

## CHAPTER 37

# Rapid Determination of Pu Content on Filters and Smears Using Alpha Liquid Scintillation

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### ABSTRACT

This chapter discusses a technique for rapidly determining plutonium content on filters and smears using alpha liquid scintillation. Filter and smear samples will be analyzed daily for plutonium ( $^{239}\text{Pu}$ ) content during projected waste retrieval operations at the Radioactive Waste Management Complex (RWMC) of the Idaho National Engineering Laboratory. Daily monitoring will allow for trending of airborne and surface contamination. Present analysis techniques are time consuming, as both numerous naturally occurring isotopes, such as uranium and thorium daughters, and inert solids must be removed prior to counting to avoid interference with Pu detection. Alpha liquid scintillation (ALS) in conjunction with microwave digestion was investigated as a technique for rapid Pu analyses. Advantages offered by ALS are short turnaround time and field use with acceptable accuracy. A state of the art Photon Electron Rejecting Alpha Liquid Scintillation (PERALS) Spectrometer with pulse shape discrimination (PSD), and an oil filled photomultiplier tube counting chamber with 99.7% counting efficiency and 99.95% rejection of beta and gamma pulses, was used. Relatively clean filter samples could be directly counted in an all purpose scintillant, bis 2-ethylhexyl phosphoric acid (HDEHP), 4-biphenyl-6-phenylbenzoxazole (PBBO), toluene, and naphthalene. Laboratory preparation of soil samples and smears with high inert solids content was accomplished by dissolution of the sample in nitric and hydrofluoric acids using a microwave digestion system in teflon pressure vessels. The Pu in the dissolved sample was extracted into tertiary amine nitrate and counted in a HDEHP or 1-nonyldecylamine sulfate (NDAS) containing extractive scintillant. This method is applicable to the determination of total plutonium in air filters, smears, and soils. The minimum detectable activity (MDA) for direct counting of air filters is about 100 pCi/g (3.7 Bq/g) for an hour count. If the sample is dissolved and Pu extracted, activities near 1 pCi/g (0.037 Bq/g) can be seen with a 20 min count.

### INTRODUCTION

Filter and smear samples will be regularly analyzed over the course of the day for  $^{239}\text{Pu}$  content during projected waste retrieval operations at the Radioactive Waste Management Complex (RWMC) of the Idaho National Engineering Laboratory. Daily monitoring will allow for trending of airborne and

surface contamination. Airborne contamination collected on filters and surface contamination collected on smears are the two normal forms of samples expected from the contamination monitoring system.

Alpha liquid scintillation (ALS) techniques developed with beta and originally used the same equipment as beta scintillation counting.<sup>1-3</sup> A specifically designed alpha liquid spectrometer (PERALS)<sup>4</sup> with 99.7% counting efficiency, 99.95% rejection of beta and gamma pulses, 5% (250 keV) resolution for energies in the Pu region of 5162 keV and 0.02 cpm electronic background was tested.

Relatively clean filter samples were directly counted in an all purpose scintillant, bis 2-ethylhexyl phosphoric acid (HDEHP), 4-biphenyl-6-phenylbenzoxazole (PBBO), toluene, and naphthalene. This formulation was found to be the optimum for ALS when compared to common beta cocktails.<sup>3,4</sup> Routine treatment for soil samples and smears with high inert solids content, however, requires laboratory dissolution and two extractions, first into a tertiary amine nitrate, and second into a HDEHP or 1-nonyldecylamine sulfate (NDAS) containing extractive scintillant.<sup>4,5</sup>

Special sample preparation techniques, such as microwave digestion, are important in ALS. Microwave digestion quickly reduces solid samples to an extractable form<sup>6</sup> within a nitrate system. Microwave digestion in specially designed, closed, raised-pressure, teflon vessels has been used for dissolution of a variety of materials and is currently being considered as an alternate EPA method for standard open vessel wet ashing techniques.<sup>7</sup> With the proper organic extractants, filters can be directly counted and soil samples extracted and counted by PERALS. This should be possible in a short amount of time (about 1 hr), in the field and with acceptable accuracy and peak discrimination against natural background components in the soil.

This chapter is a scoping study to test procedures needed in preparing samples, standards, and blanks for the PERALS system and gives preliminary results of filter and soil Pu analysis. Screening samples in less than an hour was tested rather than routine analytical analysis.

## APPARATUS

Until recently adaptation of existing beta detectors was the only way to perform alpha liquid scintillation spectrometry.<sup>1,2</sup> However, these detector systems did not provide good spectrometric results. To obtain good results, we needed an alpha only detector with (1) improved counting chamber design with no air gap, (2) improved pulse shape discriminator (PSD) to separate alpha from beta and gamma pulse continuum, (3) multichannel analysis (MCA) rather than the pulse height analysis (PHA) counting of energy regions, (4) elimination of most quenching, (5) lower background through the rejection of afterpulses characteristic of cosmic radiation, and (6) improved efficiency through rejection of unwanted luminescence.

McDowell<sup>4</sup> has designed a workable ALS instrument called a Photon-Electron Rejecting Alpha Liquid Scintillation Spectrometer (PERALS). Currently an improved alpha liquid scintillation design is manufactured exclusively by Oak Ridge Detector Labs (ORDELA). The ORDELA PERALS Model 8200B detector uses pulse shape discrimination (PSD) and an oil filled photomultiplier tube counting chamber giving: 99.7% counting efficiency, 99.95% rejection of beta and gamma pulses, 5% (200 keV) resolution at energies in the Pu region (5162 keV), 0.02 cpm background.

