operating voltage is normally +500 V DC. An external power supply may be used if the power supply can provide 1 mA at the required +500 V DC. Circuitry is provided for both internal and external bias supply options to disable the high voltage from the PMT when the sample chamber is opened.

SHIELDING

As with other alpha particle detectors, there is no need for substantial shielding from cosmic and terrestrial radiations. The PERALS® unit mounts in a standard unshielded NIM or an aluminum case. However, the manufacturer uses “mu-metal” (Ni-Fe-Mo alloy) to shield the PMT from external magnetic interference.

BACKGROUND

The PERALS unit exhibits excellent detector background characteristics. Normally, the detector background of a scintillator for the 4.0 to 7.0 MeV energy range is about 0.00002 cps (0.001 cpm) with high purity extractive scintillators without reagents. For the same energy range, a reagent background is about a factor of ten higher.

As a result of the low background achieved and a detection efficiency near 100 percent, the figure of merit (efficiency^2/background) and minimum detectable activity are better for the PERALS system compared to other types of alpha particle counting units. Typical detection limits for the alpha emitters may range from 0.0005–0.024 Bq/L depending on the sample volume, interferences and counting time of the test source.

DARK ADAPTATION OF SOURCES

Test sources prepared in a recommended extractive scintillator and counted in a PERALS system do not have to be dark adapted prior to the measurements. The liquid scintillation cocktail selected by the manufacturer, (e.g., PBBO* scintillator in toluene) does not have the normal light sensitivity/luminescence characteristics found in other cocktails used by a typical liquid scintillation counting system.

CHANNEL OVERLAP

In a typical commercial liquid scintillation counting system that distinguishes between alpha and

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* 2-(4'-biphenylyl) 6-phenylbenzoxazole

beta particle interactions in a cocktail by voltage pulse height, there may be alpha pulses registered as beta pulses and vise versa. This false registration of the alpha or beta pulses is known as "crosstalk." Normally, crosstalk becomes more severe as the level of quenching of the test-source increases (see Section 15.4.5.4, "Quench"). As a result of the photon-electron rejection circuitry, voltage pulses from beta particles and photon-generated electrons are not registered (less than 0.1 percent) and cannot overlap into the alpha pulse region.

15.4.5.2 Calibration- and Test-Source Preparation

Some actinides (U and Th) and transuranics (Np, Pu, Am, and Cm) have been measured by a procedure that involves extraction scintillation techniques (Passo and Cook, 1994). An extraction agent, e.g., bis(2-ethylhexyl) phosphoric acid (HDEHP), is mixed either with a toluene or a di-isopropylnaphthalene (DIN) based cocktail. The alpha emitting nuclide in an aqueous sample is extracted into an organic extractant–scintillator mixture and counted by the PERALS system.

A manufacturer has combined an organic extractant with a scintillator to produce six cocktails that can be used for a variety of alpha emitting nuclides and counted by a liquid scintillation counter, preferably the PERALS. A specific method for uranium in drinking water using an extractive scintillator and the PERALS system has undergone an interlaboratory comparison study that has been published by ASTM as D6239. The PERALS system had sufficient spectral resolution to resolve the alpha peaks of ^{234}U and ^{238}U and to estimate the ^{234}U : ^{238}U activity ratio. In addition, a ^{232}U yield tracer may be resolved. Duffey et al. (1997) have published a detailed method for the analysis of uranium in drinking water using the PERALS system that includes the results of the ASTM method.

Dacheux and Aupiais (1997), in their evaluation of the PERALS® counting system in comparison to typical radiochemistry: alpha spectrometry for ^{232}Th, $^{234,/238}$U, ^{237}Np, $^{238,\,239}$Pu, $^{241/243}$Am, and $^{244/248}$Cm in aqueous solutions used the extractive scintillators of ALPHAEX $_{\alpha}^{®}$, URAEX $_{\alpha}^{®}$ and THOREX $_{\alpha}^{®}$. The authors provide a sequential method of separating the thorium, uranium, plutonium, americium, neptunium, and curium elements, including the oxidation-reduction steps for proper elemental extraction into the extractive scintillators. A similar study for ^{239}Pu in aqueous solutions using ALPHAEX $_{\alpha}$ and THOREX $_{\alpha}$ was reported by Aupiais (1997). Using the method described, a detection limit of 4.8×10^{-4} Bq/L was quoted for a 24 hour counting interval and a 250 mL sample. Recommendations as to use of tracers for ^{232}Th, $^{234/238}$U, $^{238,/239}$Pu and $^{244/248}$Cm are provided based on the ~ 300 keV alpha peak resolution of the instrument.

Escobar et al., has used the RADAEX $_{\alpha}^{®}$ extractive scintillator cocktail for the analysis of ^{226}Ra in water samples by a typical (non-PERALS) LS counting system (Escobar et al., 1999) for sample volumes greater than 19 mL. The authors followed the manufacturer's recommendations for sample preparation prior to extracting the radium into the extractive scintillator. Sample dissolved radon interference, which is extracted with the radium, was eliminated by heating and stirring the samples for one hour at 60 °C. Accurate results were obtained for ^{226}Ra concentrations in the range of 0.38–2.36 Bq/L in the presence of ^{230}Th and ^{210}Po added interferences. A detection limit of 0.024 Bq/L was quoted for a one liter sample and a 12,000 s counting time.

In addition to the use of PERALS® for the analysis of the long-lived alpha emitting radionuclides in water, other reported applications include high-level waste samples (Dewberry et al., 1998) and airborne uranium (Metzger et al., 1997). Additional references to radioanalytical methods may be obtained from the manufacturer.

15.4.5.3 Detector Calibration

The settings and calibration of a PERALS unit are established by the manufacturer prior to delivery. The calibration is performed using a ^{226}Ra reference source (with cocktail) so that the 6 MeV ^{218}Po alpha particle produces a 6 volt output pulse for input into an analog-to-digital convertor/computer or multichannel analyzer. A detection efficiency of about 99 percent and a FWHM resolution less than 300 keV can be obtained for most applications when calibrated. If a tracer is to be used, the alpha energy of its emission should be sufficiently different from the alpha energy of the nuclide of interest to prevent peak interferences requiring corrections, e.g., greater than 700 keV.

15.4.5.4 Quench

Two types of quenching may be encountered in liquid scintillation counting: chemical or color quenching. Color quenching results in a reduction of the scintillation intensity (as seen by the photomultiplier tubes) because of absorption of the fluor scintillation by colored materials present in the cocktail. This results in fewer photons per quanta of particle energy reaching the PMT and a reduction in counting efficiency. Chemical quenching results in a reduction in the scintillation intensity because of the presence of materials in the scintillation solution that interfere with the process leading to the production of light resulting in fewer photons per quanta of particle energy and a reduction in counting efficiency.

In order to minimize the effects of oxygen quenching, the test-source/scintillation-cocktail combination is sparged with toluene-saturated argon. The manufacturer has developed methods or recommends methods that minimize color quenching of the test sources. The ferric ion is a known color-quenching agent (also for the standard LSC and LS cocktails) that shifts the energy spectrum to a lower energy. A yellow test-source color exhibits the most color quenching. Removal of the Fe^{+3} ion or reducing it to Fe^{+2} (e.g., addition of ascorbic acid) prior to the addition of the extractive scintillator to the sample is recommended. The Fe^{+2} ion is not extracted into the extractive scintillator.

In order to determine the extent of any color quenching, a test-source spectrum should be compared to a spectrum obtained from spiking the extractive scintillator with the nuclide of interest.

15.4.5.5 Available Cocktails

Currently, six proprietary extractive scintillators are available to the user for analyzing the more important long-lived naturally occurring or manmade alpha emitting nuclides. The commercially available extractive scintillators include: ALPHAEX$_{\alpha}^{®}$, POLEX $_{\alpha}^{®}$, RADAEX $_{\alpha}^{®}$, THOREX $_{\alpha}^{®}$, and URAEX $_{\alpha}^{®}$. In addition to the above elements, the extractive scintillator RADON $_{\alpha}^{®}$ also has been developed for radon. The extractants used usually have distribution coefficients greater than 1,000. The quantitative recovery of a nuclide in a test solution will depend on both the distribution coefficient and the volume ratio of extractive scintillator to aqueous solution. The use and selection of the extractive scintillator is based on the valence state of the nuclide in the test solution. Controlled aqueous ionic phase conditions must be established to ensure maximum nuclide extraction and unquenched counting conditions. These conditions vary considerably from an acidic media, an acidic sulfate media, or a basic nitrate media.

15.4.5.6 Troubleshooting

The manufacturer has provided a troubleshooting section within the instrument instruction manual that primarily deals with the electronic aspects and setup of the PERALS$^{®}$ spectrometer. In addition, the manual contains several sections on sample preparation, radiochemical procedures, alpha-emitting nuclide measurements, coincidence measurements and theory of operation. Not all of the items discussed in Section 15.5.3.4 on liquid scintillation counting troubleshooting apply to PERALS$^{®}$ because of its uniqueness (e.g., LS cocktail dark adaption). However, certain aspects of LS sample quenching apply to both applications even though sparging of the test-source/LS cocktail with toluene-saturated argon is unique to PERALS. Specific information on troubleshooting of the procedures and instrumentation can be obtained from the manufacturer.

15.5 Beta Detection Methods

15.5.1 Introduction

Radioactive decay by beta particle emission is generally accompanied by one or more gamma-ray emissions; the latter normally is much easier to identify and quantify. Beta-particle counting typically is more difficult, because of the additional source preparation and associated complications resulting from the effects of backscatter, scattering, and absorption in the source material (NAS/NRC, 1962). Since beta particles are not emitted monoenergetically, there is additional difficulty in obtaining quantitative measurements. Guidance on beta particle counting can be found in industry standards (ASTM D1890; D3648; E1329) and publications (NCRP, 1978; Knoll, 1989; Lapp and Andrews, 1964; Price, 1989; PHS, 1967a; Mann et al., 1991; Wang and Willis, 1965; Watt and Ramsden,1964).

Accurate beta-particle measurements will depend upon the degree and extent to which the various parameters that affect the measurement process under considerations are evaluated. For beta particle counting, the items that should be considered include:

- Beta-particle energy or energies, including conversion electrons;
- Radiation detector characteristics;
- Material and geometry (including source-to-detector distance) of the final source mount;
- Form and thickness of final source for analysis; and
- Radionuclide purity of final source.

For certain beta-detection methods, beta-particle attenuation in the air/detector window, self absorption and backscatter corrections to the detector efficiency may be necessary depending on the beta-particle energy, detection system and final source form. Various beta-detection systems, such as liquid scintillation, have been developed to minimize the need for such corrections but these systems may have characteristics that require other type of detector efficiency corrections, e.g., color or chemical quenching. The potential of detector contamination from test-source measurements is a function of the type of detector used and the stability of the final test-source composition. The inherent beta-particle background of the various detection systems should be evaluated and its contribution removed from the test-source measurement result. Many of these items are discussed in Sections 15.2 and 15.3 on the preparation of sources.

The radiation detectors used for beta-particle measurements include an end window Geiger-Mueller tube, gas proportional chamber, liquid scintillation counter, plastic scintillators, and solid-state detectors. Each of these detectors is discussed in subsequent subsections. The end window Geiger-Mueller tube, plastic scintillators, and solid-state detectors have limited laboratory applications for beta-particle detection. Since the end-window Geiger-Mueller tube and gas proportional counters have similar characteristics and operational requirements, these two beta-particle detectors are discussed in the same subsection.

“Gross” beta counting of evaporated samples, wherein a multitude of beta-emitting radionuclides may exist, is typically used for screening of water samples. The application of such methods may be targeted for a specific radionuclide or a category of radionuclides, such as the naturally occurring nuclides or a specific radionuclide in a facility effluent. However, extreme caution should be applied to the interpretation and use of such results without a full specific radionuclide characterization of the water source under investigation. This type of analysis is to be considered “gross” and, in most cases and for a variety of sound technical reasons, the gross measurement result does not equal the sum of the radionuclides contained in the sample.

When specific radiochemistry is performed the beta-emitting radionuclide of interest will be isolated, concentrated and converted to a desired final chemical and physical form. Under these circumstances, the beta detection system should be calibrated for the radionuclide, chemical composition of the final test-source form and the range of final test-source masses expected from chemical recovery.

The beta particle measurement system should be calibrated with standards traceable to a national standards body such as NIST and its subsequent performance held to established measurement quality requirements through the use of instrument QC checks (Section 18.5.6, "Summary Guidance on Instrument Calibration, Background, and Quality Control"). In addition, appropriate instrument QC should be established for background, voltage plateau, quenching, resolution, and alpha-beta crosstalk (Section 18.5.4.2, "Self-Absorption, Backscatter, and Crosstalk").

Certain aqueous beta-emitting radionuclide calibration standards and sources are available from NIST or from a radioactive source manufacturer (complies with ANSI N42.22) that supplies NIST-traceable standards. The long-lived pure beta-emitting radionuclides available from NIST include: ^{3}H, ^{14}C, ^{63}Ni, ^{129}I, ^{89}Sr, ^{90}Sr, ^{99}Tc, ^{228}Ra, and ^{241}Pu. The majority of the gamma-emitting radionuclides also emit beta particles in the nuclear transformation process. Refer to Table 15.4 for the availability of known beta-emitting radionuclides. Contact a radioactive source manufacturer that supplies NIST-traceable standards for the availability of other pure beta or beta/gamma-emitting radionuclides (ANSI N42.15).

TABLE 15.4 — Nuclides for beta calibration

Purpose	Nuclide	Reference
Specific Nuclide Analyses	^{3}H, ^{14}C, ^{63}Ni, ^{89}Sr, ^{90}Sr (also ^{90}Y), ^{99}Tc, ^{129}I, ^{131}I, ^{228}Ra (also ^{228}Ac), and ^{241}Pu	Various Methods
Gross Beta	^{137}Cs	ASTM D3648
Gross Beta	^{137}Cs	EPA, 1980
Gross Beta	^{137}Cs	ASTM D1890
Gross Beta	^{137}Cs and ^{90}Sr/Y	APHA (1998), Method 7110

Beta detectors should be calibrated according to their intended use, i.e., nuclide specific or gross beta measurement applications. An example of detector calibration for the specific radionuclide of ^{90}Sr can be found in ASTM D5811. Gross beta measurements, as the name implies, are non-specific to a given beta-emitting nuclide and typically require no chemical separations or purification steps. The most common applications for gross beta measures are health physics swipes for contamination surveys, air particulate filter papers from air monitoring programs, and evaporated surface or ground water onto a metal planchet. For gross beta-particle measurements, the instrument's calibration is related to a reference nuclide, typically one that is specified by a laboratory client, measurement quality objectives, or by regulatory requirements. Typical beta-emitting reference nuclides for gross beta analyses include ^{137}Cs, ^{90}Sr/Y, ^{99}Tc, or ^{40}K. Table 15.4 lists beta emitting calibration standards for beta analysis referenced in various national standards.

Aqueous radioactive standards can be prepared in the appropriate geometry for LS or Cerenkov counting or through chemical processing, precipitated, electroplated, or evaporated as a final test-source form for counting by a GP, plastic, or solid-state beta-detection system.

15.5.2 Gas Proportional Counting/Geiger-Mueller Tube Counting

The end-window Geiger-Mueller (GM) tube and the GP counting chamber are the two most prevalent types of detectors used for field and laboratory beta particle counting applications. However, because of its dual use for alpha and beta particle counting, the GP (chamber) counter is used almost exclusively by radioanalytical laboratories. The end-window GM tube counter cannot differentiate between alpha and beta particles because of its operating characteristics. In other words, the total number of ion pairs produced to generate a voltage pulse is independent of the primary ionization (alpha or beta particle interaction), which initiated the detection event. The end-window GM counter is typically used with a survey meter for field or laboratory applications such as the beta measurements of surface contamination, health physics swipes, air filters and soil measurements. Several types of commercially available GP counters are described in Section 15.4.2, on page 15-20.

15.5.2.1 Detector Requirements and Characteristics

Beta particles entering the sensitive region of the detector produce ionization that is converted into an electrical pulse suitable for counting. The number of pulses per unit time is directly related to the disintegration rate of the test source by an overall efficiency factor. This factor combines the effects of test-source-to-detector geometry, test-source self-shielding, backscatter, absorption in air and in the detector window (if any), and detector efficiency. Because most of these individual components in the overall beta-particle detection efficiency factor vary with beta energy, the situation can become complex when a mixture of beta emitters is present in the sample. The overall detection efficiency factor may be empirically determined with prepared standards of composition identical to those of the test-source specimen, or an arbitrary efficiency factor can be defined in terms of a single calibration source, such as ^{137}Cs or another nuclide. Gross counts can provide only a very limited amount of information and therefore should be used only for screening purposes or to indicate trends.

For both window-type gas proportional and end-window GM counters, the thickness of the detector window should be selected to reduce transmission losses from beta particle absorption in the window. The severity of the beta absorption in the window is a function of beta-particle energy and window material and thickness. Estimates of the transmission of beta particles through GM tube walls and windows have been evaluated by Price (1964). These transmission loss estimates are also applicable to the thickness of a window on a GP detector. For ^{14}C with a maximum beta energy of 154 keV, the transmission through a 4 and 0.9 mg/cm^2 window thickness would be approximately 35 and 79 percent, respectively. For the same window thicknesses, the transmission of beta particles from ^{64}Cu with a 580 keV $E_{\beta\text{max}}$ would be about 87 and 97 percent, respectively. Most commercially available gas proportional counters offer detector windows that are thinner than 0.09 mg/cm^2 (e.g., 0.08 mg/cm^2).

Various GP counter characteristics, including detector size, counting gas, window thickness, restrictions on size of test-source mounts, etc., are presented in Section 15.4.2.1. Typical values for the important operational parameters for GP beta-particle counting are provided in Table 15.5.

TABLE 15.5 — Typical operational parameters for gas proportional beta counting

Background count rate	24–50 counts/hour (0.007 to 0.014 cps)
Length of voltage plateau	200 V DC using P-10 gas
Slope of voltage plateau for well-designed detector	2.5%/100 V DC for an electroplated source
Windowless detector efficiency $-\ \dfrac{100\times\text{count rate}}{\alpha\ \text{emission rate}}$	≤60% for an electroplated ^{90}Sr/Y source including backscatter
Windowed efficiency $(0.5\,\text{mg/cm}^2$ thickness) $-\ \dfrac{100\times\text{count rate}}{\alpha\ \text{emission rate}}$	≤45% for an electroplated ^{90}Sr/Y source including backscatter

At least one instrument manufacturer has engineered a windowless GP counter available as either a sequential multiple sample (test source) GP counters and multiple detector single sample (test source) GP counters. The units available typically have lower beta background and higher detector efficiency specifications compared to the windowed GP counters.

SHIELDING

Most GP systems used for beta particle measurements have shielding to reduce the beta background count rate. Shielding reduces the beta background by absorbing some of the components of cosmic radiation and radiations emitted from materials in the surroundings of the measurement system. Ideally, the material used for the shielding should itself be free of any radioactive material that might contribute to the background.

