

This document addresses effective techniques for low-level radiochemical methods for alpha-spectrometry with a focus on appropriate techniques for analyzing air-filters, water samples, and soils for actinide elements, Th, Pa, U, Np, Pu, Am, Cm (as well as other trivalent trans-curium elements). A complete procedure for each element, for each matrix, is beyond the scope of this summary. Here, for each matrix, a brief summary is presented for producing elementally pure alpha-counting sources for these three matrices. References to published methods and research are provided for the reader to develop the final techniques.

The basic procedure for environmental radiochemistry can be divided into four parts:

- 1) Sample Preparation (e.g., tracer additions, digestions, dissolutions, precipitations).
- 2) Radiochemical Separations (e.g., ion-exchange, extraction chromatography).
- 3) Source Preparation
- 4) Counting

Radioactive tracers are added at the beginning of the Sample Preparation step. Choice of tracer will depend on the analyte of interest. Since counting is virtually the same for each matrix, the needed hardware (detectors, chambers, vacuum controllers, etc.) and software are handled as a separate section.

### Sample Preparation

#### Air-Filters

Air-filter monitoring is a common methodology for identifying air-born radionuclides attached to particulates. Air-filters are typically collected on some periodic basis for analysis. Since, in many cases, the alpha-decay energies of many of the radionuclides overlap, highly purified alpha-counting sources must be prepared to ensure that misidentifications and false positives are minimized.

#### *Air Filter Digestions*

Glass-fiber filters are perhaps the most common filtering medium used for air monitoring. It is suggested that the filters should be completely dissolved, as actinides may be present in highly insoluble forms that are not broken-down in acid leaching procedures. Glass-fiber filters (and most soil particles) are soluble in a hydrofluoric acid (HF)/nitric acid (HNO<sub>3</sub>) medium. To achieve total dissolution, samples are digested for several hours to days in the mixed acid solution. In some cases, samples must be melted at high temperature (a process known as fusion) to achieve total dissolution of soil particles.<sup>2,3</sup> In these cases, the molten sample is allowed to cool and is redissolved in the HF/HNO<sub>3</sub> solution. The solution of HF and HNO<sub>3</sub> is evaporated to dryness to volatilize HF. The inside walls of the beaker are rinsed carefully with HNO<sub>3</sub> to gather residual HF. Evaporation is repeated to ensure that all HF residual is removed from the matrix. The sample is then dissolved in an acidic medium and readied for analytical separations.

#### Water Samples

Monitoring of environmental water quality, both in surface waters and groundwater aquifers, is an important part of a total-site-monitoring program. Although methods are available for much larger sample sizes, it is assumed that the sample size is roughly on the order of liters for this description. Although rain is the largest source of groundwater, the matrix is highly dependent on the rock formations in which the water is held and may vary widely. All groundwater samples should be acidified to minimize the adsorption of actinides to the walls of the collection bottle. Tracers should be added after acidification. Despite the variability of the groundwater matrix, a number of well-established techniques have been developed for actinide analysis.

#### *Water Sample Preparation*

A number of effective techniques can be devised for pre-concentration of actinides in water samples. A common technique is co-precipitation with calcium phosphate CaHPO<sub>4</sub>. The CaHPO<sub>4</sub> precipitation is effective in co-precipitating all actinides from a basic medium (for most matrices, co-precipitation is virtually quantitative). A further advantage of this technique is that reduction-oxidation control is unnecessary (III, IV, and VI states are precipitated). Samples are first acidified by adding HNO<sub>3</sub> to pH<2 (to inhibit adsorption to the walls of the sample bottle). Once acidified, tracers (and Ca<sup>2+</sup>) are added, time is allowed (or agitation applied) for mixing and the sample is transferred to an appropriate glass beaker. After heating for some time interval, the pH of the solution is raised to pH 8-9 with concentrated ammonium

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hydroxide  $\text{NH}_4\text{OH}$ . This produces a whitish-gray flocculent, or floc. The floc is heated for several hours and allowed to settle. The supernatant may be discarded and the floc wet-ashed several times with  $\text{HNO}_3$  and hydrogen peroxide  $\text{H}_2\text{O}_2$ . After wet-ashing, samples are dissolved in an acid medium for analytical separations.

## Soils

Soils present the greatest challenge to the radiochemist. The soil matrix is highly variable and can contain high concentrations of non-radioactive matrix interferences<sup>3-5</sup>. However, despite the complexity of the soil matrix, recent advances in separations chemistry have helped to ensure a higher degree of success for actinide analysis of larger soil samples. Here we assume that sample size will be roughly on the order of one to ten grams.

### *Soil sample preparation: leaching, total dissolution, or fusion*

The data quality objective and the source term of the analyte radionuclide of interest help to determine the method of choice for soil sample preparation. For example, if one is expecting that the soil environment being investigated contains highly-insoluble plutonium associated with reactor core material or plutonium metal fabrication facilities, then a fusion technique might be the method of choice to ensure total dissolution. On the other hand, if the monitoring activity is around a discharge area where potential releases are more likely to be in a more soluble form, then a leaching procedure might be the more appropriate and cost effective approach. A total dissolution technique of  $\text{HF}$  and  $\text{HNO}_3$  is an effective (less costly) alternative to a fusion. Only the most refractory geochemical forms (e.g. zirconium oxides) are resistant to total dissolution by  $\text{HF}$  and  $\text{HNO}_3$ . In this procedure, a soil sample is weighed into a Teflon beaker of appropriate size. A one to one mixture of  $\text{HF}/\text{HNO}_3$  is added, so that the ratio of acid to soil is about 30 mL acid:1 g soil. The sample is heated at medium heat (covered) for several hours and then evaporated to dryness. The inside walls of the beaker are rinsed carefully with  $\text{HNO}_3$  to gather residual  $\text{HF}$ . Evaporation is repeated to ensure that all  $\text{HF}$  residual is removed from the matrix. The samples are then dissolved in boric acid (to dissolve rare-earth fluorides that may be present), combined with an appropriate acid medium for analytical separations.