A PERALS spectrum of <sup>226</sup>R and its daughters is overlaid on a typical one using silicon surface barrier alpha spectrometry (Figure 1). This comparison shows the radium, radon and polonium peaks resolved in both systems. The 250 keV for Pu resolution of PERALS, noted in the first peak when compared to about 20 keV in the surface barrier spectrum, does not allow resolution of the two <sup>226</sup>R peaks at 4.6 and 4.78; thus <sup>241</sup>Am, always found with <sup>239</sup>Pu, are also seen as one peak on the PERALS system.

Analysis equipment includes: the CEM 81D microwave digestion unit, assorted sizes of separatory funnels (30 to 500 mL), adjustable hot plates, heat lamps, a balance capable of weighing to 0.1 g, a dry argon sparging apparatus, (Figure 1), 10 × 75 mm culture test-tubes, cork stoppers, parafilm, and lambda pipettes. The ALS spectrometer was powered by a Canberra Model 3120 High Voltage Power Supply. Data is transferred through a Canberra Model 18075 A to D Converter to a Canberra MCA system 100 operating an IBM PC, for peak detection and analysis.

Four types of reagents are used in the procedure: (1) mineral acids for sample dissolution and organic stripping, (2) inorganic salts for oxidation state adjustment, (3) large organic amines or phosphates for sample extraction, and (4) scintillation grade organic reagents and fluors for cocktail preparations. High purity reagents decrease the probability of various unwanted reactions, minimize introduction of undesirable quenching species, and reduce background.

## PROCEDURE

This section describes the ALS analytical scheme. The results give a preliminary performance evaluation of the ALS system, microwave digestion, and organic extraction as an analytical tool for both directly analyzed and digested/extracted filter and soil samples.

Certain air filters and smears may be counted directly in the extractive scintillator. Swipe or smear samples and lightly coated air filters must be relatively clean, contain mostly alpha activity, have low beta-gamma activity and have low inert solid content. If the sample contains a large amount of soil or matter, it will require digestion and extraction.

Sample dissolution was accomplished by wet ashing in nitric and hydrochloric acids using hydrofluoric acid to break down silicates. A microwave

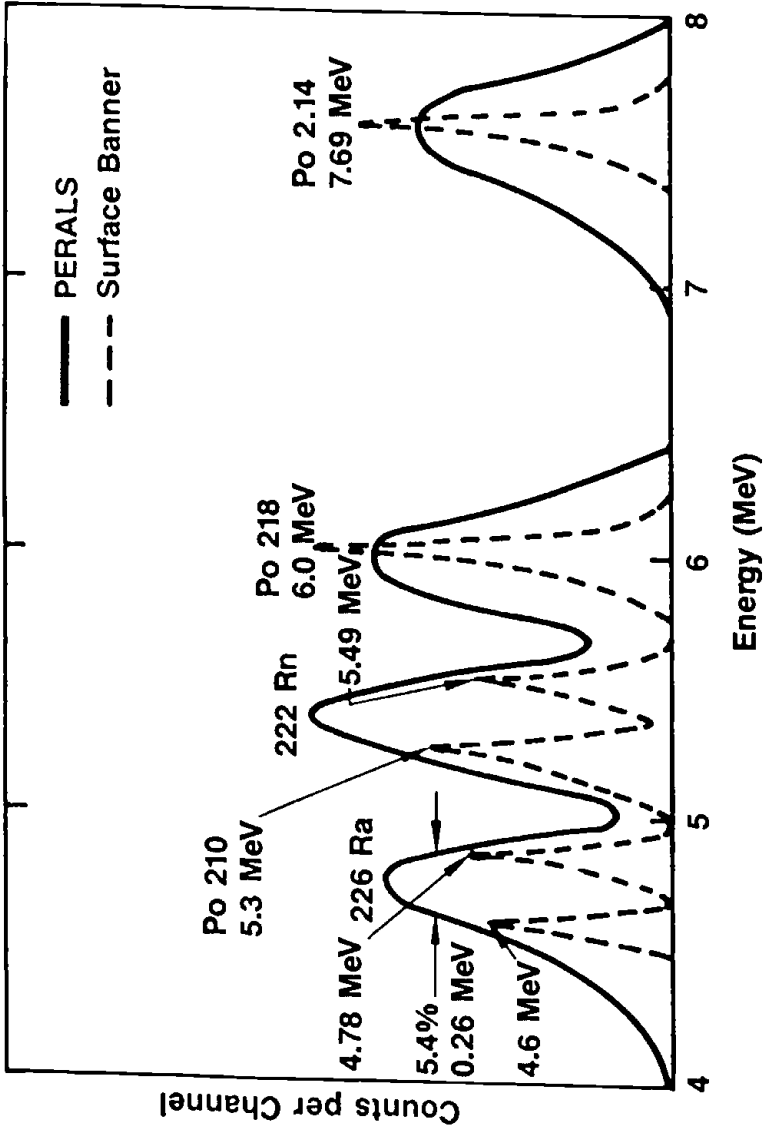


Figure 1. Surface barrier and PERALS  $^{226}\text{Ra}$  spectrum.

digestion system with teflon pressure vessels contained the HF and reduced dissolution time.

The sample (soil, smear, or filter) is weighed, placed in a 120 mL high temperature teflon vessel, and a 7:3 mixture of aqua regia and hydrofluoric acid is added. The cap is tightened on the vessel to a prescribed torque. This allows the acid mixture to become pressurized to 120 psi. At this pressure, the temperature of the solution reaches 150°C and the HF remains in solution longer than in an open system. The microwave is operated for 5 min at full power (650 watts) then 10 min at 50% power.

