7.0 SAMPLE ANALYSIS

7.1 Introduction

Samples collected during surveys for decommissioning purposes should be analyzed by trained individuals using the appropriate equipment and procedures. This manual assumes that the samples taken during the survey will be submitted to a well-established laboratory for analysis, using either in-house or contractor laboratory services. Whether the licensee uses in-house or contractor laboratory support, there should be written procedures that document the laboratory's analytical capabilities for the radionuclides of interest and a QA/QC program which assures the validity of the analytical results.

The most commonly used radiation detection measuring equipment for survey field applications has been described in Section 5.0. Many of those general types of devices are also used for laboratory analyses, usually under more controlled conditions which provide for lower detection limits and greater delineation between radionuclides. Laboratory methods often also involve combination of both chemical and instrumental technique to quantify the low levels expected to be present in samples from decommissioning facilities. This section describes laboratory methods applicable to most types of radiological surveys supporting license termination to assist the Manual user in selecting appropriate procedures for specific applications.

7.2 Prior Considerations

To reemphasize the point made in Section 3.0, a thorough knowledge of the radionuclides present, along with their chemical and physical forms and their relative abundance, is a prerequisite to selecting laboratory methods. With this information, it may be possible to substitute certain gross, that is, nonradionuclide specific, measurement techniques for the more costly and time-consuming wet chemistry separation procedures, relating the gross data back to the relative quantities of specific contaminants. The individual responsible for the survey should be aware that chemical analyses require lead times which will vary, according to the nature and complexity of the request. For example, a lab may provide fairly quick turnaround on gamma spectrometry analysis because computer-based systems are available for interpretation of gamma spectra. On the other hand, soil samples which must be dried and homogenized will require much longer lead time. Some factors influencing the analysis time include (1) the nuclides of concern, (2) the type of samples to be analyzed, (3) the QA/QC considerations required, (4) the availability of adequate equipment and personnel, and (5) the required detection limits.

For relatively, simple analyses, such as gross alpha and gross beta counting of smears and water samples, liquid scintillation spectrometry for low-energy beta emitters in smear and water samples, and gamma-spectrometry of soil, it is usually practical to establish in-house laboratory capabilities. The more complicated and labor-intensive procedures, such as alpha spectrometry, Sr-90 and low-energy beta emitters (H-3, Ni-63, etc.) samples should be considered candidates for contract laboratory analyses.

Analytical methods should be capable of measuring levels below the established release guidelines, detection sensitivities of 10 to 25% of the guideline should be the target. Although laboratories will state detection limits, these limits are usually based on ideal situations and may not be achievable under actual measurement conditions. Also, remember that detection limits are subject to variation from sample to sample, instrument to instrument, and procedure to procedure depending upon sample size, geometry, background, instrument efficiency, chemical recovery, abundance of the radiations being measured, counting time, self-absorption in the prepared sample, and interferences from other radionuclides present.

7.3 Sample Preparation

Various degrees of sample preparation may be necessary prior to direct measurement and/or wet chemistry procedures. The only treatment for smears (filter papers) before gross alpha/beta counting will be to wait until short-lived naturally occurring radon daughters, which may have been collected along with the other radionuclides of concern, have decayed to negligible levels. For the Ra-222 and the Ra-220 series decay times of 4 hours and 72 hours, respectively, are typically used. If liquid scintillation analyses are necessary, the smears may require oxidizing to separate the carbon-14 and tritium and place it into a liquid form for analysis; or the smears may need to be cut into small pieces before placing into the counting vial, to reduce the chances of attenuation of the scintillations by the smear papers.