Commercially available low-background GP systems typically have 102 mm of lead surrounding the test-source and cosmic-guard (anti-coincidence detection system) detectors. For a sequential sample GP counting system, the lead shielding may weigh several hundred kilograms depending on the shielding configuration. With the shielding included, a sequential sample GP counting system may weigh up to 360 kg. Portable GP counting systems with less shielding are available but their beta-particle backgrounds are higher.

BACKGROUND

The GP detector's beta background is principally due to the secondary electrons generated from the interaction of cosmic radiation and photon radiations emitted from materials in the surroundings, including the detector shield and housing. Some contribution to the background also may come from beta particles originating in the materials surrounding the detector that may enter the sensitive volume of the detector.

Most of the commercial GP counting systems have passive detector shielding and active cosmic guard (anti-coincidence counting detectors/circuits) components to reduce a detector's beta background. The efficiency of the cosmic guard to reject coincident high-energy cosmic radiation is greater than 99 percent. The anti-coincidence detector surrounds, or is in close proximity to, the primary counting chamber and detects interaction events that are caused by radiations from cosmic rays and the inherent radioactivity in the building and surrounding materials. The anti-coincidence circuitry prevents detector events from being registered that have occurred simultaneously in both the primary test-source-counting and coincidence-counting detectors. Without shielding and anti-coincidence counting detector/circuitry, the background of a GP counter operating at the beta plateau would be about 50 cpm.

The beta-particle background for a GP counting system will depend upon detector size. For some commercial units with a 57.2 mm diameter detector and a 0.08 mg/cm^2 window thickness using P-10 gas, the beta-particle background count rate commonly is about 51 counts per hour (0.85 cpm). A background of 24 counts per hour (0.4 cpm) also may be obtained for some commercial units. These background values apply to GP counting systems with passive lead shielding and active cosmic guard background reduction components.

OPERATING VOLTAGE

The operating voltage of a GP counter used in the beta-particle counting mode depends on the counting gas used, the amplifier and voltage discriminator settings, and the mode of beta-particle discrimination, i.e., voltage pulse height discrimination or simultaneous alpha- and beta-particle counting. A generic discussion on these parameters is provided on page 15-23 for GP counting systems .

Prior to the operation of a gas proportional counter, the operating voltage of the detector must be determined in conjunction with the other operating parameters. Normally, the manufacturer of the unit recommends the voltage discriminator and amplifier gains settings. The user typically places an electroplated beta source into the counting position and increases the detector bias voltage in discrete 25 or 50 V DC increments while recording the observed source count rate at each voltage setting. Figure 15.3 illustrates a typical voltage response curve for a commercial window type gas proportional counter detector using P-10 counting gas and a massless ^{90}Sr/Y source (Canberra, 2002). The operating plateau for beta counting is between 1,400–1,600 V DC. For most commercial GP units, the slope of this plateau should be $\leq$ 2.5 percent per 100 volts over a 200-volt range. When using the separate alpha plateau then beta (plus alpha) plateau counting modes, the alpha count rate on the beta plateau must be determined at the alpha and beta plateau voltages selected during calibration, (i.e., determining the ratio of the alpha-particle count rate on the beta plateau to the alpha-particle count rate on the alpha plateau). For test-source measurements, the observed beta-particle count rate must be adjusted for the alpha-

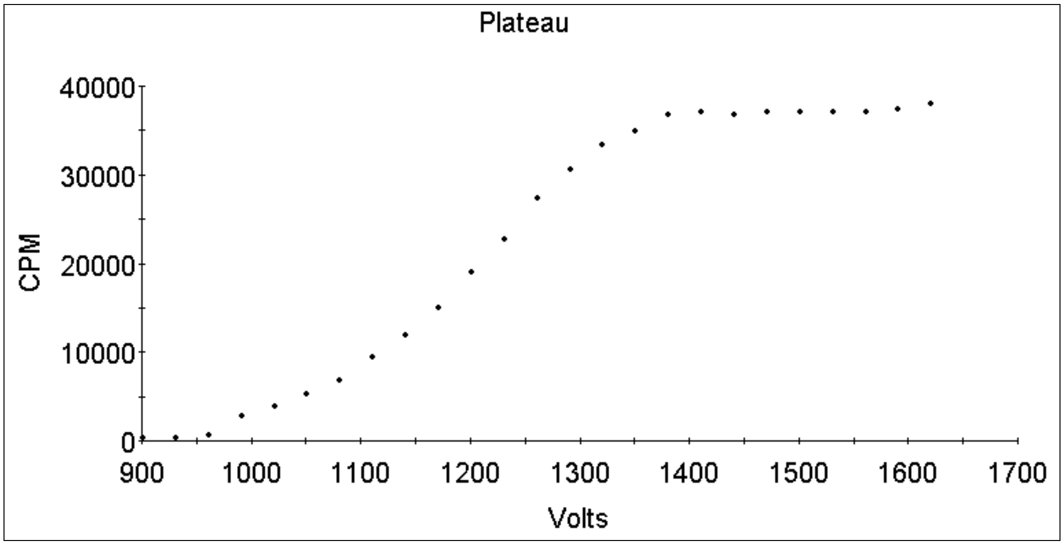


FIGURE 15.3 — Beta plateau generated by a ^{90}Sr/Y source on a GP counter using P-10 gas

particle count rate on the beta plateau by applying a correction factor using this ratio. The observed increase in the alpha-particle count rate on the beta plateau varies according to the alpha-emitting nuclide. The difference between the count rates on the two plateaus will be accentuated for nuclides that have both alpha and photon emissions, e.g., ^{241}Am.

For the simultaneous alpha and beta counting mode, the detector operating voltage is located on the beta particle plateau. For this counting mode, the voltage discriminator setting for alpha detection is set so that only a small fraction (less than 1.0 percent) of the alpha detection events will be registered as beta detection events.

15.5.2.1.4 CROSSTALK — REGISTRATION OF ALPHA PULSES AS BETA PULSES

Modern proportional counters are capable of electronically discriminating between alpha and beta interactions in the detector. As discussed on page 15-24, this differentiation is accomplished by identifying the two types of particles based on the resultant voltage pulse heights from their interactive events in the detector. Those pulses whose heights exceed an experimentally established voltage (pulse) discriminator level are registered as alpha counts and those falling below this level are recorded as beta counts. The dynamic range of the voltage separation between the alpha and beta voltage pulses varies by detector design and manufacturer. If the voltage discriminator is not properly set, a fraction of high-energy beta particles may be recorded as alpha particles. In addition, severely degraded alpha particles, because of their self absorption in a test source of significant masses, may be recorded as beta particles. This missclassification of alpha and beta counts is referred to as “crosstalk.” The degree of spillover varies according to detector design and GP counter manufacturer.

For some commercial GP counters, crosstalk may occur for both modes of GP counting, i.e., alpha then beta plateau counting and simultaneous alpha and beta counting. For electroplated beta particle sources, the crosstalk is minimum for both counting modes when the voltage (pulse) discriminator is properly set. However, certain alpha emitting radionuclides ^{230}Th, ^{235}U, ^{238}U, ^{241}Am, ^{238}Pu, ^{239}Pu) have multiple low-energy conversion electron/photon emissions that may be registered as beta particles. The user should review the decay scheme of the nuclide of interest to gain a perspective on the extent of the possible alpha-to-beta crosstalk.

For both counting modes, corrections should be made to the beta count rate to remove the portion contributed by alpha particles. Since the fraction of the alpha counts occurring in the beta channel depends on the source mass, a crosstalk curve should be developed. This can be accomplished concurrently with the self-absorption calibration for the alpha emitting radionuclide selected. A crosstalk response curve is generated by recording the beta counts from the alpha self-absorption determination at all source masses and plotting the crosstalk fraction (alpha-particle count rate in beta channel/alpha count rate in alpha channel) as a function of source mass (Section17.4, "Data Reduction on Non-Spectrometry Systems"). Beta-particle count rates then can be corrected for the influence of the alpha particles at all source thicknesses.

15.5.2.2 Calibration- and Test-Source Preparation

For specific nuclide beta particle counting by a gas proportional counter, chemical separations are typically performed to isolate the radionuclide of interest from other beta emitting radionuclides. Beta measurements are performed on chemically isolated pure beta emitters (beta decay not accompanied by a gamma-ray) and also in cases when better detection capabilities (increased sensitivity) are required to meet detection limits, such as, ^{89}Sr, ^{90}Sr, ^{99}Tc, ^{131}I, ^{134}Cs, and ^{137}Cs (EPA, 1980). Test sources measured in a proportional counter are usually prepared by electrodeposition, coprecipitation, or evaporation (Blanchard et al., 1960). The comments on chemical reactivity of source-contained materials and contamination given in Section 15.3 apply.

Test- and calibration-source preparation techniques and applications for GP counting are presented in Section 15.3. These preparation techniques have been presented in a fairly generic manner but with identification of the applications to alpha and beta counting. Refer to the section for information on preparing test and calibration sources for beta particle radionuclides applicable to gas proportional counting.

Preparation of beta calibration and test sources by precipitation/coprecipitation applicable to gas proportional counting also is discussed in Section 15.3. The techniques include precipitation of the radionuclide with the element of interest (e.g., Cu^{131}I) and co-precipitation of a radionuclide with a chemically similar element that forms a precipitate (e.g., NdF$_3$ – ^{239}Pu). Table 15.1 (page 15-12) provides a listing of the common precipitates and coprecipitates used for both beta- and alpha-emitting radionuclides.

15.5.2.3 Detector Calibration

Calibrations for beta particle measurements can be accomplished for either the beta (plus alpha) plateau counting mode or the simultaneous alpha and beta counting mode. However, for both modes of operation, calibration sources should be prepared in a manner identical to the method used for test-source mounting. This may include massless or electroplated sources, microprecipitated (less than 200 µg) sources and low-mass (1–125 mg) sources. For accurate results, beta self-absorption curves (for both operating modes) and crosstalk corrections (simultaneous counting mode) during the source calibration should be developed.

Beta-particle attenuation should be considered for windowed GP counting applications. Beta-particle attenuation can result from the interaction of a beta particle with the air, detector window, or the matrix atoms of the final test source. Beta-particle air attenuation is a function of the distance between the test source (or sample) and the detector's particle-entrance window. Under most applications for beta-particle counting, this factor typically is insignificant compared to the other sources of beta-particle attenuation. Consideration of the detector's window thickness and its beta-particle attenuation becomes important when evaluating low-energy beta particles, such as ^{14}C. Normally, the air and detector window attenuation factors are determined as a combined beta attenuation-efficiency factor that includes the test-source self-absorption for a given application. In most applications, a backscatter factor for the material composition (Z value) of the final test-source mount is included into a combined attenuation-backscatter-efficiency factor or—more simply—the combined detector efficiency correction factor.

Beta-particle counting systems should be calibrated with the specific radionuclide under investigation or a surrogate radionuclide of similar beta energy having a comparable final test-source composition and configuration. However, it should be mentioned that moderate to severe calibration biases may occur depending on the severity of the departure from the chemical composition of the final test-source matrix and the beta energy of a surrogate. For this reason, using an surrogate radionuclide is discouraged unless the availability of the radionuclide of interest is nonexistent. Corrections between the surrogate and radionuclide of interest should be determined and applied to test-source results, as appropriate. For electroplated plated test sources, a correction factor needs to be determined if the plating material of the surrogate is not the same as that used for the test sources.

Certain aqueous beta-emitting radionuclide calibration standards and sources are available from NIST or from a commercial radioactive source manufacturer that complies with ANSI N42.22. Refer to Section 15.4 for the availability of known beta/gamma-emitting radionuclides. Contact a radioactive source manufacturer for the availability of other NIST-traceable pure beta- or beta/gamma-emitting radionuclides (ANSI N42.15).

The counting efficiency (ε) is determined by counting a calibration source to accumulate sufficient net counts (approximately 10,000) to provide a relative (1σ) counting uncertainty of about 1 percent and dividing the resultant net count rate (cps) by the beta-emission rate of the source (β/s). The beta emission rate is determined by the source activity (Bq) times the beta abundance per disintegration.

$$\varepsilon = \frac{\text{Measured Net Count Rate (cps)}}{\text{Bq} \times \text{fractional } \beta \text{ abundance}}$$

For a nuclide specific or reference nuclide counting efficiency, the same equation is used but without the beta abundance factor. The uncertainty of the detector efficiency factor can be calculated using the methods described in Chapter 19.

For health physics swipes and air particulate filter samples, a calibration source is prepared by spiking an unused filter with the appropriate calibration solution. For health physics swipes, the entire surface of the filter may be spiked. However, only the active area of an air filter is spiked with the calibration solution. The retainer ring and gasket holding down the filter determines the active area to be spiked. Depending on the filter composition (e.g., glass fiber filter), the filter matrix may cause some wicking of the solution away from the surface. In order to prevent the wicking effect, the surface of the filter may be sprayed with an acrylic lacquer and dried prior to spiking the surface.

Self-absorption of beta particles is not as pronounced as with alpha particles, because the charge and mass of beta particles are significantly smaller. Scattering, and particularly backscatter from the source mount, is much more pronounced for beta counting than for alpha counting (Blanchard et al., 1957). To reduce scatter, plastic mountings are often used to mount sources for beta counting (EPA, 1980). The effects resulting from self-absorption and scattering can be minimized by preparing test sources in a standardized constant thickness, or using a correction factor based on an empirical calibration curve for different thicknesses (Friedlander et al., 1981; Tsoulfanidis, 1983). If test sources of varying mass are to be counted for beta activity determination, a self-absorption curve should be prepared. The method used is identical to that described under alpha calibration for proportional counters, except that a beta-emitting reference material is used.

Instrument calibration for a specific nuclide measurement should be calibrated with the radionuclide of interest. In some cases, a radionuclide whose beta emission has the same energy as the nuclide of interest may be used as long as the self-absorption characteristics are similar. An example is the calibration of the GP counter for ^{228}Ac (β_{avg} = 404 keV) by using ^{89}Sr (β_{avg} = 589 keV) (EPA, 1980).

In cases where finite test-source thicknesses are unavoidable, beta-source measurements can be adjusted to account for self-absorption (PHS, 1967a). Typical applications for such self-absorption curves include $SrCO_3$ (^{89}Sr and ^{90}Sr), Cu^{131}I, and gross-beta analysis. In order to determine the change in counting efficiency as a function of source thickness or mass, a self-absorption curve should be developed. Calibration sources containing a known amount of the radionuclide of interest are prepared in varying thicknesses (mass) and counted. Self-absorption curves for gross beta-particle measurements are constructed most frequently using reference material containing ^{137}Cs, ^{90}Sr/Y, ^{99}Tc, or ^{40}K. The self-absorption curve is constructed by counting planchets containing varying mass of material but with a known amount (sometimes constant) of added radioactivity. A discussion on the preparation of a self-absorption curve that relates the self-absorption factor to a zero-thickness efficiency is discussed in Section 15.4.2.3, "Detector Calibration." Most radioanalytical laboratories generate a self-absorption curve by determining the counting efficiency as a function of source mass in milligrams or mg/cm^2 without normalization to the "zero thickness" efficiency. Test sources prepared for gross beta measurement are counted in the exact geometry as those used to prepare the absorption curve. The material forming the matrix for the self-absorption calibration source should, when possible, be identical to that expected in the test sources to be analyzed. For the lower to intermediate beta particle energies, the detector efficiency factor is a function of beta energy, final sample mass and source composition. For beta particles having a maximum beta energies greater than 1,500 keV, the detector efficiency factor is nearly constant over a final sample mass range of 0 to 5 mg/cm^2. For sufficiently thick sources, the number of beta particles interacting with the detector will reach a limit and the count rate becomes independent of the source thickness.

Figure 15.4 illustrates a typical self-absorption curve for ^{90}Sr/Y in a dry residue generated from evaporated tap water. Note that this self-absorption curve is multi-component, where the resulting curve is a composite of the self-absorption effects of the low-energy ^{90}Sr ($E_{\beta max}$ = 546 keV) and the high-energy ^{90}Y ($E_{\beta max}$ = 2.28 MeV).

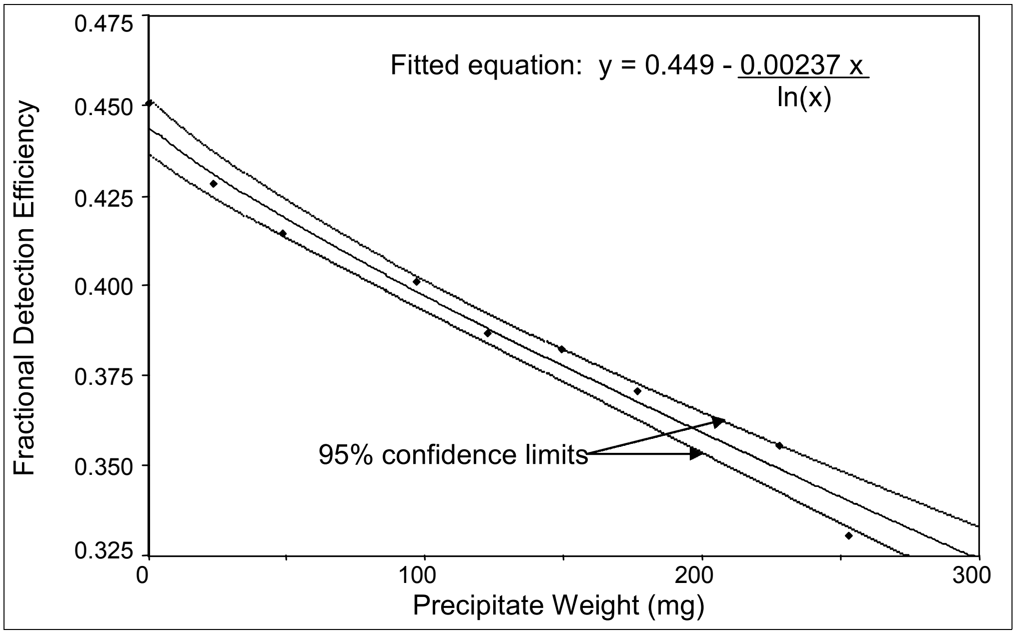


FIGURE 15.4 — Gas proportional counter self-absorption curve for ^{90}Sr/Y

15.5.2.4. Troubleshooting

Various problems that may arise when counting calibration or test sources on a GP counter are discussed in Section 15.4.2.4. These may include both instrumentation- and test-source preparation related issues. Instrumentation related problems should be identified through the instrument's operational quality control checks that include periodic detector response and background measurements. Section 18.5.6 ("Summary Guidance on Instrument Calibration, Background, and Quality Control") in Chapter 18 provides guidance on the frequency for these types of QC measurements for a GP counter.