## Separations Chemistry

The separation method will depend on the elements of interest for the test. Numerous methods are available, employing ion-exchange, liquid-liquid extraction and, most recently, extraction chromatography. For example, separation of Am and Pu can be accomplished using a column technique, employing extraction chromatography, using a resin such as EiChrom Industries Tru-resin™. In short, the digested and dried sample is dissolved in dilute nitric acid and transferred to a 2-mL extraction chromatography column. The solution is allowed to pass through the column and the eluant (containing interfering common ions) is discarded. Actinides are extracted into the stationary phase. Am and Pu are then separated by taking advantage of differences in the chemistry of these two elements.<sup>3-10</sup> The choice of technique will depend on the analyte(s) of interest and the potential interferences.

## Source Preparation

Alpha source preparation is a critical step in environmental sample analysis. The ideal alpha source consists of a virtually massless, monomolecular layer of alpha-emitters which means that spectral resolution is critical. Two basic methods are available for preparation of high quality alpha-counting sources. Electrodeposition provides the best spectral resolution in source preparation.<sup>10</sup> However, micro-precipitated sources using microgram amounts of rare-earth elements can provide excellent spectral resolution, while having the advantage of rapid sample throughput.<sup>11-12</sup>

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## Alpha Spectrometry Hardware and Software

### ALPHA-ENSEMBLE Alpha-Spectrometry System

ORTEC's integrated alpha spectroscopy hardware solution consists of the ALPHA-ENSEMBLE 2- to 8-channel spectrometer. Up to eight ULTRA ion-implanted solid-state detectors may be ordered with the ALPHA-ENSEMBLE. The ALPHA-ENSEMBLE is delivered with the detectors pre-installed and tested as an integrated data acquisition unit with MAESTRO-32 MCA emulation software.

This spectroscopy system will operate from a single PC, with a fully-functional 32-bit Windows 2000/XP/Vista compliant software program, complete with built-in Microsoft Access database and QA functions. The system allows for almost immediate out-of-the-box operation. No multiple component setup is required. A single ALPHA-ENSEMBLE unit contains up to eight independent alpha chambers. The system is expandable to more than 200 chambers, all operable from a single PC. A high performance o-ring, set into the face of each chamber, provides for excellent vacuum reliability. All electronics (detector bias, vacuum controls, current) are monitored for each detector and can be viewed simultaneously for each ALPHA-ENSEMBLE.

### ULTRA Ion-Implanted Silicon Detectors

ULTRA ion-implanted silicon detectors are the most advanced charged-particle detectors ever produced. Both the entrance and the back contact are ion-implanted. The entrance is an extremely thin boron implantation (~500 angstroms Si equivalent). Since no epoxies are used to mount the ULTRAS, the distance between the silicon surface and the top of the mounting can is <1mm which provides for maximum efficiency. The rugged front contact is easily cleaned with a solvent moistened cotton swab and is impervious to finger contact. ULTRAS are available in surface area sizes from 300 mm<sup>2</sup> to 1200 mm<sup>2</sup> and in low background configurations (-AS series).

### Ion Recoil Contamination Avoidance Package

For low-level environmental and radiobiology alpha spectrometry analyses, it is recommended to use an ion recoil contamination avoidance system. The ALPHA-ENSEMBLE has a vacuum control to allow the user to set the proper vacuum for ion recoil avoidance. The only additional requirement would be to provide a reverse-biased sample tray (model RCAP-ST) for each chamber to attract any escaping ions back to the sample.

### AlphaVision-32 Alpha-Spectrometry Analysis Software

AlphaVision-32 software provides a complete solution for alpha-spectral collection and analysis. It includes the capability for controlling the MCB hardware, collecting alpha spectra from solid state detectors, analyzing the results by one of several methods and generating reports. Results are stored in convenient Access databases and QA functions are built in.

The way in which a software package interacts with the user is a very important consideration from the point of view of the person who must make repeated measurements. AlphaVision-32 employs all the advantages of the Microsoft Windows system and has been carefully designed to provide the friendliest possible environment in which the alpha spectroscopist may perform his or her work.

Extensive menus are provided for the operation of all acquisition and analysis functions, such as controlling acquisition, setting analysis parameters, calibrating detectors, and editing libraries. Graphical display of individual detector status, along with logical user-defined grouping of the detectors in the system, result in an interface that provides on-line status for up to 128 alpha detectors. Data are automatically archived in a simple Microsoft Access database. Reports are generated directly using Access or by using an add-on Report Writer. Alpha-nuclide libraries are extracted from industry-accepted standard libraries.<sup>13</sup>



Group	Name	D1	D2	D3	D4
7			OK	OK	OK
8		OK	OK	OK	OK
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10		OK	OK	OK	OK
11		OK			
12					
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# Sample Preparation for Low-Level Alpha Spectrometry: Air Filters, Water and Soils

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