Soil and sediment sample preparation includes removal of sticks, vegetation, rocks exceeding about 0.6 cm (1/4 inch) in diameter, and foreign objects. If non-volatile elements are the only contaminants of concern the samples are dried at approximately 110° C for a minimum of 12 hours; volatile radionuclides (H-3, Tc-99, and iodides) must be separated from the sample before drying to avoid loss of the radionuclide of interest. Dried samples are homogenized by mortar and pestle, jaw crusher, ball mill, parallel plate grinder, blender, or a combination of these techniques, and sieved to obtain a uniform sample. Sieve sizes from 35 mesh to 200 mesh are recommended for wet chemistry procedures. In addition, samples for chemical separations are also usually ashed in a muffle furnace to remove any remaining organic materials that may interfere with the procedures. Sample weights must be determined after drying and ashing procedures to enable referencing contamination levels back to weights of dry soil. To reduce the number of analyses required, multiple systematic or random samples from the same averaging region, i.e. equal aliquots from same grid block and same depth layer, may be combined into one composite sample. Traceability of components in a composite sample must be maintained, and the remainder of the individual samples should be retained to enable their analyses, in case the average value suggests the possibility of a hot-spot at one of the systematic or random sampling locations.

Water samples are usually prepared by filtration of suspended material using a 0.45 micrometer filter and acidification with nitric or hydrochloric acid to a pH of less than 2. This permits separate analyses of suspended and dissolved fractions and, if preparation is not performed promptly following collection, prevents loss of dissolved radionuclides by plating out on container surfaces.

7.4 Analytical Procedures

This section briefly describes specific equipment and/or procedures to be used once the medium is prepared for analysis. The results of these analyses, that is, the levels of radioactivity found in these samples, are the values used to determine the level of residual activity at a site. In a decommissioning effort, the release guidelines are expressed in terms of the concentrations of certain nuclides. It is of vital importance, therefore, that the analyses be accurate and of adequate sensitivity for the nuclides of concern.

An excellent source of information on a variety of topics, from detection equipment to chemical procedures, is equipment vendor literature, catalogs, and instrument manuals. Other references that should be considered are available from such organizations as National Council on Radiation Protection and Measurements (NCRP), the U. S. Environmental Protection Agency (EPA), the American Society of Testing and Materials (ASTM), the American Society of Mechanical Engineers (ASME), the DOE Technical Measurements Center (Grand Junction, CO), and the Environmental Measurements Laboratory (EML, formerly the Health and Safety Laboratory) of the U. S. Department of Energy (DOE). Table 7-1 provides a summary of the common laboratory methods with estimated detection limits.

TABLE 7-1
TYPICAL MEASUREMENT SENSITIVITIES FOR LABORATORY RADIOMETRIC PROCEDURES ASSOCIATED WITH TERMINATION SURVEYS

Sample Type	Radionuclides or Radiation Measured	Procedure	Approximate Measurement Sensitivity
Smears (filter paper)	Gross Alpha	Low-background gas proportional counter; 5-min. count	5 dpm
		Alpha scintillation detector with scaler; 5-min. count	20 dpm
	Gross Beta	Low background gas proportional counter; 5-min. count	10 dpm
		End window GM with scaler; 5-min. in count (unshielded detector)	80 dpm
	Low Energy Beta (H-3, C-14, Ni-63)	Liquid scintillation spectrometer; 5-min count	30 dpm
Soil Sediment	Cs-137, Co-60, Ra-226 (Bi-214)*, Th-232 (Ac-228)*, U-235	Gamma Spectrometry- Intrinsic germanium detector (25% relative efficiency); pulse height analyzer; 500-g sample; 15-min. analysis.	1-3 pCi/g
	U-234, 235, 238; Pu-238, 239/240; Th-228, 230, 232; other alpha emitters	Alpha spectrometry - pyrosulfate fusion and solvent extraction; surface barrier detector; pulse height analyzer; 1-g sample; 16-hour count	0.1-0.5 pCi/g
Water	Gross alpha	Low-background gas proportional counter; 100-ml sample, 200- min. count	1 pCi/l
	Gross beta	Low background gas proportional counter; 100-ml sample, 200-min. count	1 pCi/l
	Miscellaneous gamma emitter	Gamma spectrometry - 3.5 l sample 16-hour count	10 pCi/l
	Miscellaneous alpha emitter	Alpha spectrometry - 100 ml sample; 16-hour count	0.1-0.5 pCi/l
	H-3	Liquid scintillation spectrometry; 5-ml sample; 30-minute count	300 pCi/l

*Indicates number of daughter series, measured to determine activ[illegible]vel of parent radionuclide of primary interest.