Inaccurate results can occur from the misuse of a specific nuclide detector calibration or if the test sources are prepared differently than the calibration sources. It is important that a laboratory and its client cooperatively decide on the nuclide of interest for gross beta measurements as well as the chemical composition of the self-absorption curve that may be used. Some clients may want the laboratory to use the gross beta reference nuclide that the nationally recognized performance evaluation programs incorporate into their gross-alpha test samples. Inaccurate results also will occur when a beta-detector efficiency factor for a massless calibration source is applied as the detection efficiency for air particulate filter or swipe test sources. These test sources normally have some amount of radioactivity/particle penetration into the fibers of the filter or swipe material and may contribute to self absorption depending on the beta energy.

15.5.3 Liquid Scintillation

When beta measurements involving pure beta emitters of low energy are required, they are often performed using liquid scintillation spectrometry, because sample preparation is easy and counting efficiencies are relatively high (Herpers, 1986). Although it is the preferred method for measuring low-energy, pure beta-emitting radionuclides, (e.g., ^{3}H, ^{14}C, ^{35}S, and ^{63}N) it is a well-established procedure for measuring numerous other beta-emitting radionuclides, including ^{45}Ca, ^{32}P, ^{65}Zn, ^{141}Ce, ^{60}Co, ^{89}Sr, ^{55}Fe, ^{87}Rb, ^{147}Pm, and ^{36}Cl (Hemingway, 1975).

Liquid scintillation counting (LSC) avoids many sources of error associated with counting a solid source, such as self-absorption, backscattering, loss of activity during evaporation because of volatilization or spattering, and variable detection efficiency over a wide beta-energy range. In addition to the improvement in the detection capability offered by LSC over other beta counting techniques, sample preparation time and counting times may be significantly shorter. Sample preparation involves only adding a soluble or dispersable sample aliquant to a scintillation cocktail to form a liquid test source. Because every radioactive atom is essentially surrounded by detector molecules, the probability of detection is quite high. Radionuclides having maximum beta energies of 200 keV or more are detected with essentially 100 percent efficiency. Liquid scintillation can, at times, be disadvantageous because of chemiluminescence, phosphorescence, quenching, or high backgrounds (especially in older instruments). However, better coincidence circuitry and use of certain types of shielding (e.g., bismuth germanate) have been able to reduce backgrounds in newer instruments.

The observed count rate for a liquid-scintillation test or calibration source is directly related to the beta (plus conversion electron) or positron emission rate in most cases. The important exception is beta emitters whose maximum energy is below 200 keV. Low-energy beta emitters, such as tritium (^{3}H, $E_{\beta max} = 18$ keV) or ^{14}C ($E_{\beta max} = 156$ keV), have a significant number of emissions that have energies in the range of 0.7 to 4 keV. Beta-particle energy is converted to photons through interaction with the solvent and fluor. It takes about 150 eV to produce one photon. Thus, a 150 keV beta particle will produce about 1,000 photons. These photons are then detected by the PMTs in the LSC instrument. The PMTs are arranged so that the test or calibration source is positioned between them. Thus, when a nuclear decay event produces photons, each of the PMTs will detect about half of them. If these photons are produced from the same decay event within the source, it is likely that they will occur in each detector within about 20 ns of each other. The electronic circuitry of the detectors is established such that only those events that yield counts in each PMT within 20 ns are recorded are recorded as valid counts. This is the coincidence function of the LSC instrument. The calibration of liquid scintillation counting detectors is given in ASTM E181. In this energy range, the efficiency of producing a photon in the cocktail is poor because of two reasons: an inability to exceed the necessary quantum threshold and pulse-summation effects. Thus, the overall efficiency of detection in an unquenched sample approaches about 65 percent for ^{3}H and 94 percent for ^{14}C.

15.5.3.1 Detector Requirements and Characteristics

For measurements in which data are expressed relative to a defined standard, the individual correction factors cancel whenever sample composition, sample mass, and counting configuration and geometry remain constant during the standardization and tests.

Liquid scintillation counting systems use an organic phosphor as the primary detector. This organic phosphor is dissolved in an appropriate solvent that achieves a uniform dispersion (this combination is commonly referred to as the “cocktail”). A second organic phosphor often is included in the liquid scintillation cocktail as a wavelength shifter. The sample then is added to this cocktail to form the test source. The beta particles interact with the solvent and primary phosphor to produce photons. The wavelength shifter efficiently absorbs the photons of the primary phosphor and re-emits them at a longer wavelength more compatible with the photomultiplier tube. Most liquid-scintillation counting systems use two photomultiplier tubes in coincidence. The coincidence counting arrangement minimizes spurious noise pulses that occur in a single photomultiplier tube and thus provides lower background. The requirement that both photomultiplier tubes respond to each event has a slight affect on the overall detection efficiency of $E_{\beta max}$>200 keV; however, system response to $E_{\beta max}$<200 keV will be significant.

Another approach to LSC without the use of organic phosphors is Cerenkov counting. When a high-velocity charged particle passes through an optically transparent dielectric medium whose index of refraction is greater than one, excess radiation is released in the ultraviolet range of energies. This is known as "Cerenkov radiation" (Kessler, 1986). In order to produce Cerenkov radiation, the condition $\beta \cdot n > 1$ must be met; where n is the refractive index of the medium and β is the ratio of the particle velocity in the medium to light velocity in a vacuum (Knoll, 1979). Wavelength shifters are usually employed to convert the ultraviolet Cerenkov radiation to the visible range. Although Cerenkov counting efficiencies are about 20 to 50 percent (Scarpitta and Fisenne, 1996), lower than when organic phosphors are used, mixed waste disposal may be eliminated.

The assessment of the effectiveness of the overall system detection is based on the figure of merit (FOM) concept. This is a numerical value that is used to describe the entire counting system (cocktail plus detector). The FOM generally is obtained by the following formula:

$$\text{FOM} = \frac{(\text{Efficiency of the sample detection})^2}{\text{Detector blank background}}$$

Thus, the larger the FOM, the lower will be the limit of detection. A lower blank background, a more efficient cocktail, or a better photon detection system can achieve a larger FOM.

OPERATING VOLTAGE

The voltage of the detector is established based on the characteristics of the PMT. This is usually about 1,000 volts DC. The voltage of the PMT should not be changed because this would affect the overall quantum yield of photoelectrons produced by the decay event. Generally the voltage is a fixed parameter by the instrument manufacturer and not adjustable by the user.

SHIELDING

Most liquid scintillation units come with the sample chamber enclosed within the instrument. The manufacturers have provided a mechanism (usually a source "elevator") by which the source is moved into a shielded position (chamber) between the two PMTs. No additional shielding is usually required for LSC instruments. However, building location and room materials of construction can affect the overall background that the LSC instrument experiences. Instruments are constructed with standard shielding materials to account for routine background radiation. The potential for other than routine background radiation should be assessed prior to selecting a location for the instrument. Shielding from UV-visible radiation is discussed under the section on dark adaptation.

BACKGROUND

There are several different sources of background radiation that could affect liquid scintillation analysis:

- Building construction materials;
- Reagents used in analysis (this is the blank and is usually assessed separately from background" radiation);
- Scintillation vials;
- Presence of an energy source (reactor or accelerator);
- Presence of other radionuclides that have beta or gamma emissions that are contaminating the sample or test source under analysis;
- Stray light into the instrument; and
- Scintillation cocktail (this is the blank and is usually assessed separately from background radiation).

Although there is some capability to differentiate certain beta-particle energies, there is a wide overlap in beta particle spectra. Thus, background counts that take into account the process—as well as the instrument, reagents, and scintillation vials—should be performed routinely. Routine monitoring of background is significantly different for LSC with respect to other detection methods because the cocktail is the primary detector. For example, any component of the sample (chemical or physical) that can affect the cocktail and is not reproduced in the background test-source measurement can introduce additional uncertainty. Controls should be in place to identify and correct variations in background measurements. Variations of background and background quench also should be monitored for potential impact on results.

Another way to help achieve low backgrounds is to use scintillation-grade organic phosphors and solvents prepared from materials containing low concentrations of ^{14}C, such as petroleum. The counting vials may be made of low-potassium glass or plastic to minimize counts because of ^{40}K. Liquid scintillation provides a fixed geometry from a given size counting vial and liquid volume.

DARK ADAPTATION

The photomultiplier tubes are sensitive to any light which they detect. Stray room light will cause a signal leading to a higher background. The instruments are constructed so that they are light tight, and interior surfaces are generally black to prevent light transmission by these surfaces from stray light.

Chemiluminescence, the production of light by a chemical reaction with a molecule, can be troublesome in liquid scintillation counting. However, the duration of chemiluminescence is generally short, and waiting a few minutes after mixing the reagents will allow the effect to dissipate before counting starts. Phosphorescence, the emission of light caused by photon interaction with a molecule, will cease a short time after being placed in the dark. This is referred to as being "dark adapted" (Faires and Boswell, 1981).

The two factors which can produce the phosphorescent effect on the cocktail are external UV light and heat. Each of these work by a similar mechanism. Energy is transferred to the fluor (either by UV excitation or heat) and the fluor excites/de-excites yielding photons in the detection range of the PMT. These events can contribute to the total background and increase the detection limit of the analysis or could lead to falsely elevated sample results. Interference from UV light from lamps or the sun is avoided by dark adapting the source in the LSC vial for at least 30 minutes prior to analysis. To avoid differences in background because of thermal excitation, most instruments have internal thermostats to maintain constant temperature during the analysis. These instrument characteristics allow sufficient time for phosphorescent and luminescent states, unrelated to the radioactivity measurement, to undergo de-excitation prior to counting the source.

CHANNEL OVERLAP

The traditional concept of "channel" for liquid scintillation was an energy range that corresponded to the majority of the energy distribution of a particular radionuclide's beta particle distribution. Counting in "channel 1" indicated tritium, or "channel 2" indicated ^{14}C. The size of the channel was determined by setting discriminator levels. The amount of quench in a test source would cause a spillover of the higher energy distribution beta particles to the lower channels. Also, the high energy distribution of a lower energy beta could cross into the higher energy beta channel. This was referred to as "channel overlap." In older instruments, the sample-channel-ratio method was used to separate the components. Recent advances in liquid scintillation instruments have made it easier to eliminate or account for this overlap. Similar to gamma spectrometers, liquid scintillation units now divide the energy output of the PMT into more discrete channels (usually about 1,000). Mathematical modeling of the spectrum shape based on these discrete channels allows more refined techniques to be used to account for channel overlap.

15.5.3.2 Calibration- and Test-Source Preparation

Gaseous radionuclides most often measured include tritium, both as a vapor (^{3}HOH) and in the elemental form (^{3}H-H), ^{14}CO$_2$, and the noble gases, ^{37}Ar, ^{41}Ar, ^{85}Kr, ^{222}Rn, ^{131m}Xe, and ^{133}Xe. Tritiated water vapor is often collected by condensation from a known volume of air (EPA 1984b). The air is drawn first through a filter to remove all particulates and then through a cold trap submerged in a bath at sub-zero temperatures. A measured aliquant of the collected water is analyzed by liquid scintillation spectrometry (EPA, 1984b). Tritiated water vapor sometimes is collected by pulling air through a trap containing materials like silica gel (SC&A, 1994) or through a molecular sieve. After collection, the water is distilled from the silica gel, collected, and counted in a liquid scintillation spectrometer.

Gaseous products of oxidation or combustion can be trapped in a suitable media, such as water for ^{3}H, ethanolamine for ^{14}C, peroxide for ^{35}S, and then analyzed by liquid scintillation spectrometry (NCRP, 1978). For this method, it is very important to de-aerate the liquid prior to introducing the gas since gaseous components may cause quench. The temperature should be carefully controlled since gas solubilities are generally inversely proportional to the temperature (NCRP, 1978).

Tritium is the radionuclide most often measured by liquid scintillation counting (DOE, 1997; EPA 1979; Lieberman and Moghissi, 1970). The primary step in preparing water samples for counting is distillation in the presence of an oxidizing agent, such as $KMnO_4$, to separate the tritium labeled water from dissolved solids, including interfering radionuclides, and any organic material that may be present. An aliquant of the distillate is then mixed with a cocktail and counted in a liquid scintillation spectrometer. To measure tritium in samples of other matrices, the water in the sample can be removed and collected by distillation as an azeotrope, for example, *n*-hexane or cyclohexane (Moghissi, 1981; EPA, 1979). An aliquant of the collected water is then mixed with a liquid scintillator and counted as described above for water samples.

Tritium can be concentrated in a sample of water if lower detection limits are required. The concentration process, electrolysis, uses the isotopic effect caused by the mass difference (three times) between ^1H and ^3H (DOE, 1997; EPA, 1984a). Tritium becomes enriched in the liquid phase as electrolysis continues. Generally, 50 mL of the laboratory sample is placed in an electrolysis cell and a current of about three amps applied. Electrolysis is continued until the volume reaches about 5 mL. More sample can be added to the cell during the electrolysis, if greater sensitivity is necessary for the measurement. The concentrated laboratory sample is then distilled in the presence of an oxidizing agent, such as $KMnO_4$, and treated like a water sample (see above).

Environmental and biological samples also can be analyzed for total ^3H (that contained in both the water and fibrous fractions) by quantitatively combusting the laboratory sample, collecting the water formed, and analyzing it by liquid scintillation spectrometry (DOE, 1997). In another case, both ^3H and ^{14}C can be measured simultaneously (EPA, 1984b). The laboratory sample first is freeze-dried to remove and collect the water fraction. The tritium in the water is measured directly by liquid scintillation spectrometry. The fibrous (freeze-dried) material is combusted and the H_2O and CO_2 are collected. As before, the ^3H in the water is measured directly by liquid scintillation spectrometry, while the ^{14}C is first converted to benzene or captured as CO_2 and then counted by liquid scintillation spectrometry.

15.5.3.3 Detector Calibration

When the quenching of a group of test sources is predictable, e.g., distilled drinking water (EPA, 1980; ASTM D4107), a counting efficiency is determined for the group by placing a known quantity of reference material in the source medium and scintillation solution under identical conditions (vials and volumes) as the test-source medium.

Except for test sources with very predictable amounts of quenching, it is necessary to determine a counting efficiency for each laboratory test source. Two methods of determining counting efficiency are available: internal standardization and external standardization (NCRP, 1978).

Internal standardization for quench correction is by the method of standard additions. This involves the counting of two aliquants of the sample, one being the sample and the other is an identical aliquant that has been spiked with a known amount of the radionuclide being determined. The degree of quench then can be determined from the spiked aliquant and applied to the unspiked aliquant (DOE, 1995). This method does not require a curve for correction but decreases throughput because two test-source counts are required. For these reasons, the use of an external standard is the more widely used technique to correct for quenching (Horrocks, 1973).

One external standard method is called the "external-standard channels-ratio" (Baillie, 1960; Higashimura et al., 1962). In this method, a series of vials is prepared containing a known amount of reference material and varying amounts of the medium being evaluated. Windows in the energy spectrum are set for a high- and low-energy region. The vials are counted and the ratios of low-to-high count rates are recorded for each quenched source. A quench curve is then prepared by plotting the ratios of low-to-high energies as a function of counting efficiency. The efficiency of an unknown test source can then be determined from its low-to-high energy ratio during counting.

The second external-standard method employs an external gamma-ray source that generates Compton electrons in the scintillation solution. A quench curve is then prepared by plotting a parameter obtained from the external standard spectrum against counting efficiency (Kessler, 1989).

QUENCH

Quenching, which is probably the most prevalent interference in liquid scintillation counting, can be defined as anything which interferes with the conversion of radionuclide decay energy to photons emitted from the sample vial, resulting in a reduction of counting efficiency. Two types of quenching may be encountered in liquid scintillation counting: chemical or color quenching. Color quenching results in a reduction of the scintillation intensity (as seen by the PMTs) because of absorption of the fluor scintillation by colored materials present in the cocktail. Thus, a reduction in counting efficiency occurs after the particle energy has been transferred to the fluor. Chemical quenching results in a reduction in the scintillation intensity because of the presence of materials in the scintillation solution that interfere with the process energy transfer to the fluor also leading to a reduction in counting efficiency. Chemical quenching results in a reduction in the scintillation intensity because of the presence of materials in the scintillation solution that interfere with the process leading to the production of light resulting in fewer photons per quanta of particle energy and a reduction in counting efficiency. Suspended solids and opaque materials also will cause quench in the cocktail, because they physically obstruct the light path to the PMTs.

One can have all three types of quenching present in a test source. Although the mechanisms of chemical and color quenching may be different, they both affect the number of photons reaching the detector. Therefore, the measured sample counts should be corrected for quenching effects so that the radioactivity in the test source can be quantified. Some of the stronger chemical quenching agents are alkyl bromides, iodides, nitrates, mercaptans, and ketones (NCRP, 1978). Yellow provides the most significant quench.

The quantitative measure of quench can be seen in the beta particle spectrum of the quenched *versus* unquenched test source. Not only does quench reduce the total number of photon events received by the detectors, but it also shifts the distribution of the events to lower energy. This causes the $E_{\beta\mathrm{max}}$, as well as the other mathematical characteristics of the beta curve, to shift to lower energies.

Quench may play an important role in the analysis for surface contamination levels of low-energy beta-only emitters, such as ^{3}H, ^{14}C, ^{63}Ni, ^{135}Cs, etc. As discussed in Section 10.6, swipes are used for assessing gross surface contamination levels. Thus, chemical separations or sample cleanups are not usually performed, and the entire swipe will be inserted into the scintillation vial. Several different parameters affecting quench will also affect determining the consistency of the results if direct analysis of the swipe is used. Some of these factors are:

- Material from the surface analyzed which dissolves in the cocktail yielding either a chemical or color quench;

- Insoluble detritus that can become suspended in the cocktail, interfering with the emitted fluor radiation reaching the PMT;

- Adhesives or adsorbent materials used in the swipe material itself may react with the fluor, or may interfere with the transfer of energy to the fluor; and

- The degree of transparency of the swipe material to the counting system (i.e., the photons emitted by the fluor may be absorbed by the swipe material).

When this type of analysis is being performed, either a dry or wet swipe could be used. However, the analyst should ensure that the conditions cited above are accounted for by performing a test of the particular swipe and the surface type to assess their affect on quench.

COMPENSATION FOR QUENCH

Most liquid scintillation spectrometers manufactured after about 1965 have a method of assessing the quench level in a solution compared to the standard, allowing for correction of the quench. Historically, quench was accounted for by establishing a quench curve for the instrument or by using standard additions. A quench curve is made by taking a standard and analyzing several replicates under conditions of varying amounts of added “quench” agent. Typically, any strong color agent could be used as the quench.