Vessels are uncapped and 5 mL of nitric and 5 mL of 30% hydrogen peroxide are added to drive off chloride and fluoride ions and oxidize minute traces of organic matter. The sample is placed in a 30 mL beaker, and 3 mL aluminum nitrate is added to tie up free fluoride, prevent calcium fluoride precipitation, and adjust the ionic strength. Volume is reduced to 5 mL by evaporation to remove high acidity, chloride, and fluoride ions, giving a pure nitrate system. The solution should be about 1 *M* nitric acid and 3 *M* total nitrate.

The dissolved sample is converted to a suitable oxidation state for extraction into an aqueous immiscible scintillator. Pu is primarily in the +6 state after nitric acid digestion. It is brought to +4 by reduction with ferrous sulfate or potassium metabisulfite (if the system contains appreciable iron). Any Pu +3 present is raised to +4 with sodium nitrite. After addition of these reagents the solution must be contacted immediately with the tertiary amine or Pu will disproportionate back into multiple oxidation states.

After ionic strength and oxidation state adjustments, Pu is extracted into the high molecular weight (> 300) tertiary amine such as tri-octyl amine or, as used here, the proprietary formulation, Adogen-364. The amine is nitrated by contact with 0.7 *M* nitric acid before extraction. The purity of this amine is critical. Any primary or secondary amines present may keep the Pu from being extracted, bind it to the amine so it can not be stripped, or extract unwanted ions. Due to time constraints the purity of the amine could not be assayed and purifying procedures could not be undertaken. The main concern in the extraction step is the removal of Th, U, and any colorant such as iron. Removal of other elements in the extraction procedure is not as crucial in this method as the sample will not be plated out on a surface as a solid.

The acid solution is transferred to a 30 mL separatory funnel and shaken with the amine for several minutes by an automatic shaker. The Pu is stripped from the amine nitrate, which is highly quenched, and put into an organic with less quenching. It is stripped with a solution of 1 *N* sulfuric or perchloric acids and a small amount of an associated salt of each acid, lithium perchlorate or sodium sulfate. Salt provides a surface for Pu to adhere to upon evaporation and prevents Pu from plating on the container sidewall.

Acidity and volume of the stripped solution is reduced by heating. This also destroys any residual amine. The type of acid determines the final extractive scintillant. An extractive scintillant containing HDEHP was used for perchloric acid, NDAS for sulfuric. A diluent, 2-ethylhexanol, was to the trioctyl-

lamine nitrate ( $\text{TANO}_3$ ) as an aid to stripping into 1 *N* sulfuric acid. The pH of the perchloric solution for HDEHP extraction should be greater than one, as the extractant is a weak acid. The pH for the sulfate system can be between zero and two.  $\text{K}_2\text{S}_2\text{O}_8$  is added to ensure the Pu + 4 for the perchloric system. Other than the extractants HDEHP or NDAS, the scintillant cocktails are formulated the same for either system with solvent, enhancer, and fluor.

A matrix standard soil was specially prepared to a 100 pCi/g concentration of Pu homogeneously distributed, and chemically and physically bound to the soil. Soil for the standard was obtained from the RWMC at an 8 ft depth near the location of the proposed retrieval effort. Soil was dried at 105°C in a laboratory oven and sieved through a 35 mesh screen (525  $\mu\text{m}$ ) followed by a 200 mesh screen (75  $\mu\text{m}$ ). Both fractions were weighed with more screened soil added until a total of 1 kg of screened soil was obtained.

The 1 kg of soil was then spiked by taking approximately 100 g from each fraction, wetting completely to a slurry consistency, and adding an accurately weighed aliquot of  $^{239}\text{Pu}$  stock solution. These slurries were mixed thoroughly, dried, ground, resieved, and then mixed in a special dual cylinder mixer. Enough  $^{239}\text{Pu}$  spike was added to each fraction so that the activity concentration was approximately 100 pCi/g. The final blended product had an activity concentration of 102.3 pCi/g. Sieving of the soil was done to enhance the particle size fraction that was less than 10  $\mu\text{m}$ . This is the respirable fraction and should be the same size as found on most of the smears and filters to be analyzed.

An above background sample of Pu contaminated soil that had been environmentally aged and may have been "high fired" was obtained from the same source as most of the waste, Rocky Flats Plant, and used as another matrix standard. This soil has a high silica and low clay content, a more refractory (hard to dissolve) Pu oxide, and Pu that is more intimately bound to the soil. The RFP soil was obtained by RFP personnel, downwind from a former drum storage area. The Pu originated 20 years ago from leaking drums that contained contaminated cutting oil. The oil held a suspension of <3  $\mu\text{m}$  Pu particles. This area was decontaminated in 1969 and covered with an asphalt pad.<sup>9</sup> The estimated  $^{239}\text{Pu}$  concentration was 1000 pCi/g.

The RFP soil was dried and sieved to determine particle size distribution. The finest particle size range, less than 45  $\mu\text{m}$  was used for most of the tests as this approximates air deposition or filter samples more closely than the bulk soil. A similar sized sample from the RWMC standard was also used for this reason. Both matrix standards, RWMC and RFP soil, were used to test the sample dissolution and extraction efficiencies and verify elimination of background interferences.

Matrix blanks were used to test the method, particularly the contribution of natural background alphas and reagent impurities to the peak. For a blank soil known to be Pu free, a subsurface soil sample from a basement excavation, presumably having no Pu fallout, was used. This soil was counted directly or was dissolved, extracted, and counted. Differences between the matrix stan-

dards and the matrix blank were used to determine the minimum detectable activity, as well as how the ALS system and chemistry is distinguishing Pu alpha from those alpha naturally in the soil.