7.4.1 Smear (Filter Paper) Counting

As a precaution against accidental contamination of the laboratory facility, it is prudent to first screen smears by gamma spectrometry or gross GM counting. If little contamination is expected, all smears collected at the facility (or in a particular survey area) may be assayed at once by placing all the smears on the detector. This will provide a broad screen for expected and unexpected contaminants. If contamination is detected, the smears should be recounted in smaller groups until the contaminated smears are isolated. Since the procedure is nondestructive, it will not interfere with subsequent analysis of the smears. When performing such screening, the smears should be left in their protective "envelopes" to avoid cross contamination.

Gross alpha/gross beta. The most popular method for laboratory smear analysis is to count both gross alpha and gross beta levels in a low-background proportional system; both automatic sampler changer and manual detector instruments are used. Such systems have low backgrounds, relatively good detection sensitivity, and the capability of processing large quantities of samples in a short time. Using counting times of several minutes, measurement sensitivities of less than 10 dpm alpha and 20 dpm beta can be achieved. Filter papers can also be measured using standard field instruments, such as alpha scintillation and thin-window GM detectors with integrating scalers (see Section 6.0 on instrumentation). The measurement sensitivities of such techniques are not nearly as low as the low-background proportional system; however, for 5-minute counting times, alpha and beta levels below 20 dpm and 100 dpm, respectively, can be measured. One of the major drawbacks to such a procedure is that it is very labor intensive.

Filter papers can also be covered with a thin circle of zinc sulfide scintillator and counted for gross alpha using a photomultiplier tube attached to a scaler. While such a system provides a sensitivity comparable to that of the low-background proportional counter, it is not usually automated and is, therefore, a labor intensive method.

Liquid Scintillation. Smears for low-energy beta activity (for example H-3, C-14, and Ni-63) can be placed directly into a scintillation cocktail and counted on a liquid scintillation spectrometer. The counting efficiency may be reduced; but as a screening method, this process will yield reasonable results. With the spectrum capability of the newer instruments, the analyst can (in most cases) identify the specific beta emitter(s) present. The introduction of the sample into the liquid scintillation medium produces **quenching**, a reduction in the efficiency of the scintillator as a result of the introduction of the sample. To evaluate the effect of quenching, an external standard may be used or a known amount of the identified radionuclide (referred to as an internal standard or spike) may be added to the sample after initial measurement and a recount performed to enable determination of the detection efficiency for the specific sample. It should be noted that even with the identification of the nuclide(s) on the smears, this is still a gross analysis; and caution is advised in trying to infer too much from this information.

7.4.2 Soil/Sediment Analysis

Gamma Spectrometry. After the soil or sediment has been prepared and placed in an appropriate container, the samples are counted. The analysis of soil or sediment is dependent on the radionuclides of interest. If the contaminants could include gamma emitters, the sample will be analyzed using gamma spectrometry (a non-destructive analysis that can identify and quantify multiple gamma-emitting nuclides). It is prudent to subject at least a representative number of soil or sediment samples to gamma spectral analysis, even if no gamma emitters are expected, as a check on the reliability of the identification of potential contaminants. Either solid-state germanium detectors or sodium iodide scintillation detectors may be used; a sodium iodide system typically has a higher detection efficiency but is not able to provide the resolution of the solid state detector, which is capable of resolving gamma photopeaks, having energies which differ by as little as 0.5 to 1 keV.

Although state-of-the-art systems include inherent computer-based spectrum analysis capabilities, it is important that an experienced analyst carefully review each spectrum, because at the low concentrations typically encountered ir decommissioning surveys, resolutions, interferences, peak shifts, and linearity may not be readily apparent. Spectra should also be reviewed for gamma-photopeaks, not previously identified as principal facility contaminants of concern. Special attention should be given to those radionuclides which may have difficult to resolve photopeaks, for example Ra-226 (186.2 keV) and U-235 (183.7 keV), and select, secondary photopeaks or daughter photopeaks for calculations. An example would be the use of a daughter in the Ra-226 decay series, Bi-214 (609 keV peak), as an alternate for determining the quantity of Ra-226 present. When using such an approach, it is also necessary that the equilibrium status between the parent and the daughters be known.