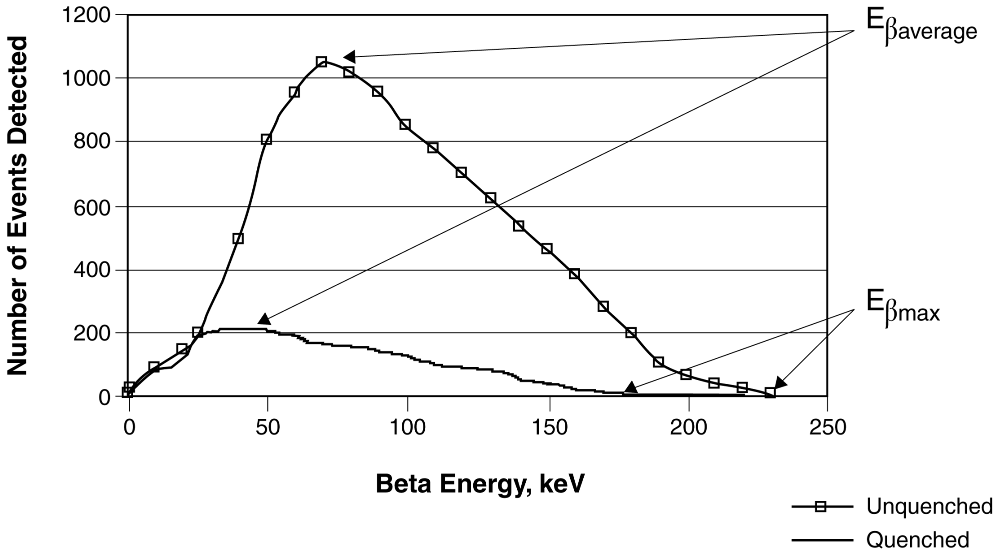


FIGURE 15.5 — Representation of a beta emitter energy spectrum

Figure 15.5 shows the effect that quench would have on the beta spectrum. Note first that the average beta energy is shifted to a lower energy. Second, the total number of events at each energy is lower than the unquenched source.

Historical quench corrections include channels ratio, external standard, and internal standardization. More recent methods are the H-number and tSIE methods. One of the methods used to assess the quench is the H-Number technique (Horrocks, 1970). Fundamentally, the beta-particle spectrum generated in the cocktail by a standard external gamma source (^{137}Cs) is analyzed over the energy range of the instrument. Each energy interval receives a number of counts corresponding to the generated Compton events (these are significantly greater than the test-source output pulses because of the gamma intensity). The inflection point of the beta curve at the high end of the energy distribution is assigned a channel number for that solution with no added quench. Increasing levels of quench shifts this inflection point to lower channel numbers. The quench is a measure of the change in the channel number of the inflection point compared to the unquenched solution.

Another method uses the transformed spectral index of the external (tSIE) standard (Kessler, 1989). This technique uses the energy distribution of the entire spectrum as generated by an external ^{133}Ba source when it is exposed to the cocktail. The accumulation of this energy spectrum takes a few seconds and the events produced are far greater than those of the test source because of the intensity of the ^{133}Ba source. The effects of the radioactivity in the sample are independent of this measurement.

The manner in which quench affects the electron distribution produced by the external source will be the same for standards and samples, since quench is the interference of energy transfer. With environmental samples, the degree of quench for all practical purposes is independent of the material that causes the quench ("quench is quench," regardless of the cause).

The fluors used in cocktails are susceptible to excitation by both light (artificial room light or sunlight) and heat. Furthermore, these materials also will have phosphorescent states, which can have significant lifetimes (minutes). It is important to ensure that the standards for quench-curve preparation and the sample are "dark adapted" for the same period of time prior to their analysis. This allows all of the phosphorescent states to de-excite and not add to the measured counts, and helps to ensure that the interference form other sources of excitation are minimized.

The level of quench affects the measurement uncertainty of the analysis in two ways. First, it decreases the net count rate of the test source. Since the relative measurement uncertainty is directly proportional to the square root of the counts, the relative uncertainty increases. This uncertainty can be directly quantified. Second, the measure of quench itself is not exact and will be characterized by a Gaussian distribution at a specific quench for a specific test source. Additionally, the quench function is generally exponential. This means that the determination of quench in an individual test source is made from a smoothed curve. Unless a specific effort is made to assess this uncertainty component, it is not accounted for in most software analysis of the final calculation. Minimizing the quench will minimize the increase in the combined standard uncertainty of the measurement.

Beta particles, unlike alpha and gamma rays, are emitted in a continuum up to an $E_{\hat{a}\max}$ (Figure 15.5). The continuum covers a wide range of energies, so that different beta-emitting radioisotopes having different energies may have overlapping energy continua. The average beta particle energy is roughly one-third of the $E_{\hat{a}\max}$. This energy generally has the highest population of all the beta particle energies emitted by that particular radionuclide. As an example ^{90}Sr has an $E_{\hat{a}\max}$ of 546 keV and ^{89}Sr has an $E_{\hat{a}\max}$ of 1,490 keV. Their beta-particle spectra overlap significantly. They cannot be separated chemically. Neither of these two isotopes is a strong gamma emitter. Thus, the analysis of these two beta emitters sometimes is performed indirectly, using liquid scintillation, by using the ingrowth of ^{90}Y and mathematically solving for the initial concentrations of ^{89}Sr and ^{90}Sr.

A liquid scintillation spectrometer detects beta-particle events as a result of beta energy transfer into a liquid medium, which promotes the formation of photons in the UV/visible energy region. The transfer is an indirect process. The beta particle distributes its energy through solvent "excimers" to an organic fluor, which de-excites by releasing the UV/visible photons. Any component of the cocktail that affects the energy transfer process will have a significant effect on the analysis. Other controllable aspects of the cocktail are:

- The ratio of the sample volume to solvent-to-fluor volume;
- Preparation of the quench curve;

- Stability of the cocktail; and
- Dark adaption of the cocktail.

Each analytical procedure for scintillation analysis should find the sample-to-fluor volume that provides the maximum response. Part of this process is that the analyst is ensuring that sufficient fluor exists to convert the beta particles to UV/visible region photons (i.e., scintillator capacity). Once this ratio is established, a quench curve is made using the same ratio of sample-to-fluor solution.

The most significant aspect of liquid scintillation analysis is accounting for quench in the sample and standards to the same extent (or by an equivalent methodology), so that the analytical results are reproducible and accurate.

Beta and alpha particles both will induce a fluorescent spectrum in the liquid scintillation cocktail. The beta spectra originate at zero energy and cover a large range of energies. The alpha-particle distribution is much different, in part because of the discrete energy distribution. Although the liquid scintillation process has transformed the original energy of the beta particles to a measurable quantity on this spectrometer, the distribution of the actual beta-particle energies is exactly the same as the distribution of the UV light detected by the spectrometer. It is difficult to distinguish one beta emitter from another for this reason of continuous beta-particle energy, unless the beta-particle energies are very different. Alpha analysis using liquid scintillation is less complicated because of the distinct energy emitted by the alpha particles. The signal from the alpha particles can be distinguished from that of the beta because of the delay time for the fluor excited state to decay. Because alphas have such a significant energy directly imparted to the fluor, a triplet state of the excited electron is achieved.

This state must first decay to the singlet electron state before fluorescence can occur, as in beta interactions. The Δt for this process is about 35 ns, so it can be segregated electronically from any beta signal. The problems of quench will occur in alpha as in beta spectroscopy, since quench occurs not with the actual radioactive decay mode, but with the energy transfer from the fluor to the detector. Refer to section 15.4.5 (“Photon Electron Rejecting Alpha Liquid Scintillation”) for details about a method of performing alpha analysis in liquid scintillation media.

COCKTAIL

The liquid scintillation cocktail is the combination of the scintillator (primary and secondary) and solvent. The combination of the cocktail with radionuclide solutions is referred to as the “test source” or “calibration source.” The scintillators are organic materials which over time can undergo decomposition. As with other organic compounds of this type, they are light and heat sensitive. Thus, it is important to protect them from light and heat to minimize their degradation during laboratory storage.

The test source also will be susceptible to degradation because of changes in temperature and addition of chemicals from the sample. It is therefore important to know how much sample to add to the fluor solution and how long it can be stored without degradation.

The ratio of fluor solution to sample (which comprises the cocktail) should be optimized for each radionuclide and sample type analyzed. This can be done by first selecting a final volume of the cocktail that will fill a vial to 80-90 percent of its volume. Then, make several combinations by varying the ratio of a standard radionuclide to the fluor solution so that the final volume is constant. Count all the vials for the same time period and find the ratio that achieves the highest relative count rate.

15.5.3.4 Troubleshooting

There are many areas involving the processing of a sample by liquid scintillation analysis where errors can be introduced. Identified here are some of the more common problems that have been experienced with suggestions on how to correct them:

- Routine background check is above upper control limit on QC charts
  - Insufficient dark-adapt time
  - Light leak has developed into the instrument
  - Contamination of the fluor solution with a radionuclide calibration solution
- Routine QC check of test source (using a flame-sealed, unquenched source) is below lower control limit
  - Wrong channel or range selected
  - Smudges on scintillation vial
  - Decay correction not used or improperly applied
- Test-source count rate appears to change during count interval
  - Cocktail separation has occurred during the count interval
  - Background has changed during the count interval
  - Insufficient dark adapt period
  - Temperature change of instrument
- Instrument check with unquenched source yields low readings
  - Source not fully inserted into instrument
  - Decay correction not used or improperly applied
- Test-source or QC count rate is unusually high
  - Contamination in cocktail from another radionuclide or higher concentration
  - Insufficient dark adaptation

15.6 Gamma Detection Methods

This section describes the measurement of gamma-ray activity. Since gamma radiation is a penetrating form of radiation, it can be used for nondestructive measurements of samples of any form and geometry as long as calibration sources of the same form and geometry are available. Radionuclides separation followed by sample digestion can be used to improve the detection capability of gamma-ray-remitting analytes by concentrating the analyte and reducing interferences. Attenuation of gamma radiation is generally small, but because of variations in sample density, sample thickness, container shape, or container thickness, it must be corrected either by using calibration sources that match the sample/container densities and containers or by appropriate mathematical formulas (Modupe et al., 1993; Venkataraman et al., 1999):

Photons interact with matter in one of three ways:

- Photoelectric effect, where all energy is transferred to an electron in the absorber matrix;
- Compton scattering, where an electron in the absorber matrix is scattered and only part of the initial photon energy is transferred to that electron; and
- Pair production, where the photon energy is converted to positron-electron pair in the vicinity of a nucleus.

For the photoelectric effect, the entire gamma energy is transformed into a detector pulse, eventually resulting in the full-energy peak (FEP) observed in the gamma spectrum. The Compton scattering effect is seen as continuous, broad band radiation (referred to as the "Compton continuum"), which terminates at the Compton edge. This is a distinct decrease in the recorded counts in the continuum. This edge occurs between 150 and 250 keV below the FEP. The remainder of the energy is carried away by the scattered gamma ray. Pair production requires a minimum gamma ray energy of 1,022 keV, since the sum of the rest masses of a positron-electron pair is this amount.

The energy of the gamma ray in the pair production effect is split between the formation of the positron and electron. The positron is a very short-lived particle and annihilates an electron in the absorber matrix. This annihilation process creates two 511 keV photons. These may or may not be detected by the detector. The energy spectrum recorded from this event may have five distinct peaks that appear to be gamma rays: the FEP (1,275 keV), a single escape peak (FEP-511 at 765 keV), a double escape peak (FEP-1,022 at 254 keV), a 511 keV peak, and a sum peak (FEP+511 at 1,786 keV). Figure 15.8 (page 15-80) shows some of these additional peaks.

The extent to which each of these effects is seen depends upon the gamma ray energy, the sample matrix, and the detector material. The mass attenuation coefficient is a measure of the probability that a gamma ray will interact with the absorbing medium. Figure 15.6 shows the relative mass attenuation coefficients of each of the three predominant photon interactions with high-purity germanium.

Since different radionuclides emit distinct and discrete spectra of gamma radiation, the use of an energy discriminating system provides identification and quantification of all the components

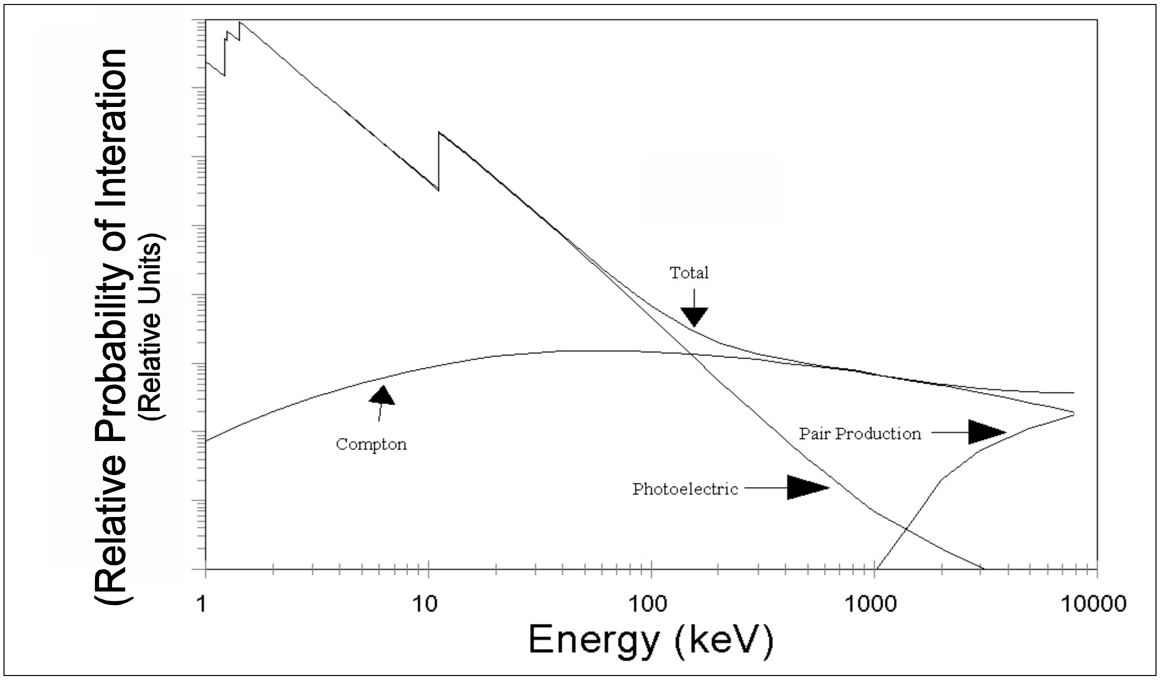


FIGURE 15.6 — Gamma-ray interactions with high-purity germanium

present in a mixture of radionuclides. General information on gamma-ray detectors and gamma counting is covered in the literature (Friedlander et al., 1981; ICRU, 1992; Knoll, 1989). Recent applications of gamma counting are given in several ASTM Test Methods (ASTM C758, C759, D3649).

Gamma counting is generally carried out using solid detectors since a gas-filled detector will not provide adequate stopping power for energetic gammas. The more commonly used solid detectors are discussed in this section.

15.6.1 Sample Preparation Techniques

Important considerations in preparing calibration sources for gamma-ray spectrometry are geometry (shape), size, and homogeneity (uniformity) of the source. Calibration sources can be in any reproducible shape or size, but the radionuclides need to be uniformly distributed throughout. A counting container that allows the source to surround the detector, thus maximizing the geometrical efficiency, is referred to as a "Marinelli" or "reentrant" beaker (Hill et al., 1950). It consists of a cylindrical sample container with an inverted well in the bottom of the beaker that fits over the detector.

Two important advantages of gamma-ray spectrometry are the ability to measure more than one radionuclide simultaneously and the elimination or reduction of sample dissolution and radionuclide separations (i.e., gamma-ray spectrometry can be a nondestructive sample analysis).

15.6.1.1 Containers

Source configurations for nondestructive analyses generally are selected to optimize counting efficiency for the particular sample type and its expected activity. This also means that the containers are selected to minimize attenuation of the particular gamma rays, and to have sufficient integrity to keep the sample intact. For quantitative analysis, the calibration and test sources (samples) are counted in the same type of container. Different types of containers might be used for qualitative analyses.

15.6.1.2 Gases

Sample containers for gasses will generally have a provision so that the container may either be evacuated (using a vacuum pump) or purged (having sufficient sample so that the container may be flushed with approximately 10 sample volumes). This is generally accomplished using inlet and outlet isolation valves. These may be constructed of either plastic, stainless steel, or glass. These containers are then brought to atmospheric pressure, which minimizes losses because of pressure differential, during storage, transport and counting. Analysis at pressures other than atmospheric may be made, however, a correction using the ideal gas laws needs to be made.

Sample containers for gaseous or atmospheric samples may use concentration devices to enhance the detection limits for certain radionuclides. A concentrated sample matrix, such as a solid, represents the aerosol collected. The detector calibration needs to be performed with a matrix and source container that matches the test source and container. Examples of this are:

- Charcoal canisters (aluminum cans that contain inlet and outlet retention elements and are filled with charcoal and may be impregnated with potassium iodide, KI or triethylene diamine [TEDA]), used for iodine or noble gas collection.

- Molecular species filtering (EPA, 1990) that collects four primary species of iodine on separate cartridges so that they can be measured individually. Air is pulled first through a particulate filter and then through the cartridges placed in series.

- Zeolite canisters (aluminum cans that contain inlet and outlet retention elements and are filled with silver-alumino-silicate materials) for iodine collection.

In each of these cases the distribution of the radionuclide on the medium most likely will not be uniform. This is especially true for the filled canisters where the flow inlet end will have a significantly higher loading than the outlet, unless the medium has gone to saturation. The positioning of the sample container on the detector in a reproducible geometry to that of the standard becomes very important for these types of samples.

15.6.1.3 Liquids

Containers normally used for liquid analysis are:

- Marinelli beakers of 0.25 to 4 L to measure liquid sources (water, milk, and food samples blended to a uniform slurry);
- Plastic bottles of standard sizes such as 250, 500, or 1,000 mL; or
- Scintillation size vials (20 mL) for samples of more significant activity.

If greater counting efficiency is required, the source size can be reduced, allowing a greater amount of the laboratory sample to be counted and in a more favorable geometry. Examples of such processes are:

- Reducing the volume of water samples by evaporation;
- Reducing the volume of water samples by coprecipitating the desired radionuclides and collecting them on filter paper; and
- Concentrating the radionuclide on a resin.

It should be noted that the final sample configuration should not only be homogeneous, but should also match the geometry of the standard used to calibrate the detector.

A radionuclide in solution may be purified by chemical techniques (i.e., impurities removed), after which the solution can be transferred to a planchet and evaporated to dryness, as described above. Evaporation of a laboratory sample after purification is used by the EPA to measure ^{228}Ac in the analysis for ^{228}Ra (EPA, 1984a), and sources of thorium, isolated from marine carbonates, have been prepared by evaporation for measurement (Blanchard et al., 1957). For the analysis of test sources having significant solids containing low-energy gamma emitters, absorption curves can be prepared. Solid samples may need to be air-equilibrated prior to counting to ensure that a consistent moisture film is present, which is accounted for by self-absorption measurements in standards and samples.

In the case of all dry sources, steps should be taken to prevent solids from exiting the test-source mount or container, which will affect the measurement and, in time, contaminate the detector.