The Pu and Am concentration of the standard and blank soil was determined by the Rocky Flats Plant, Golden, CO, UNC Geotech at Grand Junction, CO; and the INEL. They used dissolution and extraction, followed by conventional alpha spectrometry and whole sample counting of Am by gamma ray spectrometry. RFP and INEL used gamma ray spectrometry of  $^{241}\text{Am}$  and assumed a 10:1 ratio of Am to Pu. UNC used total dissolution, organic extraction, ion exchange, precipitation, and alpha spec for Pu and Am. The results averaged 1010 pCi/g Pu and 110 pCi/g Am for the suspendable (less than 100  $\mu\text{m}$ ) portion of the soil. The blank had less than the detectable (about 0.1 pCi/g) for both isotopes.

Following sample preparation, samples were purged of dissolved oxygen and dried before insertion in the oil filled counting chamber. In direct filter analysis, occluded air on the filter was also removed. A filter disc, smear, or portions there are folded and pushed with a lambda pipette into the counting test tube so it takes up no more space than the one mL volume scintillation solution. Air is removed by bubbling dry argon, saturated with toluene, through a lambda pipette while probing with the pipette to remove all bubbles from the test-tube. The paper becomes transparent and seems to disappear. A transfer lambda pipette tip was used as a sparging lance. Water in the gas is removed with molecular sieve and metallic sodium. Bubbling through toluene saturates the gas with the scintillant solvent so the sample volume remains constant.

The test tube is corked and sealed with parafilm, wiped clean, and placed in the sample holder oil bath. The light tight cap is replaced, the high voltage activated, and counting on the ALS spectrometer initiated. A directly prepared sample will count with near 100% efficiency if the alpha activity is on the surface of the fibers in a very thin layer. This method works best on samples with ultrafine particulates, such as air filter samples with only respirable size particulates. Sparged samples sealed with parafilm may last for several weeks, but slow evaporation of the scintillant still occurs. Only glass sealing and dark storage will ensure long term stability.

Two types of calibration are necessary in the ALS system: energy and amplitude. Energy calibration is done by extracting Pu from the standard aqueous solution into the same scintillant in the same manner as the sample. The peak energy of the sample should match that of the standard. Instrument and extraction efficiency are verified with check standards and spikes, assuming near 100% counting efficiency. When directly counting samples the calibration for both energy and amplitude is difficult, as color and chemical quenching shifts the spectrum, and inclusion of alphas in some particles lowers the efficiency. Results for direct counting of various types of blanks, prepared calibration standards, and standard spiked soil are given below.

## RESULTS

This section discusses results of analysis of soils and filters on the PERALS system, both directly without treatment and following microwave digestion and extraction of the sample. Three experimental parameters will be reviewed as they apply to both direct analysis and analysis after dissolution and extraction: efficiency, resolution, and background. Optimum is 99.7% efficiency, 5% resolution, and <0.02 cpm background for the entire process (dissolution, extraction, and counting). Precision for these parameters, for direct and extracted soil standards, blanks, soil blanks, and soil spikes, for problems encountered, and for further work necessary are discussed.

Background includes electronic noise, cosmic rays, and chemical impurity contributions to the final count rate. Efficiency is the percentage of the analyte extracted and pulses successfully detected by the instrument and converted to the count rate. Resolution is the degree of energy separation of one group of pulses from another and the location on the energy scale of a specific peak. Precision is the stability of the instrument and reproducibility of the other parameters.

### Resolution

Energy resolution, the separation of two alpha peaks by energy and the energy location on the spectrum, has both instrument and chemistry contributions. Resolution depends on the amount of light per pulse received; thus an efficient and stable scintillator and diffuse reflector are necessary. The characteristics of a PM tube and its physical relationship to a sample are critical to maximizing this parameter. The detector uses an oil-filled cavity, eliminating the air gap between sample and phototube. This prevents spectrum distortion caused by refractive index discontinuity and improves resolution.

Figure 1 shows a PERALS alpha spectrum for  $^{226}\text{R}$  and its daughters overlaid with a surface barrier spectrum.<sup>9</sup> The radium, radon, and polonium peaks are resolved in both systems. The weak 4.6 MeV radium, however, is not resolved from the strong 4.78 MeV radium, illustrating the practical limitations 5% resolution. The resolution of the major peak is about 20 keV in the surface barrier spectrum and 250 keV in the PERALS spectrum.

Resolution is needed to separate background nuclide activities from those activities of Pu in the soil. Energy stability is important in identifying the peak. The separation of the Pu peak from that of background Th depends on energy stability and resolution. A spectrum of a naturally occurring alpha emitter, Th, is shown with that of Pu in Figure 2 after one week of ingrowth. The separation of the single Pu peak (5.1 MeV) from the major Th (4.2 MeV) and daughter peaks (6.0 and 7.7 MeV) can be seen.