Soil/sediment analysis by gamma spectrometry can be performed with relatively large samples, using geometries, such as a 0.5-liter Marinelli beaker and 100 to 400 ml cans or jars. With counting times of one-half hour or less, many commonly encountered radionuclides can be measured with measurement sensitivities of several pCi/g when using such sample geometries.

Alpha Spectrometry. Radionuclides emitting primarily alpha particles are best analyzed by wet chemistry separation, followed by counting to determine amounts of specific alpha energies present. Samples are fused at high temperatures into fluoride and pyrosulfate fluxes. This process ensures that all chemical species are in an ionic state that is more readily dissolved. (The process of leaching certair chemical forms of radionuclides from the soil matrix has been found to be less consistent than total dissolution of the sample matrix.) After dissolution, barium sulfate is precipitated to carry the alpha emitters out of solution. The precipitate is dissolved and the various nuclides are separated by oxidation-reduction reactions. After final separation and cleanup, the nuclides of interest are co-precipitated (with either neodymium or cerium fluoride) and collected on a filter paper. This precipitate is then counted using a solid-state surface barrier detector and alpha spectrometer.

A known amount of tracer radionuclide is added to the sample before the chemical separation, to determine the fraction of the radionuclide recovered in the procedure. This also provides a "calibration" of the analytical system for each sample processed. Lower limits of detection are less than 1 pCi/g using standard alpha spectrometry methods. Sample quantities for such procedures are typically a few grams or less.

Liquid Scintillation. If tritium is a radionuclide of concern, the tritium is separated by adding a known amount of low-tritium water and distilling the sample to collect the moisture. An aliquot of the collected moisture is then placed in a scintillation cocktail and counted using a liquid scintillation beta spectrometer. The activity is then related to the quantity of soil in the sample procedure or to the natural moisture content of the sample. Detection sensitivities below 1 pCi/g can be obtained with this method. An alternate technique utilizes an oxidizer to convert tritium to water vapor which is collected in a cryogenic liquid bubble trap. This is a faster method, but the amount of sample which can be processed is smaller and the sensitivity is, therefore, poorer than the distillation method.

A recently introduced analytical technique uses liquid scintillation counting to measure alpha-emitting contaminant concentrations. This system is known as PERALS (photon electron rejecting alpha liquid scintillator). While it does not provide the sensitivity and resolution capabilities of conventional alpha spectrometry, the wet chemistry procedures are less rigorous and results are obtainable in about one fourth of the time.

Other procedures. Analysis of soil/sediment samples for most pure beta radionuclides, such as Sr-90, Tc-99, and Ni-63, requires wet chemistry separation, followed by counting using liquid scintillation or beta proportional instruments. Each radionuclide (element) requires a specific procedure for the chemical separation; such detail is beyond the scope of this manual and the reader should consult the references given above for further information. As with the alpha spectrometry techniques, a known amount of tracer is added to the sample to determine recovery. Lower limits of detection of less than 1 pCi/g are achievable using standard methods.

7.4.3 Water Sample Analysis

Water samples may be directly counted for gamma emitters using equipment described for soil/sediment samples. Because the guideline levels for unrestricted use are much lower for water than for soil, the larger sample volumes (1 to 3.5 liters) and longer count times (up to 12 or 16 hours) may be necessary.

Gross alpha and gross beta analyses are conducted as screening techniques by evaporating a small (10 to 100 ml) volume of water to dryness and counting on a low-background gas proportional system. Measurement sensitivities of 1 pCi/l are obtainable. Because of the substantial sample thickness which may occur, self-absorption may be significant and corrections will be required. Samples containing more than 15 pCi/l gross alpha or 50 pCi/l gross beta should be analyzed for specific radionuclides. Care must be exercised when the water may contain tritium, technetium, or other volatile radionuclides. In such circumstances, direct analyses by liquid scintillation or a combination of wet chemistry and liquid scintillation may be required. Analyses for other specific radionuclides are conducted in a manner similar to that for soil/sediment.