15.6.1.4 Solids

A variety of containers are used for solids analysis such as:

- Cylindrical plastic containers of various volumes, such as the 400 mL “cottage-cheese container,” and Marinelli containers;
- Planchets and plastic culture dishes of various diameters to measure precipitates, air filters, etc.;

- Aluminum cans (like the "tuna can" configuration) of a standardized volume into which solid sources can be compressed, and sealed, if desired, to retain volatile materials; and
- 47 mm (2 inch) diameter, 0.45 µm pore size particulate filters, which are enclosed in a petri-style dish after sample collection.

Sometimes, other samples may be reduced in volume by:

- Reducing the size of vegetation samples by compression into a large pellet or by ashing, if volatile radionuclides are not of interest; and
- Reducing the size of filter samples by digestion or ashing, if volatile radionuclides are not of interest.

Many of the sizes of these containers have been retained for historical consistency (PHS, 1967a).

Solid samples analyzed directly by gamma-ray spectrometry do not need to be dried prior to analysis as do samples for alpha or beta counting. However, it is important that the sample and standard geometries match, and that the sample water content should be known so that dry-weight concentration can be calculated.

15.6.2 Sodium Iodide Detector

Sodium iodide has a high density, which makes it an attractive solid material for detecting high-energy gamma radiation. The crystal is activated with 0.1–0.2 percent thallium to improve its scintillation characteristics in the visible range. In scintillators such as NaI(Tl), the gammas interact by excitation of electrons in the valence (or bound) states of the atoms to an excited state called the conduction band. Energy is released as light (visible and UV) photons when the electrons return to the valence band. These scintillations are easily detected and amplified into useable electrical pulses by a photomultiplier tube. The NaI(Tl) detector is the recommended detector for gross-gamma or single-radionuclide counting because of its high efficiency and room temperature operation.

15.6.2.1 Detector Requirements and Characteristics

The sodium iodide crystal usually is sealed in an aluminum enclosure called a "can." The crystal is hygroscopic and sensitive to shock and fracture. The geometry of the detector "can" may be flat or well shaped, but numerous shapes have been made for specific applications. One of the most common sizes for the detectors is the 7.5×7.5 cm (3×3 inch), but they can come in many sizes, including some specially constructed to contain several hundred pounds of the scintillator. The well-shaped detectors are of higher efficiency for the same volume of detector. This particular characteristic allows almost a 100 percent efficiency (so-called 4π geometry) for low-energy gamma-emitting test sources that can fit inside the well.

A gamma energy of 300 eV will release about ten light photons when it interacts with the crystal. This is the minimum energy necessary to create a photoelectron at the first dynode of the PMT. The PMT is optically coupled to the base of the NaI(Tl) detector to minimize any loss of photons, and maximizing efficiency. The size of the final voltage pulse (referred to as the "pulse height") received from the PMT is directly related to the energy of the gamma which interacted with the sodium iodide crystal. Electronic circuitry connected to the PMT output can perform pulse-height-analysis (PHA). This is merely counting the number of events with a certain pulse height. The output of the PHA can then be stored using a multichannel analyzer (MCA which is subsequently displayed on a screen), or summed over a specified energy range (this device usually referred to as a "scaler" or a "single channel analyzer," SCA).

The following components complete the NaI(Tl) gamma-ray spectrometry system:

- HIGH-VOLTAGE POWER SUPPLY. 1,000 to 3,000 volts DC regulated to 0.1 percent with a ripple of not more than 0.01 percent.

- PRE-AMPLIFIER/AMPLIFIER. The combination shapes and linearly amplifies the PMT output to a maximum of 10 volts.

- MULTI-CHANNEL ANALYZER (MCA). The amplifier output is directed to the PHA. The PHA will sort the individual events and send them to discrete energy registers so that a count vs. energy graph can be displayed. The system usually has a low energy cut off to eliminate low energy background signals which will increase MCA processing time.

- SINGLE CHANNEL ANALYZER (SCA). A single-channel discrimination system is set with a lower and upper level discriminator (LLD and ULD). The lower limit is usually referred to as the "threshold" and the difference between the two limits is the "window." Only those pulses from the amplifier within the window will be sent to the scaler. Any pulses lying outside the preset limits are rejected. The scaler takes the sum of all counts within the window for a pre-set time. The SCA application of a NaI(Tl) detector commonly is used to analyze gamma-ray emitters (such as ^{85}Sr) when they are used to monitor chemical yield.

- BETA ABSORBER. A beta absorber of 3–6 mm of aluminum, beryllium, or poly(methyl methacrylate) should completely cover the upper face of the detector to prevent betas from reaching the detector.

Figure 15.7 is a gamma-ray spectrum of ^{137}Cs collected using a NaI(Tl) detector. The features of note in this spectrum are:

- The FEP at 661 keV;
- The Compton edge at about 470 keV;
- The backscatter peak from the detector shielding at about 215 keV;

- A broad peak at about 35–40 keV as a result of the photoelectric absorption of the 37.4 keV barium K-shell X-ray (from the Cs decay) and the 35 keV iodine K-shell X-ray (from the iodine in the detector); and
- The FWHM of about 53 keV.

One characteristic of a detector which helps to define its utility is the peak-to-Compton ratio. This is the number of maximum counts in the peak centroid channel of the FEP divided by the average number of counts in the Compton edge (ANSI/IEEE 325). For example, the peak-to-Compton ratio for ^{137}Cs would be the maximum counts in the 661 keV peak (assumed to be the peak centroid channel) divided by the mean counts per channel between the 440 and 490 keV Compton region. In Figure 15.7, this value is about 9.

Another characteristic is the FWHM of the detector. FWHM is the width of the peak at one half of the counts in the peak centroid. This characteristic is based on the range of energy levels available for the electrons to de-excite from after they have been promoted into the conduction band. Because the NaI(Tl) operates at room temperature this represents a broad range of energies. The value for the 661 keV peak here is about 53 keV. The FWHM varies slightly as a function of gamma ray energy for a NaI(Tl) detector.

A low-energy peak around 35 keV may be present as a result of the gamma-ray interaction with an iodine K-shell electron through the photoelectric effect. When the K-shell is filled by the

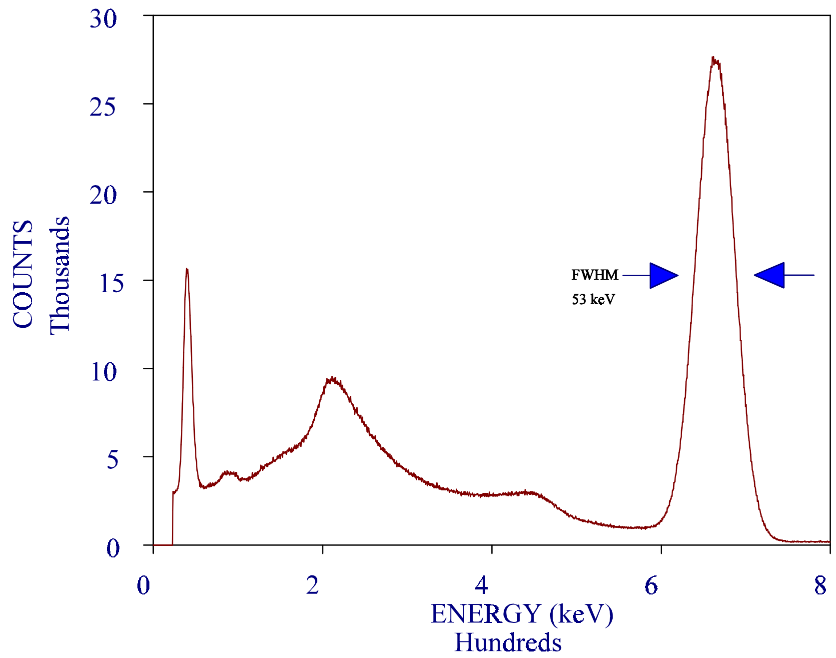


FIGURE 15.7 — NaI(Tl) spectrum of ^{137}Cs

Auger effect, the resultant release of 28 keV may be delayed enough from the original electron signal to be detected as a separate event. An additional feature (not discernable in this spectrum) is a small peak 28 keV less than the FEP, which is referred to as the "iodine escape peak." This effect is most prominent with gamma ray energies less than 150 keV. Superimposed on the low energy peak is also the X-ray emission from the decay of cesium.

Finally, the wide band at about 215 keV results from gamma rays emitted from the sample interacting with the detector shielding (usually lead) through the Compton effect. The Compton effect radiation is backscattered from the shielding to the detector. For gamma radiation in the range of 600–3,000 keV this backscatter area is from 180 to about 250 keV.

15.6.2.2 Operating Voltage

The crystal itself does not have a voltage applied to it. The voltage requirement is for the PMT. This depends on the manufacturer of the PMT, and ranges from 1,000–3,000 V DC. The remainder of the components of the system can be fed off of a 120 V AC power source. The power supply to the entire spectrometer should be on a filtered and regulated line.

15.6.2.3 Shielding

For most applications, NaI(Tl) detectors are shielded to reduce the X-ray and gamma-ray background from nonsample sources. However, the amount and type of shielding will depend on the particular application. For low-level environmental sample analyses, a typical arrangement is about a 13-cm thick lead shield (rectangular or cylindrical configuration) with its inner surfaces lined with cadmium then copper (or a thick copper sheet) to reduce lead X-rays and backscatter photons originating from the shield walls.

15.6.2.4 Background

Detectors have a certain background counting rate from naturally occurring radionuclides and cosmic radiation from the surroundings and from the radioactivity in the NaI(Tl) itself. The background counting rate will depend on the amounts of these types of radiation and on the sensitivity of the detector to the radiations. The most significant source of background for the sodium iodide detection system is the PMT. Thermionic noise is the spontaneous emission of electrons from the photocathode in the PMT, leading to a final pulse. This noise results in a background rate of about 50 cpm per cm^3 of crystal over the entire energy range. However this value is specific for each PMT used and may increase with PMT age.

Another contribution to the background can come from the PMT material itself. For low level counting applications, a quartz PMT rather than an ordinary glass PMT will yield lower count rates because of reduced levels of ^{40}K and ^{232}Th.

Shielding can also be a source of background radiation. Old lead should be used, since the contribution from naturally occurring ^{210}Pb ($t_{½} \approx 22$ y) and its progeny will lead to *bremsstrahlung* radiation from beta decay in the energy range <100 keV. Steel processed after World War II may contain small quantities of ^{60}Co.

15.6.2.5 Detector Calibration

Standards used for calibration of the NaI(Tl) detector should allow all of the photopeaks to be analyzed within a reasonable period of time (i.e., hours) and achieve less than 1 percent counting uncertainty (for the net peak area) in each photopeak used for calibration.

For a NaI(Tl) detector, the energy calibration should be checked on a periodic basis (weekly to monthly), using individual source energy standards (generally one radionuclide per source with only 2-5 gamma rays). This ensures that the individual gamma ray can be seen because of the wide energy resolution of the NaI(Tl) detector. The plot of gamma ray energy vs. channel number should yield a linear graph over the energy range used.

15.6.2.6 Troubleshooting

The three parameters that routinely should be checked and recorded are:

- Energy calibration (keV/channel),
- Counting efficiency (count rate/emission rate), and
- Gamma-ray peak resolution (FWHM).

With the exception of a complete detector or electronic component failure (no pulses are detected at the amplifier or PMT output), degradation of gamma-ray peak resolution will be the first indication that a detector is not performing properly or that electronic noise has been introduced into the counting system by electronic components, such as the pre-amplifier, amplifier, or MCA. Any indications that the detector efficiency is not within statistical limits of expected values should be recorded, and corrective action taken, because this is the parameter used to convert the observed count rate to a test-source activity. The energy calibration either should be recorded with the sample spectral data or the amplifier gain should be adjusted daily to a previously established constant value.

Sodium iodide gamma-ray spectrometry systems are extremely sensitive to both electronic and environmental conditions. Temperature changes can cause spectral shifts and improper nuclide identifications because of incorrect energy calibrations. Excessive humidity in the environment of the detection system can cause high-voltage arcing, which results in poor peak resolution or complete system failure. Poorly conditioned NIM power can introduce electronic noise that also will result in degraded peak resolution. Positioning and routing of cables among the detector, electronics, MCA, computers, and monitors may be important when evaluating electronic noise.

A nonreproducible count rate sometimes may be traced back to degraded cable connections or cracked insulation. These problems may be caused by bending, pinching, or compression of the cable during installation, or when moving shielding for the detector.

15.6.3 High Purity Germanium

The high purity germanium detectors (HPGe) have almost completely replaced the older lithium-drifted germanium detector. HPGe detectors have less than 1×10^{10} impurity atoms per cubic centimeter of germanium. The biggest advantages of HPGe detectors is that they may be warmed to room temperature without damaging the crystal, and the energy resolution is much improved over the lithium-drifted germanium detectors. Crystal sizes of more than 200 cm^3 can be made that significantly improves their efficiency over older style detectors as well.

15.6.3.1 Detector Requirements and Characteristics

HPGe detectors are maintained within an evacuated metal container (usually aluminum) referred to as the "can." The detector crystal inside the can is in thermal contact with a metal rod called a "cold finger." The combination of metal container and cold finger is called the "cryostat." The cold finger extends past the vacuum boundary of the cryostat into a dewar flask that is filled with liquid nitrogen. The immersion of the cold finger into the liquid nitrogen maintains the HPGe crystal at a constant low temperature. This helps to ensure the reproducibility of the electronic measurement as well as reduce spurious detector events (thermionic background).

In semiconductor detectors such as high-purity germanium the gamma photons produce electron-hole pairs and the electrons are collected by an applied electrical field. Detectors may have several different configurations and the location of the sensitive region of the detector is a function of how the detector was prepared. A common configuration is the cylindrical form in which the active detection region is a concentric cylinder within the entire detector crystal. This is referred to as a coaxial configuration. Additional information on the configuration and applications of HPGe detectors may be found at www.ortec-online.com, www.pgt.com, and www.canberra.com. A charge-sensitive pre-amplifier is used to detect the charge produced in the crystal, and produce an electrical pulse suitable for direct amplification. The detector pre-amplifier usually is an integral part of the detector/cold finger assembly in order to minimize the electronic noise and signal loss because of lengths of cable.

The output pulses from the pre-amplifier are directly proportional to the amount of energy deposited, which could either be total and included in the photopeak, or fractional and included in the continuum or escape peaks, in the detector by the incident photon.

Overall detector performance can be affected by count rate because reduced time constants are required which will cause some loss of resolution. When a photon interaction takes place (an event is detected), charge carriers in the form of holes and electrons are produced. The electrical field produced by the detector's high voltage bias supply causes these carriers to be swept toward the P (positive) and N (negative) layers of the detector. The time it takes the carriers to travel to the electrodes is called the "charge collection time." At very high count rates the detector continues to respond to events but the detection system may not produce reliable data. If a second (or third) event takes place while the first set of charge carriers are still in transit, the energy from the second event may not be recorded because of the detector insensitivity during the charge transfer to the electrodes. This phenomenon is known as detector "dead time." Generally the detector dead time is small compared to the ADC dead time. The ADC dead time is larger since it is processing and sorting all the signals from the detector. Another common event at high count rates is two gammas interacting with the detector simultaneously, their charge pulses getting added together, causing a sum peak. (See Section 15.6.3.3, "Troubleshooting," for a discussion of dead time problems.)

The description for electronic equipment associated with the HPGe detector is similar to the descriptions for the NaI(Tl) detector. The controls on electronic noise and voltage for each component is much more stringent for the HPGe detector.

Displayed spectra for HPGe detectors have different characteristics from the NaI(Tl) described in the previous section. HPGe efficiencies are lower for detectors equal in size to a NaI(Tl). However the energy resolution of the HPGe is much superior to that of the NaI(Tl). The energy required to cross the band gap in a germanium detector is on the order of 3 eV per event compared with 300 for NaI(Tl). Figure 15.8 shows the gamma spectrum for ^{22}Na. The FWHM of the gamma peaks here is about 2 keV, compared with the 60-70 keV for the NaI(Tl) detector. This characteristic is a function of energy and the Table 15.6 identifies how the FWHM will change for a particular detector as a function of energy.

TABLE 15.6 — Typical FWHM values as a function of energy

Energy, keV	100	600	1300
FWHM, keV	1.3	1.8	2.1

Peak-height-to-Compton ratio is another spectral parameter which is much improved for HPGe over NaI(Tl). The value for HPGe is between 30 and 50, compared to 9 for the NaI(Tl) detector.

OPERATING VOLTAGE

The germanium detector has a voltage applied directly to the crystal as opposed to the NaI(Tl) which has voltage applied to the PMT. The voltage for the HPGe is 1,000–5,000 V DC. The voltage supply unit for the detector should be on a line conditioner so that small variations in line voltage are normalized to a constant voltage. The line conditioner will also prevent power surges to the detector crystal which could destroy or severely alter its detection capabilities.

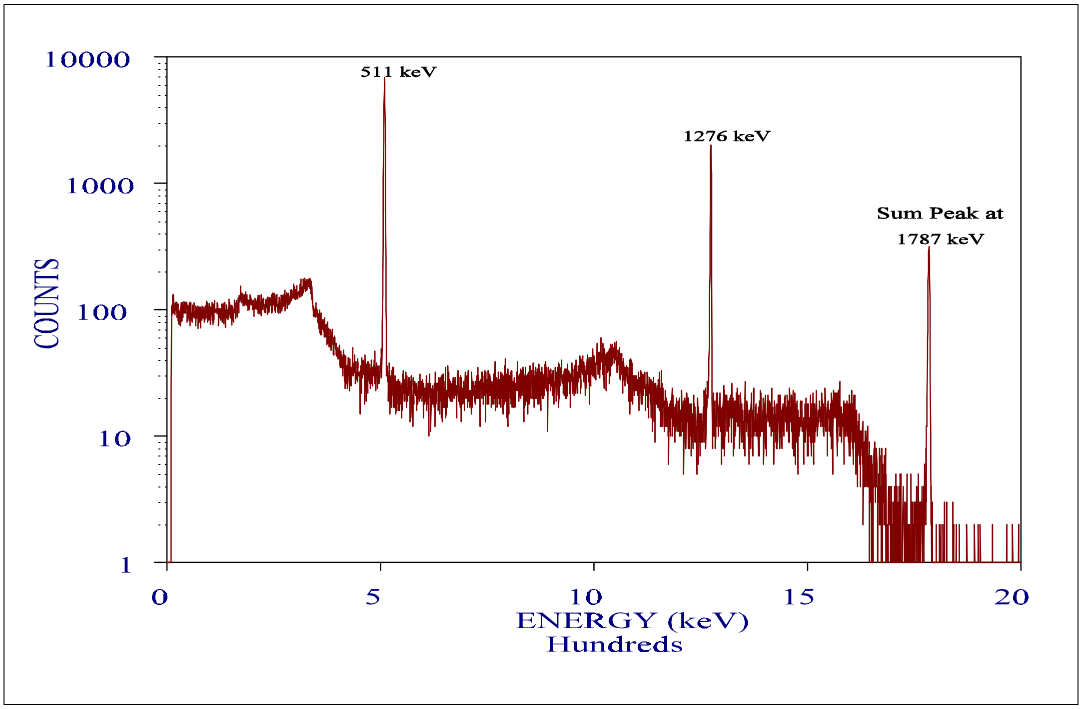


FIGURE 15.8 — Energy spectrum of ^{22}Na

Powering up a detector needs to be performed in a controlled manner at 50-100 volts/second to minimize shock to the detector crystal and maintain its performance (this is more critical for the initial 500 volts). Following this powering up a short equilibration period should be allowed prior to performing detector calibrations or QC checks. This period is somewhat detector-specific.