Table 1 gives resolution for prepared Pu standards. The full width at half maximum (FWHM) and the region of interest (ROI) width were both used as measurements of resolution. Most peaks had resolutions under 10%. We

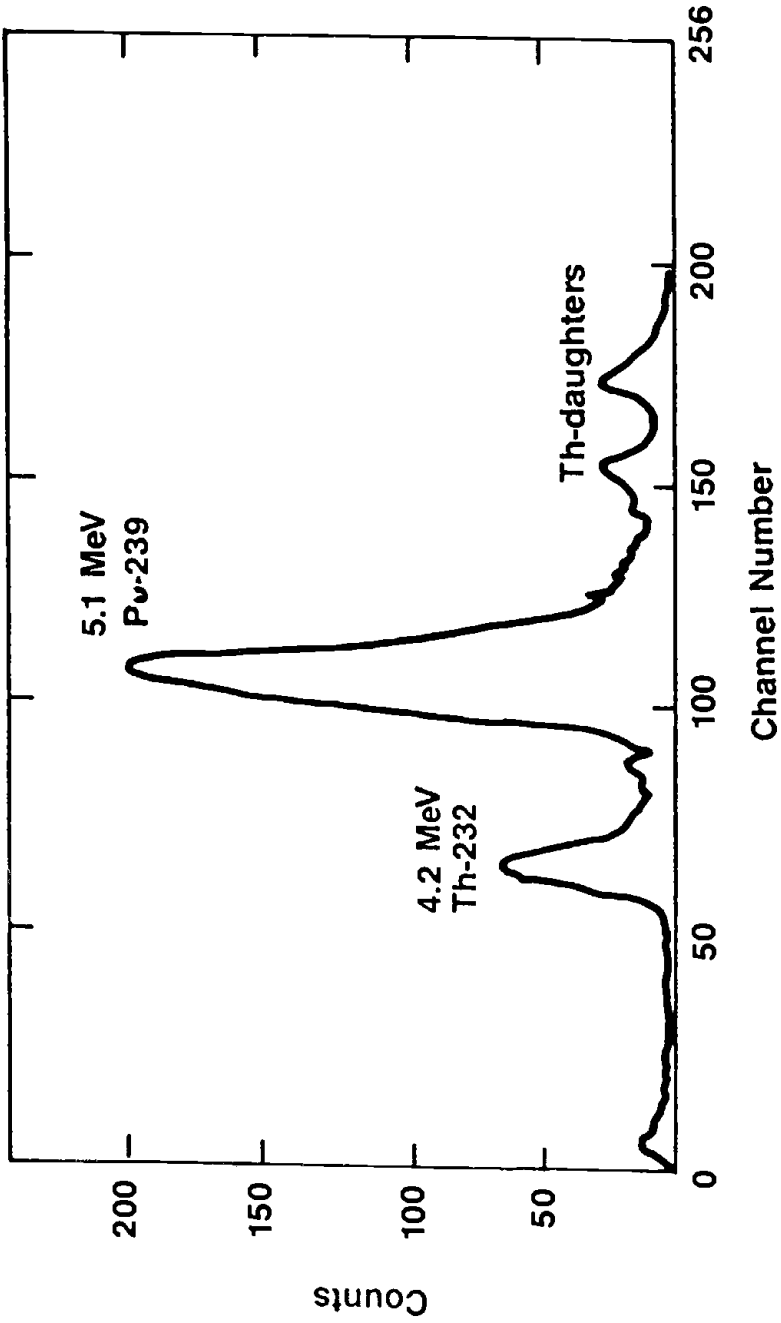


Figure 2. Plutonium and thorium standard spectrum.

**Table 1. Plutonium Peak Resolution on Prepared Standards**

Standard pCi	FWHM KeV	Resolution Percent
0.1	290	5.2
0.7	502	9.7
5.3	546	10.6
6.0	490	9.5
74.4	557	10.8
110.2	638	12.4
142.9	585	11.3
Average	515	10
Standard Deviation	111	2.2

achieved a 5.6% resolution on a low-level sample (0.1 pCi) in the the HDEHP extractive scintillant. This is the scintillant used for Pu extraction in the perchloric system and direct filter counting. Peak location is also a factor in energy calibration and peak identification. The standard deviation (1 sigma) of peak energies (location) was less than 10% that of resolution was 2.2%.

The effect of the soil on resolution was tested by using direct soil laboratory spikes. Two soils were spiked with a standard Pu solution directly in the counting tube. The Pu peak was shifted by about 10% from that of the standard without soil and broadened by 30 to 50%. A slight increase in the beta continuum region channel 5–10 was also noted. Spike recovery was 90%.

Energy shifts and loss of resolution occur when adding soil to the scintillant in direct analysis. Resolution also changes with various soil types—blank soil, spiked RWMC soil, and RFP soil. The direct soil sample method often gives a highly colored sample, which gives an energy shift toward the beta continuum region, channel 1–10. This type of quenching may also decrease counting efficiency with the loss of resolution. Energy shifting and quenching is discussed in the background and precision sections.

## Efficiency

Total efficiency is the sum of counting efficiency (the percentage of pulses successfully detected by the instrument) and the efficiency of dissolution and extraction, sometimes called chemical yield. Several types of samples were analyzed to measure these operational parameters and thus assess the quality of data achievable with the ALS system (instrument and chemistry). Efficiency of various samples and control standards in both the direct and extracted mode are given in the tables and discussion that follows. Problems and interferences that affect efficiency are given in the discussion of precision.

Table 2 gives combined counting and extraction efficiency for various soils both directly counted and digested-extracted before counting. At the current efficiency of about 20 to 25% in the direct mode, 100 pCi/g of Pu on RFP soil should be detectable on relatively clean filter samples. At this concentration (one tenth the RFP soil concentration 1000 pCi/g) and efficiency, the count

**Table 2. ALS PERALS Analysis of RWMC Standard Soil, Rocky Flats Soil, Rocky Flats Soil on Filters**

Soil Type	Method	Peak Centroid	Percent Efficiency	Percent Resolution
100 pCi/g Standard	Direct	94	45	14
1000 pCi/g RFP Soil	Direct	12	8.6	12
RFP Soil on Filter	Direct	19	28	28
Standard	Extraction	72	85	9
RFP Filter	Extraction	85	22	8

rate of 50 mg of sample is 2.2 dpm, or over ten times the background of 0.15 dpm.