SHIELDING

Detectors need to be shielded from external radiation, such as naturally occurring radionuclides emitted from building materials (particularly concrete). Shielding should be constructed of "old lead," and steel members should be used with caution, because steel fabricated after World War II may contain traces of ^{60}Co. The inner surfaces of these shields typically are lined with cadmium then copper (or a thick copper sheet) to reduce lead X-rays and backscatter photons originating from the shield walls.

BACKGROUND

Detectors have a certain background count rate from naturally occurring radionuclides, cosmic radiation, and the radioactivity in the detection equipment. Because of the processing of the germanium to remove impurities it has become a negligible source of background radiation. The specific background gamma radiation will depend on the amounts of the nuclides present and on the sensitivity of the detector to the specific gamma rays.

Ideally, the material used for shielding should itself be free of any radioactive material that might contribute to the background. In practice, this is difficult to achieve as most construction materials contain at least some naturally radioactive species (such as ^{40}K, members of the uranium and thorium series, etc.). The thickness of the shielding material should be such that it will absorb most of the soft components of cosmic radiation. This will reduce cosmic-ray background by approximately 25 percent. Cosmic-ray interactions in lead shields will produce lead X-rays that are shielded typically by cadmium and copper liners. Such a shield is referred to as a "graded shield." Six millimeters of OFHC copper also can be used to reduce the cosmic-ray produced lead X-rays without the cadmium liner. Shielding of beta- or gamma-ray detectors with anti-coincidence systems can further reduce the cosmic-ray or Compton-scattering background for very low-level counting.

The gamma-ray background spectrum for a germanium detector has two specific features. The first is the general shape of the background counts versus energy function. The shape can be described as a $1/(E_\gamma)$, or hyperbolic. Part of this response is because of the decrease in detector efficiency as energy increases. The second feature is the presence of a 0.511 MeV peak corresponding to annihilation radiation. This is because of the interaction of high energy gamma/ cosmic radiation with the lead shielding via the pair production effect. The size of this peak should be constant (in terms of counts per unit time) as long as radionuclides with gamma energies greater than 1.02 MeV are not present in the sample being counted. This peak and the general background can change under some unusual conditions (like solar flares, or the 11-year sun spot cycle).

TEMPERATURE AND HUMIDITY

Humidity can have significant effects on the many cable connections that germanium detection systems have. The change in moisture can affect cable connection impedance, which ultimately can affect peak shape. The counting room should be maintained at 40-60 percent relative humidity.

There are two separate temperature effects that can be seen. The first deals with the detector itself. The band gap in the germanium crystal is affected by the absolute temperature, so it is maintained at -196 °C using a cryostat. The cryostats are designed to have minimum thermal leakage. However, each crystal responds to different cryostat temperatures from low levels of liquid nitrogen in the dewar in which the cryostat is immersed. Many of the newer systems have low-level monitors that alert the analyst to replenish the supply of liquid nitrogen. For those that do not have feature, addition of liquid nitrogen to the dewar should take place routinely (usually about every 1–2 weeks). The detector should be allowed to equilibrate for at least one hour after the refill before it is used for analytical work.

The other temperature effect is that of the room environment on the electronics. Although the detector and the electronics may be on a conditioned line, the instability of temperature in the room can cause the pre-amplifier, amplifier, and ADC/PHA portions of the system to respond erratically. The temperature of the room should be maintained in the 21–27 °C range.

15.6.3.2 Gamma Spectrometer Calibration

Most HPGe gamma-ray spectrometry systems are calibrated with mixed gamma-ray sources in a similar matrix and with the same geometric form as the samples to be analyzed. This requires the purchase of several different calibration sources. Commercial calibration sources of single or mixed gamma-ray emitters in a matrix of known chemical composition and density can be prepared in user-supplied containers. Calibrations based upon these sources can then be adjusted to correct for any differences in composition and density between the calibration source and the test source (Modupe et al., 1993).

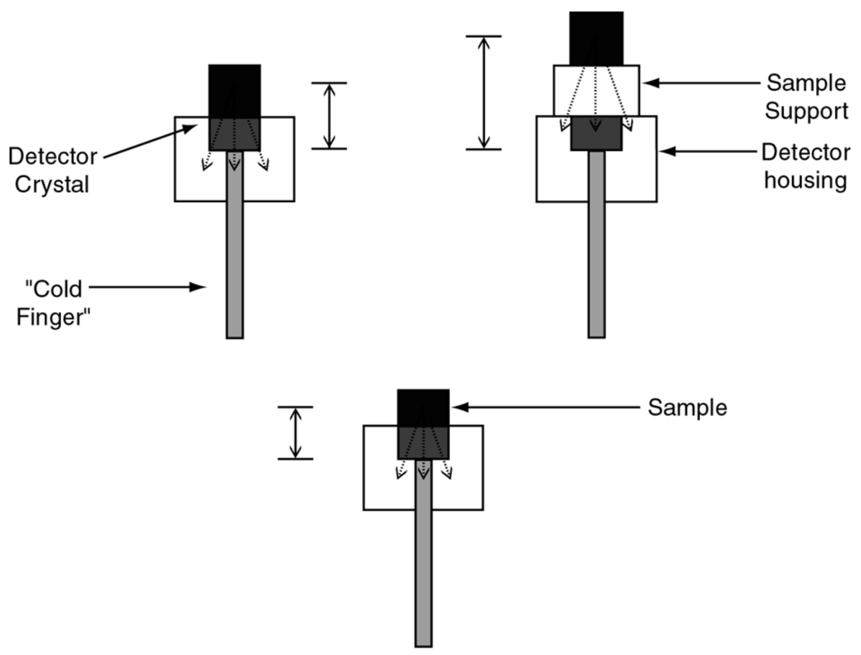
Counting efficiencies are determined by measuring a known quantity of the radionuclide(s) of interest within a similar matrix and with the same source-detector configuration as the sources requiring analysis (NCRP, 1978; ASTM, D3649). This eliminates any effect that might be caused by differences in standard and sample characteristics, e.g., density, moisture content, shape, and size. Efficiency curves may be prepared for a detector by measuring a variety of standardized sources having different photopeak energies under identical conditions as the unknown test source (Coomber, 1975; ANSI, 1991).

MARLAP recommends that calibration data for gamma-ray spectrometry calibration be obtained from the National Nuclear Data Center at Brookhaven National Laboratory (www.nndc.bnl.gov/nndc/nudat/). Data required for calibration are the half-life of the radionuclide, its gamma-ray branching ratio, and the probability of producing conversion electrons. These are readily available for common radionuclides, including ^{210}Pb, ^{241}Am, ^{109}Cd, ^{57}Co, ^{58}Co ^{141}Ce, ^{139}Ce, ^{203}Hg, ^{51}Cr, ^{113}Sn, ^{85}Sr, ^{137}Cs, ^{54}Mn, ^{88}Y, ^{65}Zn, ^{60}Co, and ^{40}K. For more information on gamma-ray spectrometry calibration, see ANSI 42.14 (also see Section 16.3.1.6 on gamma calibration.)

Figure 15.9 shows an example of three different geometries that may be used for gamma counting the same sample configuration. It is necessary to calibrate each geometry for the detector since the distance from the detector has a significant effect on the number of photons that intersect the detector. This relationship is more significant for geometries or shapes that are close to the detector's active volume.

Table 15.7 shows the efficiency of different sample container configurations for a gamma-ray detector. The efficiencies cited are for a sample container placed in contact with the germanium detector surface. Counting efficiencies were obtained using a 55 percent HPGe detector (55 percent relative to a NaI(Tl) detector of 7.5×7.5 cm.).

Recently, calibrations of gamma-ray detectors using computer software and sample geometry modeling have been shown to be accurate when compared to a traditional mixed gamma ray



The dotted arrows represent the same solid angle, which subtends the detector from the different sample geometries. Sample shape and positioning will have a significant effect on the efficiency with which the detector "sees" the sample gamma rays.

FIGURE 15.9 — Different geometries for the same germanium detector and the same sample in different shapes or position

source calibration (Mitchell, 1986; Hensley et al., 1997). An analytical advantage of this system is that the analyst may be able to analyze a smaller portion of an unknown than the size and shape used for a traditional calibration.

TABLE 15.7 — Typical percent gamma-ray efficiencies for a 55 percent HPGe detector* with various counting geometries

Energy (keV)	Filter Paper	50 cm^3 Planchet	90 cm^3 Al Can	600 cm^3 Marinelli Beaker
60	15.6	14.6	11.6	5
88	15.2	14.2	11.3	7.4
122	15.1	12.6	10.2	8.4
166	12	9.6	8	7.9
279	9.3	7.4	6	6.1
392	7.2	5.5	4.5	4.8
514	5.4	4.2	3.5	3.8
662	4.7	3.6	3	3.1

Energy (keV)	Filter Paper	50 cm^3 Planchet	90 cm^3 Al Can	600 cm^3 Marinelli Beaker
835	3.9	2.9	2.4	2.7
898	3.1	2.4	2.1	2.2
1115	3	2.3	1.9	2.1
1173	2.6	2	1.7	1.8
1333	2.3	1.8	1.5	1.6
1836	1.7	1.3	1.2	1.3

[*] Although the counting efficiencies listed above were obtained with a 55 percent HPGe detector, the calculation of counting efficiencies by extrapolation for detectors with different relative efficiencies is not possible. This is because detectors with the same relative efficiency may be of significantly different dimensions thus producing a detector/sample solid angle very different than what was used to prepare this table.

15.6.3.3 Troubleshooting

Troubleshooting can fall into two separate arenas. One for the electronic performance of the system and the second for interpretation of the gamma-ray results. The former usually involves the assessment of routinely measured parameters and careful examination of the system hardware when measurements are out of the norm. The latter involves a more fundamental understanding of the interactions of radiation with matter and detectors, and may require deductive reasoning.

ELECTRONIC MECHANICAL EFFECTS

Gamma-ray spectrometry systems have many parameters that should be monitored routinely to establish the characteristics of the system. The following should be monitored on an appropriate frequency (as discussed in Section 18.5.6 of Chapter 18, *Laboratory Quality Control*):

- Peak centroid of standards vs. channel number;
- FWHM of peaks for at least three energies over the range of 100–2,000 keV; and
- Detector efficiency of a separate source (not the calibration source) with energies at high and low keV values.

These parameters form the basis for identifying problems with the detection system. Some examples of how these parameters are used to determine the cause of problems are listed here:

- FWHM of 1,173 keV peak normally is 2.0 keV and now is 3.0 keV. Peak broadening can be a sign of low liquid nitrogen level in the dewar or warming of the cryostat. This type of effect can occur when cryostat refills are based on routine, without consideration for sudden changes in ambient temperature.

- Centroid of 662 keV peak has continued to shift steadily towards lower channel numbers:

The spectroscopy amplifier may be aging and needs replacement.

- Spectrum collection appears erratic (stop and go): Moisture condensation on cable connections can be creating variable impedance problems. Check room humidity.

- Low energy "pile-up" on a quality-control or background count appears higher than normal: Room temperature may have increased causing an increase in thermionic/electronics noise.

- Efficiency of 121 keV peak is consistent but lower than normally expected for several days in a row. Look at the test-source positioning method used in the system. Often the same detector uses plexiglass sample platforms and Marinelli beakers without the platform. If the test-source platform has not been repositioned the same as it was for the calibration source (considering that rotational positions on the detector surface are different), efficiency will be affected.

RANDOM AND COINCIDENCE (CASCADE) SUM PEAKS

At high count rates, random sum peaks may occur. Two gamma-ray interactions may occur within the resolving time of the detector and electronics and are summed and seen as one pulse. For a detector of resolving time, t, and a count rate of A counts per unit time, the time window available for summing is 2At (since the count summed could occur as early as t before or as late as t after the other count) and the probability of another count at any time is simply A. Therefore, the sum count rate will be $2A^2t$ in unit time. Random summing is strongly dependent on the count rate A. If summing occurs, it can be reduced by increasing the sample to detector distance. Therefore, if a 2,000 keV event arrives while a 1,000 keV event is in transit, the detector would see a single 3,000 keV event, producing a random sum peak, and not recording counts for the individual 2,000 and 1,000 keV gamma events. When the detector starts reporting more sum peaks than valid events, you have exceeded its count rate capability. Random pulse summing or pulse pileup can also cause peak shape and risetime problems. But the real upper limit to a detector throughput is pulse summing. This problem can be reduced or eliminated by reducing the number of events the detector sees (by moving the sample further away), collimating the sample, or using a smaller, less-efficient detector (the smaller the detector the shorter the charge collection time, which means a higher count rate limit). Modern electronics, both conventional analog and digital (pre-amplifiers, amplifiers, and analog-to-digital converters) are capable of processing 100,000 cps without any significant loss of peak resolution. This is because of the very short time constants (resolving time) these systems are capable of producing. Peak shifts also may occur with high count rates and short time constants.

Well counters that have very high efficiencies are prone to summing, because for a given source strength, the count rate is higher than for a detector of lower efficiency. For moderate and high source strengths, the trade-off is a poor one; the well counter is best suited for low-level work where its high efficiency is an important advantage.

Cascade summing may occur when nuclides that decay by a gamma cascade are counted. In this instance, a radionuclide in an excited state emits a gamma ray and de-excites to a lower energy level. The lifetime of the lower energy level is so short that the emission of a subsequent gamma ray from that state is anisotropic with respect to the first emission (the nuclear relaxation time between events is too short, and the gamma rays are emitted in the same direction from the nucleus). The second gamma ray is seen by the detector in the same timeframe as the first gamma ray. Co-60 is an example; 1,173.2 keV and 1,332.5 keV from consecutive, excited state, decay events may interact with the detector simultaneously, giving a 2,505.7 keV sum peak. Another example of cascade summing occurs when counting ^{22}Na close to the detector (Figure 15.8). The positron emitted by ^{22}Na creates a 511 keV gamma ray. When this gamma ray interacts with the detector in the same time frame as the emitted gamma ray following the positron emission, a 1,786 keV sum gamma ray is observed (511 + 1,275 keV). Cascade summing may be minimized by increasing the source-to-detector distance

ESCAPE PEAKS

Gamma-ray interaction with solid materials results in pair production formation (β^+ and β^-) when the energy of the incident gamma is greater than 1,022 keV. However, the β^+ particle can create certain artifacts by the way it interacts with matter. Once formed, the β^+ has a very short lifetime. It loses all of its kinetic energy to detector electrons in a time frame commensurate with the original event. When the β^+ particle annihilates it forms two 511 keV gamma rays. If both of these gamma rays escape the detector without interacting, a peak 1,022 keV lower than the FEP is seen. Sometimes only one of the gamma rays will escape the detector, and a peak at 511 keV lower than the FEP is realized. These two artifacts are referred to as double and single escape peaks, respectively.

The size of these peaks relative to the FEP is dependent only on the detector material and no other characteristics. The ratio to the FEP is constant and thus these peaks are usually only seen after very long count times or with very high activity samples.

MULTIPLETS AND INTERFERING GAMMA RAYS

A distinct advantage of using an HPGe detector is that it may be possible to analyze a sample for gamma emitters without radiochemical separation steps. This is possible because of the better resolution (FWHM) of the gamma-ray spectrometry system and the improvement in software, which can resolve gamma-ray peaks within a few keV of each other. For example, using a HPGe detector spectrometry system, the 1,115.5 keV photopeak of ^{65}Zn easily can be resolved from the 1,120.5 keV photopeak of ^{46}Sc. However, difficulties arise in quantifying the area under each photopeak when the two photopeaks are not separated by more than an energy differential equivalent to the FWHM peak resolution at that energy. When the differential of two gamma-ray energies is less than twice the FWHM, a single composite peak (wider than normal) may be observed in a spectrum. The composite peak is known as a “doublet” or “multiplet.” The resolution and quantification of photopeaks of a multiplet requires special software subroutines. In the previous example with ^{65}Zn and ^{46}Sc, a ^{214}Bi photopeak at 1,120.3 keV would form a multiplet peak with the 1,120.5 keV ^{46}Sc photopeak because the difference between the gamma-ray energies is less than the FWHM at 1,120 keV. In this example, a sufficient quantity of ^{214}Bi would generate an interfering gamma-ray photopeak for the ^{46}Sc photopeak, the analyte of interest. If an interfering gamma-ray peak is present, the analyst can employ one of three things:

- Find an alternate gamma line for the radionuclide where no interfering gamma ray exists;
- Allow the activity of the interfering gamma ray to decay (if it is shorter-lived) and then count the radioisotope of interest; or
- Perform radiochemical separation.

Many radionuclides emit more than one gamma ray. However, each gamma ray may not be emitted with each radionuclide decay event. This fraction of time that a gamma ray is emitted may be known as the fractional abundance or branching ratio. When a gamma ray is used to identify a radionuclide, and the radionuclide has other gamma rays that it emits, these other gamma rays should be present in the gamma ray spectrum (corrected for efficiency) in the same fractional ratio for the theoretical case. If this is not the case, then an interfering gamma ray may be present. For example, a gamma ray is found at 241 keV and potentially identified as ^{88}Kr. The fractional abundance of this line is 0.003. Kr-88 also has a gamma ray at 196 keV with a fractional abundance of 0.26. If this gamma ray is not present, or not present in the correct ratio, then an interfering gamma most likely exists. In this particular instance a likely candidate is ^{214}Pb (241.9 keV).

SPECTRUM DEGRADATION

Troubleshooting gamma ray spectra problems can be difficult. Gamma ray shape and positioning are the key characteristics that help to identify problems. The shape of a gamma-ray photopeak may appear to be Gaussian. However, it is best described by three different curves. A low-energy exponential, a middle Gaussian (about the centroid), and a high energy exponential (more drastic drop in events per energy than the low energy exponential). Upon close examination, the true gamma-ray peak will always appear to be "leaning" towards the low energy end. Listed here are some parameters that when changed cause specific effects that may be easily corrected. Some of these effects may take place during a sample count. If this happens, the effects may be more difficult to sort out.

Temperature. Changes in room temperature will affect the electronics for the amplifier and MCA units. The most common effect that can be seen from this is that the FWHM of the peak will increase (the peak will upon close up examination appear to be a true Gaussian). Usually this is most pronounced when the room temperature increases more than 3-4 °C. Maintaining the count room at a constant and moderate temperature will avoid this problem.

Humidity. Moisture within the gamma-ray detection system results from condensation on connectors. This can have irreproducible effects, because the heat generated by the electronics can cause the condensed moisture to evaporate. A common effect observed, which is related to humidity, is an irregular peak shape. A test or calibration source known to have only one gamma ray may appear to be a multiplet if humidity is effecting the system.