The direct filter analysis had a higher efficiency than direct RFP soil analysis, 9 vs 28%. The suspension of the soil in the PMT viewing area and the limited settling of contents could account for this higher efficiency. The filter samples here were highly quenched, as evidenced by the peak shifting seen in Figures 3 and 4. Some of the RFP Pu was seen in the higher channel regions, with less quenching and count rates about 3 times the soil background. Count rates for RFP and blank soil (Tables 2, 4, and 5) indicate the Pu could be distinguished from the background activities present in non-Pu-containing blank soil in the direct analysis mode.

When the spiked soil standard was counted directly, the overall efficiency approached 45% (Table 2). The efficiency for the RFP soil with a much more refractory (hard to dissolve) form of Pu was only 9%. The count rate of 0.93 cpm (Table 5) for the spiked soil in the Pu region of interest (channels 90 to 110) is over 5 times (0.16 cpm) that of the blank soil. HDEHP is the most effective extractive scintillant for direct counting in actually leaching some of the Pu. The NDAS does not leach the Pu as well as the HDEHP and has a lower blank and standard spiked soil count rate.

RFP and standard soil samples that were digested and multiply extracted have the same type of relationship between spiked soil and RFP soil held in direct counting. Extraction of Pu from the RFP soil is more difficult than the RWMC standard soil. Efficiencies for the RWMC standard soil approached 85% and the RFP soil 22%.

Some RFP soil samples were digested and extracted directly into the extractive scintillator, HDEHP. Recovery efficiencies of 25% were achieved for single extractions, 22% for multiples giving a detectable peak in 1 hr of counting for 1 g of a 1 pCi/g sample. This is about 0.55 cpm, about 5 times greater than the background of 0.1 cpm (Table 1). The peak location on the average is somewhat lower for the standard soil extract than the RFP soil. The RFP soil had a higher counting uncertainty and gave a wider peak (Figure 5). Time did not permit full development in this area, but further work should bring this extraction process up to 99% efficiency.

Table 3 lists overall efficiencies for prepared standards. The extraction and counting efficiency of 95% approach the optimum 99.7% (counting wall

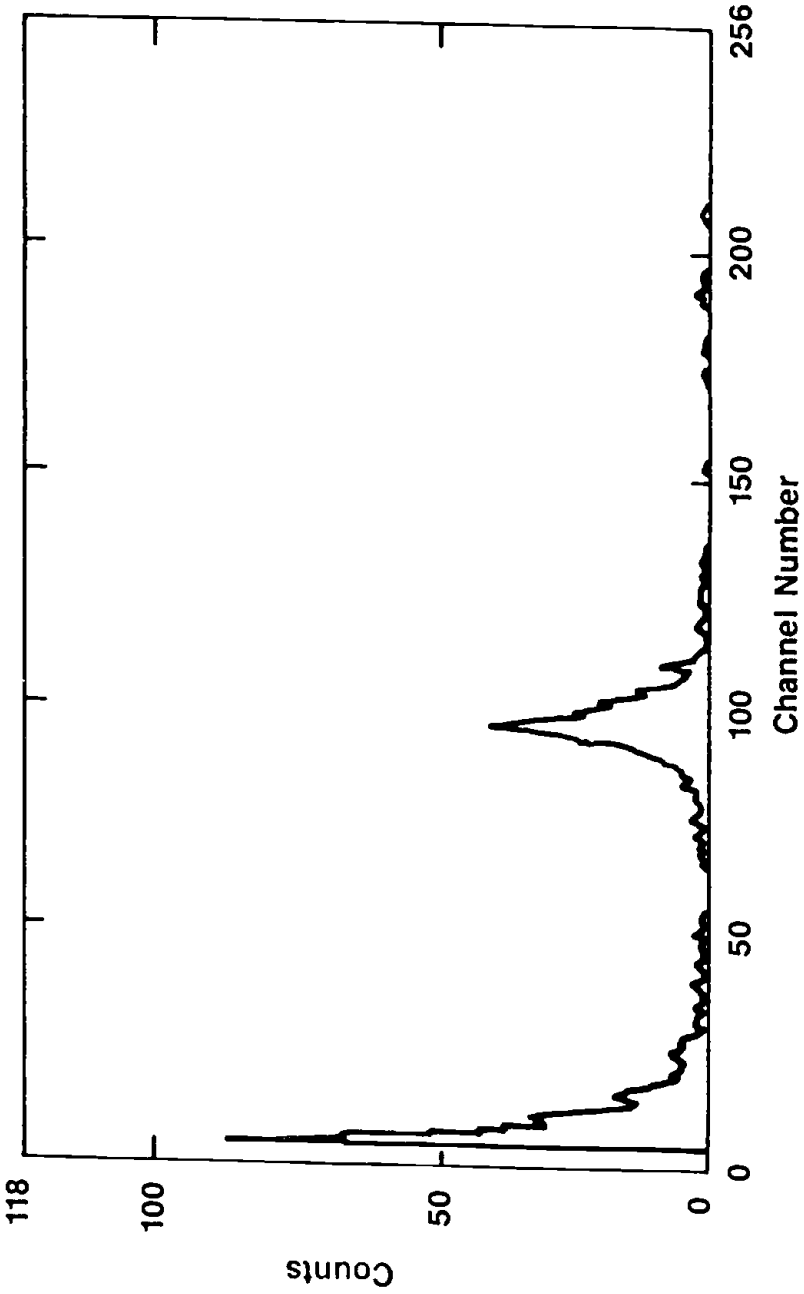


Figure 3. Direct Pu soil spectrum.

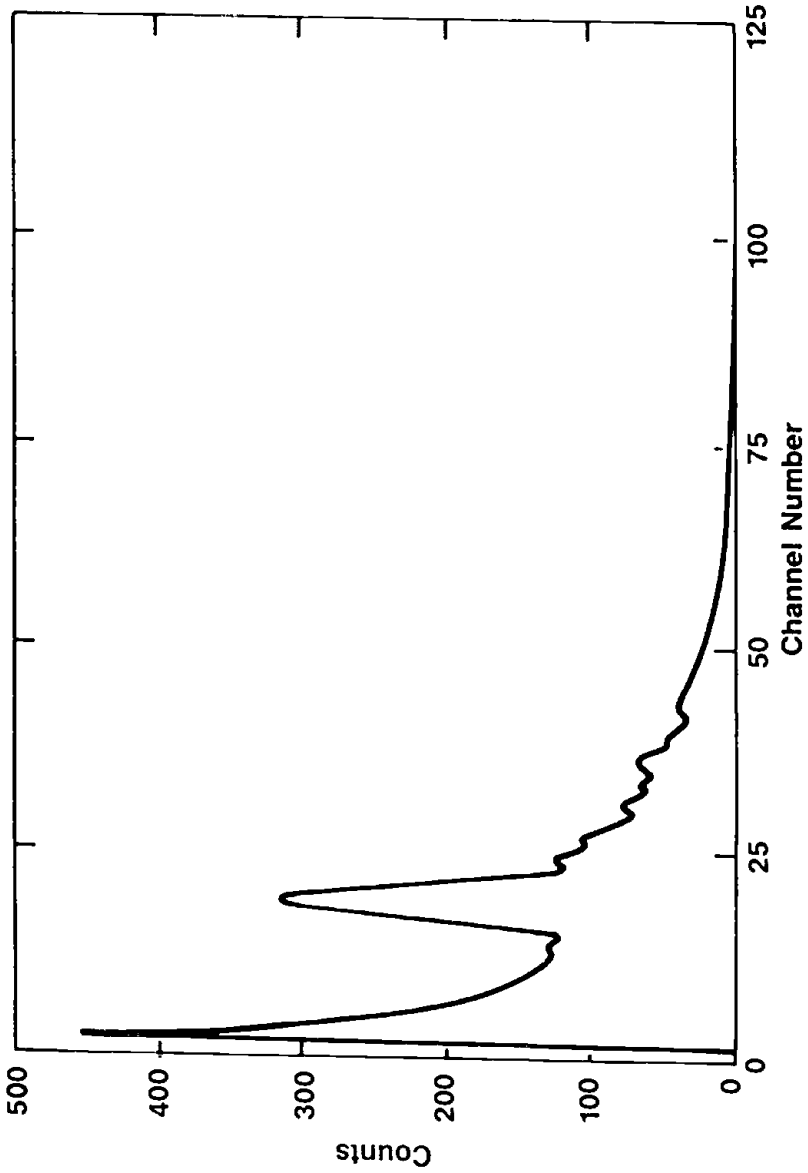


Figure 4. Direct RFP soil on filter spectrum.

**Table 3. Plutonium Efficiency on Prepared Standards**

Standard PCI	Efficiency Percent
0.1	98
5.3	92
74.0	93
88.0	95
100.9	89
142.9	101
177.0	95
Average	95
Standard Deviation	3.9

losses only). The main problem with efficiency was the extraction rather than the counting. Some standards were not in either the proper oxidation state or pH range for efficient extraction. The reproducibility of extraction was about 4%. Improvement in extraction efficiencies and consistent recoveries is desirable.

## Background

There are two types of background radiations of concern in ALS, those from the beta and gamma emissions caused by naturally occurring substances in the soil such as  $^{40}\text{K}$ , and those from other alpha emitters in the same region as Pu, such as the naturally occurring radionuclide daughters of the uranium and thorium chains. Total background is all counts in the region of interest (ROI) not from the desired element (Pu). This includes contributions from the reagents, scintillants, and other nuclides in the sample, including that of the instrument. Elimination of beta and gamma background is achieved by pulse shape discrimination (PSD). Decreasing alpha background requires clean

**Table 4. Summary of Background**

Background Type	Extractive Scintillant	Total DPM in ROI	ROI Centroid	Energy Shift Percent
Standard	HDEHP	1.69 ± 0.90	9.4	
Soil	HDEHP	1.34 ± 0.74	8.7	7
Method	HDEHP	1.58 ± 0.6	5.7	39
Standard	NDAS	0.92 ± 0.90	4.9	
Soil	NDAS	1.16 ± 0.71	4.7	4
Method	NDAS	0.71 ± 0.12	5.8	21
Standard	NDEHP	0.08 ± 0.04	105	
Soil	HDEHP	0.15 ± 0.02	92	12
Method	NDEHP	0.29 ± 0.21	81	23
Standard	NDAS	0.20 ± 0.07	75	
Soil	NDAS	0.04 ± 0.01	58	24
Method	NDAS	0.09 ± 0.07	55	28