Voltage shifts. Changes in the 120 V AC power to the high-voltage power unit, which are not compensated for by a line conditioner, will cause the peaks to move. Thus gamma rays may appear at energies several keV different from where they are expected. The software will identify the gamma rays as radionuclides, but they will be unfamiliar to the analyst. This is the key to check line voltage changes. This may or may not cause a change in the FWHM since voltage changes may only occur at discrete times (the so called “5 o’clock effect”).

Low Liquid Nitrogen. Gamma-ray FWHM will begin to increase and the low-energy pile up pulse rate will increase. The obvious fix is to add more liquid nitrogen to the dewar. However, if this happens unexpectedly (i.e., in between normal fillings), cryostat integrity or thermal contacts should be checked.

Vibration. High frequency vibration can establish electronic variations in the signals between the amplifier and ADC. One common effect is that the FWHM of the peaks will increase. Another effect is that “new” peaks that do not correspond to known radionuclides may appear. The vibration may be transmitted to the preamplifier/amplifier through the detector shielding or through the cryostat. Dampeners such as foam or rubber may help to reduce this problem.

15.6.4 Extended Range Germanium Detectors

The extended-range germanium detectors are constructed slightly differently than the normal HPGe coaxial detectors. Normally, the lithium-diffused junction (which is on the outside surface of the crystal) is about 0.5–1.5 mm thick. Also, these detectors will be encased in an aluminum detector housing. The combination of these two factors effectively shields the sensitive area of the detector from gamma rays with energies below about 40 keV. The extended range detector is a coaxial germanium detector having a unique thin-window contact on the top surface and a thin beryllium cryostat window, which extends the useful energy range down to 3 keV. The physical characteristics of the extended-range detector are shown in Figure 15.10.

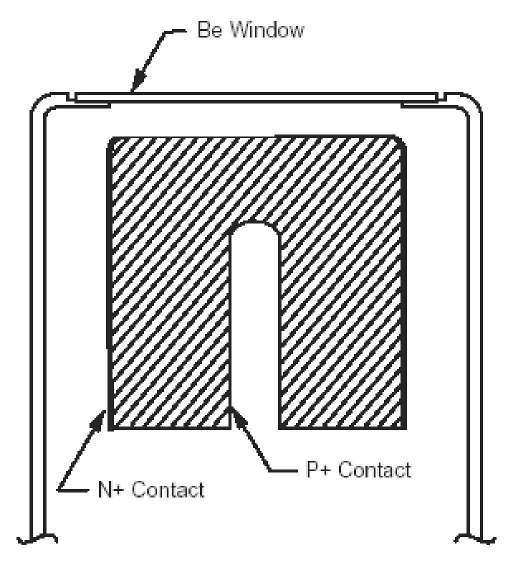


FIGURE 15.10 — Extended range coaxial germanium detector

15.6.4.1 Detector Requirements and Characteristics

The FWHM of this detector at 22 keV ranges from 0.7 (for a low efficiency detector) to 1.2 keV (for the higher efficiency detectors). The beryllium window allows for the passage of the low-energy gammas ray to the active detector area. This makes the handling of samples at the detector surface very important. It also means that if the sample container has a higher Z value than beryllium, the container may provide more shielding from gamma rays than the detector window.

Voltage requirements of the detector are similar to the HPGe detectors, and are specified by the manufacturer. The shielding requirements for this type of detector will be the same as for the standard coaxial detector. It is important to note, however, that since the range is extended into the X-ray region of elements down to aluminum, it would not be unrealistic to see X-rays from the interaction of sample gamma rays with materials of construction of the sample container, etc.

Similarly, the total background at low energies will be affected significantly, because the detector window will allow a greater number of photons to reach the detector surface (as beryllium does not shield as much as the traditional aluminum detector barriers). This also means that the ADC dead time may increase significantly because of the increased number of photons being processed by the system. Dead time increases should be monitored closely, because they will affect the quality of the peak shapes. Temperature and humidity considerations for these type detectors are similar to those of the standard HPGe detectors.

15.6.4.2 Detector Calibration

Calibration of extended-range germanium detectors is the same as for normal coaxial germanium detectors (Section 15.6.3.2, "Gamma Spectrometer Calibration"). However, since the active area allows quantification of gamma rays down to about 3 keV, additional gamma emitters with peaks in the range of 60 down to about 5 keV need to be used to perform calibration. One of the radionuclides that can serve this purpose is ^{109}Cd, which has a gamma peak at 88 keV and silver K_α X-rays (the electron capture decay converts the cadmium nucleus to a silver nucleus before the electron cascade) at 22 keV. One of the important characteristics of the detector is that the ratio of the 22 to 88 keV peak intensities should be about 20:1 for a properly operating system. Figure 15.11 shows a calibration curve for the extended range compared to the normal coaxial detector. The extended range detector has a discontinuity at 11 keV because of the germanium K-shell absorption edge.

Coincidence summing of X- and gamma-rays emitted from certain radionuclides should be considered during detector calibration. In many cases, radionuclide-specific calibrations are required, because coincidence summing effects for certain radionuclides having high X-ray emission rates produce lower than expected efficiencies for the gamma-ray energy.

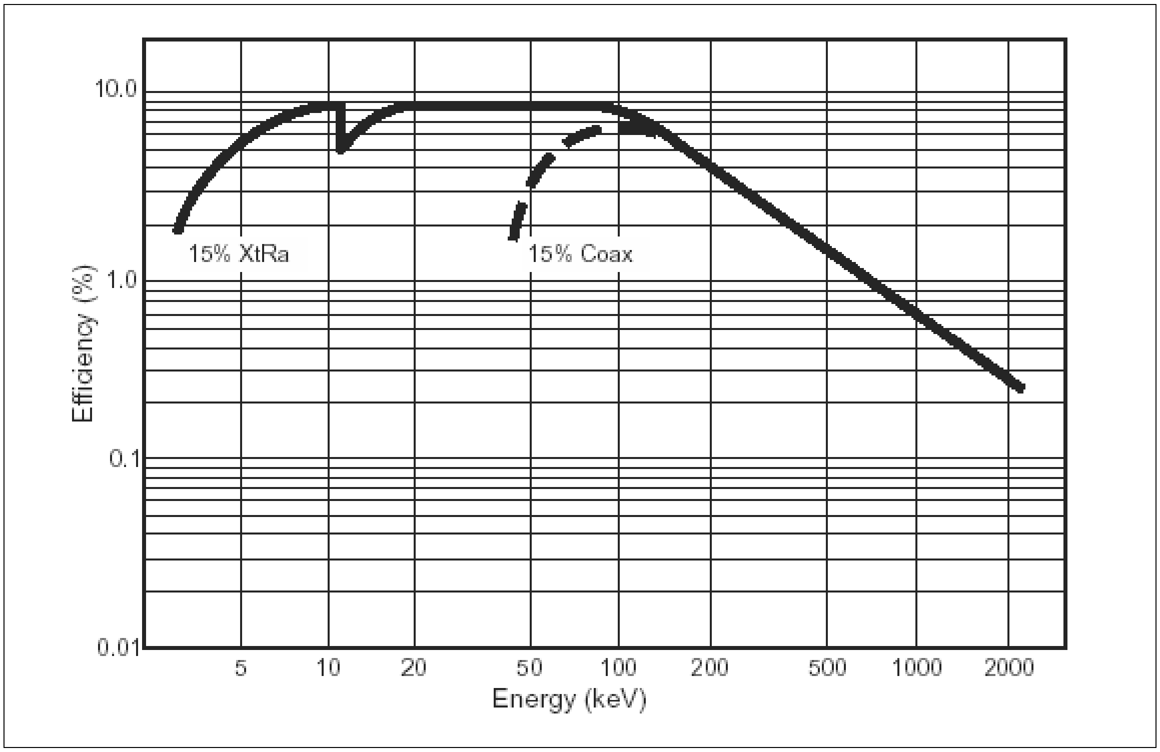


FIGURE 15.11 —Typical detection efficiencies comparing extended range with a normal coaxial germanium detector

15.6.4.3 Troubleshooting

Troubleshooting information in Section 15.5.3.3 ("Detector Calibration") applies to this detector as well. It should be noted, however, that because an extended range of energies is available, additional random sum peaks may be encountered that will be close in energy to the principal gamma rays. For example, if the source has ^{60}Co (1,332 and 1,173 keV peaks) and ^{109}Cd (22 keV peak) present, at high count rates additional peaks may be observed at 1,354 and 1,195 keV.

15.6.5 Special Techniques for Radiation Detection

15.6.5.1 Other Gamma Detection Systems

A variety of other methods and detectors are in use to analyze gamma radiation. Although they do not find general use in the analytical community, they are noted here.

OTHER GERMANIUM DETECTORS

The low-energy germanium (LEGe) detector has a thin beryllium window and a small detector volume. The intent is to focus on the gamma-ray energies in the 10–200 keV range. The small volume reduces the efficiency to higher energy gamma rays allowing good resolution of low-energy gamma rays.

The reverse electrode germanium (REGe) detector changes the positioning of the N- and P-type materials on the detector crystal. The P-type material is on the outer periphery of the crystal where the significant interaction of the gamma rays with the crystal occur. This P-type junction is less susceptible to radiation damage. Thus, the REGe is best suited for high activity samples.

MIXED ELEMENT DETECTORS

Bismuth germanate ($Bi_4Ge_3O_{12}$, or BGO) is a very effective gamma-ray absorber because of the high average Z value from the bismuth. A BGO detector acts similarly to a scintillation detector but has only about 15 percent of the efficiency of a comparable size NaI(Tl). Its advantage over the NaI(Tl) detector is that it is nonhygroscopic and shock insensitive. Its major use is for when a high photopeak fraction needs to be measured (i.e., it yields a high peak-to-Compton ratio).

Cesium iodide crystals have the highest light output of all known scintillators. However because light output is not well matched to the sensitivity of the photocathode of PMTs the yield for gamma rays is only about 45 percent of the NaI(Tl) type detectors.

Cadmium-zinc-telluride detectors do not have energy resolutions as good as HPGe, but are better than NaI(Tl) detectors. Their biggest advantage is their ability to operate at room temperature. Generally they are used for high activity sources since their size is generally small.

15.6.5.2 Coincidence Counting

In coincidence counting, two or more radiation detectors are used together to measure the same test source, and only those nuclear events or counts that occur simultaneously in all detectors are recorded. The coincidence counting technique finds considerable application in studying radioactive-decay schemes, but in the measurement of radioactivity, the principal uses are for the standardization of radioactive sources and for counter background reduction.

Coincidence counting is a very powerful method for absolute disintegration rate measurement (Friedlander et al., 1981; IAEA, 1959). Both alpha and beta emitters can be standardized if their decay schemes are such that β–γ, γ–γ, β–β, α–β, α–γ, or α–X-ray coincidence occur in their decay. Gamma-gamma coincidence counting with the source placed between two sodium iodide crystals, is an excellent method of reducing the background from Compton scattered events. Its use is limited, of course, to counting radionuclides that emit two photons in cascade (which are essentially simultaneous), either directly as in ^{60}Co, by annihilation of positrons as in ^{65}Zn, or by immediate emission of a gamma ray following electron capture decay. Non-coincident pulses of any energy in either one of the crystals will be canceled, including cosmic-ray photons in the background and degraded or Compton scattered photons from higher energy gamma rays in the test source. Thus, the method reduces interference from other gamma emitters in the test source. When two multichannel analyzers are used to record the complete spectrum from each crystal, singly and in coincidence, then the complete coincident gamma-ray spectrum can be obtained with one measurement. The efficiency for coincidence counting is low since it is the product of the individual efficiencies in each crystal, but the detection limit is generally improved because of the large background reduction (Nielsen and Kornberg, 1965). This technique is often referred to as “two-parameter” or “multidimensional” gamma-ray spectrometry.

Additional background improvement is obtained if the two crystals are surrounded by a large annular sodium iodide or plastic scintillation crystal connected in anti-coincidence with the two inner crystals. In this case a gamma ray that gives a pulse, but is not completely absorbed in one of the two inner crystals, and also gives a pulse in the surrounding crystal, is canceled electronically (Perkins, 1965; Nielsen and Kornberg, 1965). This provides additional reduction in the Compton scattering background. Germanium detectors may be used in place of the inner sodium iodide crystals for improved resolution and sensitivities (Cooper et al., 1968). An example of an assay for plutonium content using passive thermal-neutron coincidence counting is given in ASTM C1207. Another example of passive thermal-neutron coincidence counting using a moveable californium source is given in ASTM C1316.

Coincidence counters normally are employed in radioanalytical laboratories for special purposes:

- For low-level measurements when the sensitivity of a beta- or gamma-counting system is inadequate,

- When spectrometric applications are needed to discern the emissions from several isotopes whose activities are very small; or

- For the standardization of radioactive sources by absolute counting (coincidence means).

Beta-gamma coincidence counting systems have been developed for the low-level measurement of ^{131}I in milk samples (McCurdy et al., 1980; Paperiello and Matuszek, 1975). The β-γ coincidence counting system reported by McCurdy et al. (1980) consisted of a 25.4 mm diameter, 1 mm thick Pilot B plastic scintillator optically coupled to a photomultiplier tube by a 12.5 mm plastic light pipe. The beta detector PMT was contained in an aluminum housing that inserted into a 100 × 100 mm NaI(Tl) well gamma-ray detector. The beta-gamma detectors were shielded by 100 mm of lead. The outputs from both detectors were coupled to separate timing single channel analyzers (TSCA) that produced fast positive digital logic output pulses when a detector signal satisfied the SCA voltage (energy) window. Since the decay time of the voltage pulse from the plastic scintillator detector is faster compared to a NaI detector pulse, the logic pulse of the beta scintillator was delayed by 200 ns. A coincidence pulse analyzer and a scaler were used to detect and record the coincident beta and gamma events from the detected decay emissions of ^{131}I. The coincidence counting system had a β-γ coincidence background for ^{131}I of 0.00045 cps (0.027 cpm) and a detection limit of 0.4 pCi/L for a 1,300 second counting interval. Figure 15.12 shows the detector efficiency plots for a beta-gamma coincidence counting system (McCurdy et al., 1980).

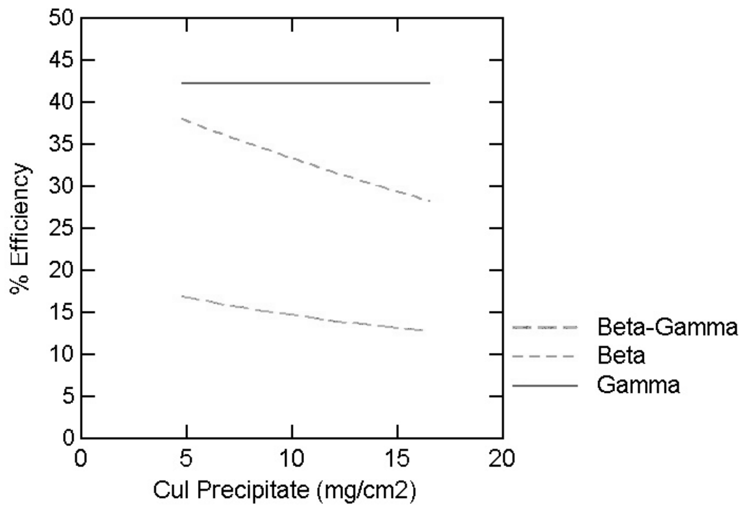


FIGURE 15.12 — Beta-gamma coincidence efficiency curve for ^{131}I

A α-γ coincidence counting system for the alpha emitting isotopes of radium has been reported by McCurdy et al. (1981). The same β-γ coincidence counting system used for the ^{131}I application was also used for the analysis of ^{228}Ra but the gamma-ray window was set for the gamma-ray photopeak for ^{228}Ac, the short-lived decay product of ^{228}Ra. For the α-γ coincidence counting application, the timing of output pulses of the TSCAs was changed to accommodate the long decay time of the alpha voltage pulse generated from the ZnS(Ag) alpha scintillator positioned next to the beta detector. The radium was coprecipitated with $BaSO_4$ and powdered ZnS(Ag) added to the final precipitate to form a 4π alpha detector. The Pilot B plastic scintillator was found to be transparent to the wavelength of the ZnS(Ag) light output. The gamma TSCA energy window was set for the 186 keV line of ^{226}Ra. The α-γ coincidence background was essentially zero for the 186 keV window over days to a week counting interval.

15.6.5.3 Anti-Coincidence Counting

Substantial background reduction can be achieved in beta and gamma counters by surrounding or covering the test-source detector with another detector also sensitive to beta or gamma radiation, and connecting them electronically so that any pulse appearing in both detectors at the same time is canceled and not recorded as a count. This is referred to as anti-coincidence shielding, and is used for obtaining very low backgrounds. This type of counter was used for many years in directional studies of cosmic rays, and was first applied to reducing the background of beta counters by Libby (1955) in his study of natural ^{14}C. The thick metal shielding (lead or iron) ordinarily used to reduce cosmic-ray and gamma-ray background should also be present, and is placed outside the anti-coincidence shielding.

Anti-coincidence shielding of gamma-ray detectors operates in a similar way, and is particularly useful in reducing the Compton continuum background of gamma rays (Nielson, 1972). Gamma rays that undergo Compton scattering and produce a pulse in both the detector and the anti-coincidence shield are canceled electronically. Ideally, only those gamma rays that are completely absorbed in the test-source detector produce a count that is recorded with the total energy of the gamma ray (FEP). There are second-order effects that prevent complete elimination of Compton scattering, but the improvement is substantial (Perkins, 1965; Cooper et al., 1968).

15.7 Specialized Analytical Techniques

Certain methods employing analyte detection techniques other than nuclear-decay emissions have been successfully used for the measurement of medium to long-lived radionuclides. Two of the three methods to be described determine the number of atoms or the mass of the radionuclide(s) of interest. The other method involves neutron activation of a limited number of the long-lived nuclides. As a result of the unavailability of a neutron source, neutron activation analysis is typically outside the capability of most radioanalytical laboratories.

15.7.1 Kinetic Phosphorescence Analysis by Laser (KPA)

Lasers can be used to excite uranium (ASTM D5174) and lanthanide complexes in solution. During or following excitation, the complex relaxes to a lower energy state by emitting photons of light that can be detected. The amount of light produced is proportional to the uranium or lanthanide element concentration.

The emitted light can be either fluorescence or phosphorescence. In either case, the detector is at right angles to the laser excitation. Fluorescent light is emitted immediately following ($<10^{-4}$ sec) the excitation of the complex. With phosphorescence, however, the emitted light is delayed, following the excitation. This enables the light source to be pulsed and the measurement to occur when the laser source is off, thus providing improved signal-to-noise over fluorescence. The light signal from organic material will decay promptly (since they have a relatively short lifetime) and will not be available to the detector, which is gated off. A pulsed nitrogen dye laser (0.1 to 0.5 mW range) often is used as the source, but other lasers can be used. Chloride and other ions can cause interference and may need to be removed before measurement.

KPA measures the rate of decay of the uranium or lanthanide characteristic energy. Measurements are taken at fixed time intervals. In aqueous solution, the uranium or the lanthanide element is complexed to reduce quenching and increase the lifetime of the complex.

An excellent reference describing the theoretical and functional aspects of a KPA unit and its application to the measurement of the uranyl ion in aqueous solutions has been written by Brina and Miller (1992) The authors reported a detection limit for UO_2^{+2} in aqueous solutions as 1 ng/L and a linear response from the detection limit to 5 mg/L. Experiences using a KPA unit for a variety of matrices that include water, urine, dissolved air filters, stack scrubber samples, soil, nuclear fuel reprocessing solutions and synthetic lung fluid were also reported. Matrices other than water may require dilution, preliminary sample dissolution and/or possibly chemical processing before analysis by a KPA unit. Consideration should be given to ensuring that the chemical yield for such processes is quantitative. Standard addition with internal standards may be needed for certain complex matrices.

There are several types of interferences that should be considered when using this method. The interferences can be differentiated into five categories: light absorption agents, such as yellow solutions and ferric iron; lumiphors, such as oils and humic acid; quenching agents, including alcohols, halides (except fluoride), and certain metals; competing reactions; and HCl. Chlorides interfere in the analysis by quenching the uranyl phosphorescence. Chemical interferences must be removed or their concentration reduced significantly by dilution to avoid inaccurate results.

KPA can be used to measure total uranium in water at concentrations greater than 0.05 µg/L (0.05 ppb). Samples above the KPA dynamic range of about 400 ppm can be diluted with dilute HNO_3 (1+19) prior to analysis. For the ASTM D5174 method, a 5 mL sample aliquant is pipetted into a glass vial, concentrated HNO_3 and H_2O_2 are added and the solution heated to near dryness. The residual is dissolved in 1 mL of dilute nitric acid, diluted with 4 mL of H_2O and a complexant is added. The 5 mL sample is analyzed by the KPA unit. Some reagents may have relatively short shelf life and need to be ordered accordingly. An interlaboratory study conducted for ASTM D5174 measured bias under 0.5 percent and between-laboratory precision (six laboratories) of 12 percent at a testing level of 2.25 ppb. For an individual laboratory, the relative precision was found to be about 4 percent at this level.

An automated KPA has also been applied to monitor uranium in stack filters and probe washes at a nuclear facility (Mann et al., 2002). The KPA was adapted to incorporate an automatic sampler and syringe pump permitting the unattended analysis of 60 samples. Methods were developed to eliminate interferences from inorganic and organic compounds. The reported detection limit was better than 1 ppb. Typical precision was about 5 percent.

Ejnik et al. (2000) have reported using KPA for the determination of uranium in urine. In this application, the researchers processed 10 mL of urine by successive and multiple dry (450 °C for 4 hours) and wet (HNO_3 and H_2O_2) ashing treatments prior to sample analysis. A detection limit of 50 ng/L and an observed concentration range between 110 and 45,000 ng/L were reported for this application.

15.7.2 Mass Spectrometry

Mass spectrometry is being used more frequently for the analysis of medium- to long-lived radionuclides. There are three types of mass spectrometers being used today for the radioanalytical applications including radiobioassay, process and waste stream characterization, effluent analysis and environmental sample analyses. The most readily available mass spectrometer for a radioanalytical laboratory is an inductively coupled plasma-mass spectrometer (ICP-MS). Some of the various ICP-MS units commercially available include single- and multi-collector magnetic-sector ICP-MS and quadrupole ICP-MS. These bench-top units are commercially available at a reasonable price. The other two types of mass spectrometers (accelerator mass spectrometers and thermal ionization mass spectrometers—see Sections 15.7.2.2 and 15.7.2.3) typically are found at national laboratories and universities or institutes, are expensive, and require special facilities including a clean-room environment for certain applications. Instrument descriptions and application references for mass spectrometry can be found in several sources (McDowell, 1963; Date and Gray, 1989; Platzner, 1997; de Laeter, 2001).

Time-of-flight plasma mass spectrometers have just recently appeared on the market. They have not yet compiled a historical record of performance that would permit reliable comparison with the ICP-MS. Similarly, Fourier-transform mass spectrometers are primarily used for research and cannot yet be considered practical for routine radiochemical analysis.

15.7.2.1 Inductively Coupled Plasma-Mass Spectrometry

ICP-MS is one of the most versatile and sensitive atomic spectroscopy techniques available. It can be used to determine the concentrations of over 70 elements. The detection limit of the technique extends down to the parts-per-billion range in soils and to the parts-per-trillion range in waters. This sensitivity makes ICP-MS an attractive complement to nuclear-decay emission-counting techniques in the radiochemical analysis laboratory. General references describing ICP-MS instrumentation, advantages and limitations of the methodology, and the potential applications of ICP-MS to radionuclide measurements include Date and Gray (1989), Platzner (1997), ASTM (STP1291), ASTM (STP1344), and Ross et al. (1993).

For very long-lived radionuclides (those with half-lives over 10,000 years, e.g., $^{234/235/238}$U, $^{239/240/244}$Pu, ^{99}Tc, ^{129}I, ^{237}Np), ICP-MS may be faster and more sensitive than nuclear-decay emission analyses. In addition, sample preparation for ICP-MS can avoid some of the analyte separation and purification steps required for nuclear-decay emission analyses, providing an additional dimension of time savings. Another important feature of ICP-MS is its ability to provide isotopic distribution information (e.g., ^{238}U vs. ^{235}U and ^{239}Pu vs. ^{240}Pu). This information is frequently useful in determining the age or origin of materials (ASTM C758, C759, C799). Typically, ICP-MS can typically detect femtograms (10^{-15} g) of a nuclide. Depending on the nuclide and required detection limit, the radioanalytical front-end chemistry may have to be conducted in a clean room or clean hood environment. In addition, high purity reagents may be required for certain radionuclides (e.g., uranium isotopes).

For more sophisticated measurements, at substantially higher cost, an ICP-MS with magnetic sector, instead of quadrupole detection can be applied. Sector instruments are capable of resolving species of very similar mass. For example, ^{99}Tc might be resolved from a contamination of ^{99}Ru with a high-resolution mass spectrometric detector. More typically, high resolution instruments are employed for their higher signal/noise ratio, and therefore superior detection limits.

The isotopic discrimination capabilities of ICP-MS make possible the calibration technique known as isotope dilution. In this procedure, a sample is analyzed for one isotope after having been spiked with a different isotope of the same element (e.g., analysis of ^{235}U might involve spiking with ^{233}U). The spiked sample is carried through all preparation and analysis steps; in this way, any matrix or procedural effects that might influence the ^{235}U signal will influence the ^{233}U signal to precisely the same extent. Final quantification relies on measuring the ratio of unknown (here the ^{235}U signal) to the known (^{233}U) signal. Isotope dilution is a way of generating highly precise and accurate data from a mass spectrometer and has been used in the characterization of many certified reference materials.

For environmental sample analysis, the elements or radionuclide of interest are normally concentrated and isolated chemically. However, for the measurement of uranium in ground and surface water, where the natural levels may be much greater than the instrument's detection limit, the samples may be diluted and then analyzed under certain conditions. Currently, there are two ASTM methods for the analysis of ^{99}Tc, ^{230}Th, and $^{232/234/235/238}$U in soils, C1310 and C1345. Natural background uranium concentrations in soil is between 3 and 5 µg/g in most geographical regions. The background thorium concentrations are slightly higher. The detection limits for uranium and thorium by the C1345 method are well below the background concentrations of these elements. The method described in C1310 has reported detection limits in soil for ^{99}Tc, ^{230}Th and ^{234}U as 12, 4, 0.7 Bq/kg, respectively. In addition, Uchida and Tagami (1999) proposed a rapid separation method using an extraction chromatographic resin for ^{99}Tc in sea- and ground water that has a detection limit of 0.3 mBq/L for 2 L samples. They also reported an ICP-MS method for the analysis of ^{99}Tc in soil that was used to measure the ^{99}Tc levels from worldwide fallout at concentrations of 5–30 mBq/kg dry (Tagami and Uchida, 1999). Ihsanullah and East (1993) published methods for the analysis of ^{99}Tc by ICP-MS for environmental media including water, soil, and marine algae with an ICP-MS detection limit of 0.004 ppb (2.52 mBq/mL).

ICP-MS has been used to analyze ^{239}Pu and ^{240}Pu in ocean sediment (Petullo et al., 1994). The analysis involved dissolution of a 20 g sample, followed by precipitation of the actinides, dissolution of the precipitate, and anion exchange for Pu isolation. A ^{242} Pu tracer was used for the chemical yield determination. Reported detection limits for ^{239}Pu and ^{240}Pu were 30 mBq/kg and 80 mBq/kg, respectively.

More recent environmental applications include the analysis of nuclides with intermediate half lives, including ^{90}Sr (Taylor et al., 2002) and ^{226}Ra (Kim et al., 1999; Lariviere, et al., 2002) in environmental media, and $^{135/137}$Cs (Epov et al., 2002) in waste waters. Lariviere et al. (2002) reported for ^{226}Ra a detection limit of 7.4 Bq/L (0.2 nCi/L) without elemental pre-concentration methods to remove interferences and 0.2 pg/L (0.007 Bq/L or 0.2 pCi/L) with a 50 times pre-concentration and elemental isolation. Their method required low sample volume (25 mL), had rapid chemistry (30 minutes) using extraction (extractant resin) chromotography, and a two minute/sample instrument measurement. Kim et al. (2002), using their chemical concentration and isolation methods, reported detection limits for water and soil of 0.00019 Bq/L and 0.75 Bq/kg, respectively.

ICP-MS has also been used for radiobioassay applications for ^{239}Pu and isotopic uranium in urine samples. The Brookhaven National Laboratory used ICP-MS to measure the ^{239}Pu concentration in urine samples from Marshall Island residents. Inn et al. (2001) evaluated the capabilities of BNL to analyze urine samples by ICP-MS in an intercomparison study to measure ^{239}Pu in synthetic urine. In the study, BNL pre-concentrated and isolated the plutonium in the synthetic urine through established and validated chemical techniques prior to analysis by mass spectrometry. Pu-242 was used as a yield monitor with each analysis. For four testing levels between 18.5 nBq/mL (18.5 μBq/L) and 278 nBq/mL (278 μBq/L), the mean of the BNL replicate (five samples) measurements for the four test levels had biases ranging from -6.8 to -20 percent. The 1σ precision for the five replicate measurements per test level was under 13 percent for all levels. The detection level was calculated to be 1,600 nBq per 200 g sample.

Lawrence Livermore National Laboratory (LLNL) has used ICP-MS coupled with chemical concentration (phosphate coprecipitation) and isolation to analyze isotopic uranium in urine samples (Hotchandani and Wong, 2002). A ^{233}U yield monitor was used with each sample (200–1500 mL). ASTM C1379 provides a test method for the analysis of urine for ^{235}U and ^{238}U by ICP-MS. Ejnik, et al. (2000) reported ^{235}U detection limits of 14 ng /L for natural uranium and 50 ng/L for depleted uranium (uranium with 0.2 percent ^{235}U) in urine, given a uranium detection limit of 0.1 ng/L. The researchers were able to determine correctly and accurately the ^{235}U : ^{238}U isotopic ratio for depleted and natural uranium in 10 mL urine samples having total uranium concentrations between 150 and 45,000 ng/L. The 10 mL samples had been treated by multiple and comprehensive dry and wet-ashing processes prior to analysis.

Nguyen et al. (1996.) reported a method for the simultaneous determination of ^{237}Np, ^{232}Th and the uranium isotopes in urine samples using extraction chromatographic sample preparation (TRU column) in conjunction with ICP-MS. They reported detection limits , using pre-concentration methods for 1/10 daily urinary excretion volume, of 13 μBq (8×10^{-4} dpm), 1.7 nBq (1×10^{-7} dpm), 33 nBq (2×10^{-6} dpm), and 7 nBq (4×10^{-7} dpm) for ^{237}Np, ^{232}Th, ^{235}U, and ^{238}U, respectively.

Lee et al. (1995) conducted an intercomparison study to evaluate the capability of the various alpha spectrometric and mass spectrometric methods for determining ^{237}Np in artificial urine samples. For this study, results from 10 different methods were evaluated in terms of bias and precision at two concentration levels (50 mBq/kg and 3.3 mBq/kg) as well as detection limits. At the time of the study, the best detection limit reported for alpha spectrometric and mass spectrometric methods were very similar (0.1 mBq/kg). However, the range of the reported detection limits was more consistent for the alpha spectrometric methods compared to the mass spectrometric methods.

15.7.2.2 Thermal Ionization Mass Spectrometry

Thermal ionization mass spectrometers (TIMS) rely on ionization from a heated filament rather than on a plasma. They provide more precise measurements than routine quadrupole ICP-MS but require substantially more operator involvement, leading to markedly reduced sample throughput compared to ICP-MS units. In addition, because of the design of most TIMS units, a limit of four samples per batch can be analyzed sequentially without reloading another set of samples. TIMS systems exist at the national laboratories and the National Institute of Standards and Technology. These units are large and are usually considered too expensive for commercial laboratory operations. In addition, facilities housing TIMS may have ventilation systems equivalent to a Class 100 clean room, depending on the application. In some cases, the initial radioanalytical chemistry is conducted in a class 100 clean room or hood.

TIMS has been successfully applied to the analysis of ^{239}Pu, ^{240}Pu, ^{235}U and ^{238}U in a variety of matrices. However, initial radioanalytical methods must be performed to isolate and concentrate the radionuclides from the initial sample. A radionuclide or isotopes in the concentrated solution would be electrodeposited on the filament used in the TIMS. For ^{239}Pu, Los Alamos National Laboratory (LANL) electrodeposits plutonium from a purified sample onto a TIMS filament with dihydrogen dinitro-sulfato-platinate. A larger quantity of platinum is then electrodeposited over the plutonium to provide a diffusion barrier that dissociates plutonium molecular species and provides high ionization efficiency. Detection limits in the femtogram range are typical, resulting in a ^{239}Pu concentration of 600 nBq/200 g sample (Inn et al., 2001). In a recent interlaboratory comparison study evaluating the capabilities of mass spectrometric methods for the analysis of ultra low quantities of ^{239}Pu and ^{240}Pu in urine (McCurdy et al., 2002), LANL's TIMS method had an estimated detection limit of 6 μBq/L. For ^{240}Pu in the samples, the detection limit was estimated to be 20 μBq/L. LANL observed good precision (about 4 percent relative standard deviation) for ^{239}Pu test levels at 28 μBq/L and above. The ^{240}Pu measurements were less precise than the ^{239}Pu measurements, 11.9 percent and 21.2 percent respectively for 32 and 16 μBq/L.

TIMS has been used to evaluate the isotopic ratio of ^{238}U : ^{235}U in urine samples. In a study reported by D'Agostino et al. (2002), five participating laboratories were provided 12 synthetic urine samples (1 kg each) containing varying amounts of natural and/or depleted urine. Various mass spectrometers were used, including sector-field ICP-MS, quadrupole ICP-MS, and TIMS. The TIMS and quadrupole ICP-MS had similar detection limits: 0.1 pg for total uranium (based on ^{238}U) and about 15 pg for a ^{238}U : ^{235}U ratio of 138 (natural abundance). The TIMS was able to measure ^{238}U : ^{235}U ratios in ranges between 138 and 220 for three test levels of 25 to 100 ng/kg, 100 to 350 ng/kg and greater than 350 ng/kg.

Additional information and radionuclide measurement applications of TIMS can be found on the Los Alamos National Laboratory and Savannah River Site websites, http://pearl1.lanl.gov/bioassay/tims.htm and http://srs.gov.

15.7.2.3 Accelerator Mass Spectrometry

Accelerator mass spectrometry (AMS) systems are routinely used by a limited number of national laboratories, universities and institutes rather than commercial or government radioanalytical laboratories. These systems are technically sophisticated, expensive and fairly large, requiring extensive laboratory space and facilities. Currently in North America, five organizations have AMS systems primarily for earth science, bioscience and environmental studies. The organizations include Woods Hole Oceanographic Institution, University of Toronto, Purdue University, University of Arizona, and LLNL.

In AMS, negative ions made in an ion source are accelerated electrostatically through a field of millions of volts. The accelerated ions pass through a thin carbon film or a gas to destroy all molecular species. After passing through a low- or high-energy mass spectrometer and various filters, the resulting ions slow to a stop and dissipate their energy in a gas ionization detector. The identity of the individual ions is determined from the ions' rates of deceleration, with the lighter ions decelerating more rapidly than the heavier ions. For AMS analysis, solid samples in the 0.1 to 1 mg mass range are pressed into sample holders.

AMS has been used for geological, biological, and environmental applications for several decades. In the1980s, AMS replaced the traditional method of scintillation counting for precise radiocarbon dating. A ^{14}C detection limit of 200 nBq (5×10^4 atoms) is typical. Tritium, used extensively as a tracer in biological and oceanographical research, can be analyzed routinely by AMS with a detection limit of 20,000 nBq. AMS can be used to measure the following low-mass cosmogenic radionuclides for earth science applications: ^{10}Be, ^{26}Al, ^{32}Si, ^{36}Cl and ^{41}Ca. In addition, ^{63}Ni, ^{129}I, and $^{239/240}$ Pu are routinely analyzed by AMS at LLNL. Table 15.8 (McAninch, 1999) provides the detection limits for these radionuclides.

TABLE 15.8 — AMS detection limits for selected radionuclides

Nuclide	Detection Limit (nBq)	Detection Limit (10^5 atoms)
^{3}H	20,000	1
^{14}C	200	0.5
^{10}Be	4	3
^{26}Al	1	0.4
^{36}Cl	3	0.3
^{41}Ca	200	8
^{63}Ni	45,000	2
^{90}Sr*	~100,000	~7
^{99}Tc*	~30,000	~600
^{129}I	1	1
$^{239/240*}$Pu	~1,000	~10

* proposed

McAninch and Hamilton (1999) compares the capabilities of the various mass spectrometric methods and fission tract analysis for the analysis of ^{239}Pu and the other actinide elements. The report includes a description of the facilities at the LLNL Center for AMS as well as the detection methods used. Additional information can be obtained online at http://cams.llnl.gov.

Recently, AMS has been used in radiobioassay to measure the ^{239}Pu in urine samples. McCurdy et al. (2002) evaluated LLNL's AMS technology for $^{239//240}$Pu bioassay measurements during an interlaboratory comparison study. LLNL's AMS method had an estimated detection limit of 6 µBq/L. For ^{240}Pu in the samples, the detection limit was estimated to be 15 µBq/L. LLNL observed good precision (under 2 percent relative standard deviation) for ^{239}Pu test levels at 28 µBq/L and above. The ^{240}Pu measurements were less precise than the ^{239}Pu measurements, about 27 percent for 16 µBq/L and above test levels.

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