**Table 5. ALS Duplicate Analysis**

Method	DPM in R01	Relative Percent Deviation	Primary Peak Channel	RPD Peak Location
Standard blank	0.14 ± 0.02	7	108	0.9
	0.15 ± 0.02		109	
Soil blank direct	0.16 ± 0.10	12	62	22
	0.18 ± 0.18		77	
RFP soil direct	2.10 ± 0.38	39	13	7
	1.14 ± 0.21		14	
RFP filter direct	4.30 ± 0.30	17	9	61
	3.63 ± 0.33		17	
Standard soil direct	0.97 ± 0.12	28	98	4
	0.73 ± 0.04		102	
Standard extraction	192.6 ± 9.4	0.6	103	11
	193.8 ± 12.8		92	
RFP soil extraction	83 ± 2.1	6	72	15
	88 ± 1.1		98	
Standard soil extraction	28 ± 0.84	31	82	0.6
	39 ± 0.4		83	

reagents and a low radon working area. Currently the method blanks give a background 4 to 10 times higher than the optimum electronic background.

Various blanks (method, standard) were prepared for both extracted and directly analyzed samples. The background contributions can also indicate the efficiency of the scintillant and show energy shifting. The method blank is blank soil directly prepared in scintillant or digested and extracted into the scintillant. The standard blank is pure extractive scintillant.

Table 4 lists the average count rates for backgrounds in two different extractive scintillants. A typical background spectrum for the HDEHP extractive scintillator is shown in Figure 6. Peak location and width for two different regions of interest (ROI) are given, one region is the area of highest background near the beta continuum, containing possible thorium peaks, the other is further down field where Pu peaks should be located. The primary channel is the center of the peak where the largest number of counts are clustered. The peak width is given by the number of channels in the region of interest. The counts per channel gives the actual background that can be used for correction of sample peaks falling in those ROIs.

Background varies more at different regions of interest than with different types of blanks. This seems to indicate that the background contribution of natural alpha emitters in soil is negligible. Near the edge of the beta continuum (peak channel 5-9) the background is about 10 times higher, 0.9 to 1.7 dpm, than in the region of interest for Pu in a clean sample, 0.04 to 0.2 dpm. The HDEHP, which is the scintillant of choice for direct soil counting, has a higher background than the NDAS. The NDAS is perhaps easier to use for the final

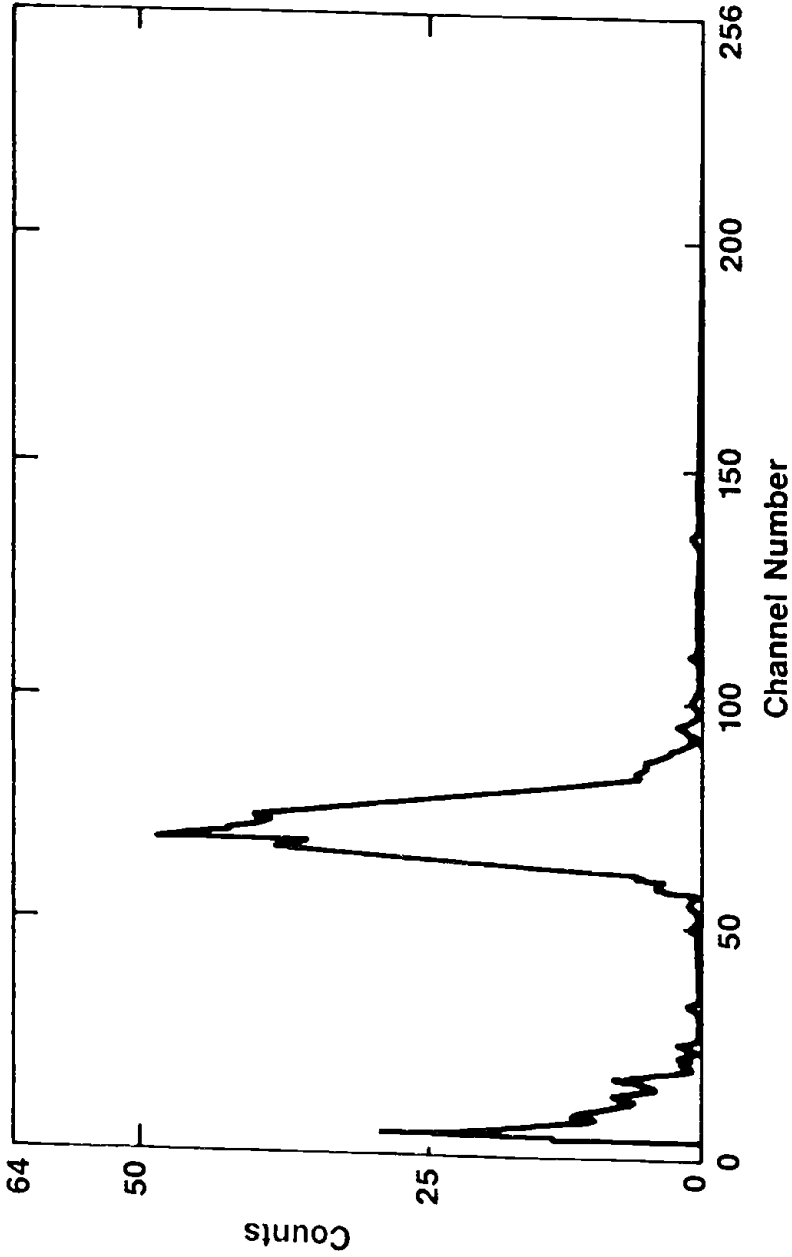


Figure 5. Extracted RFP soil spectra.

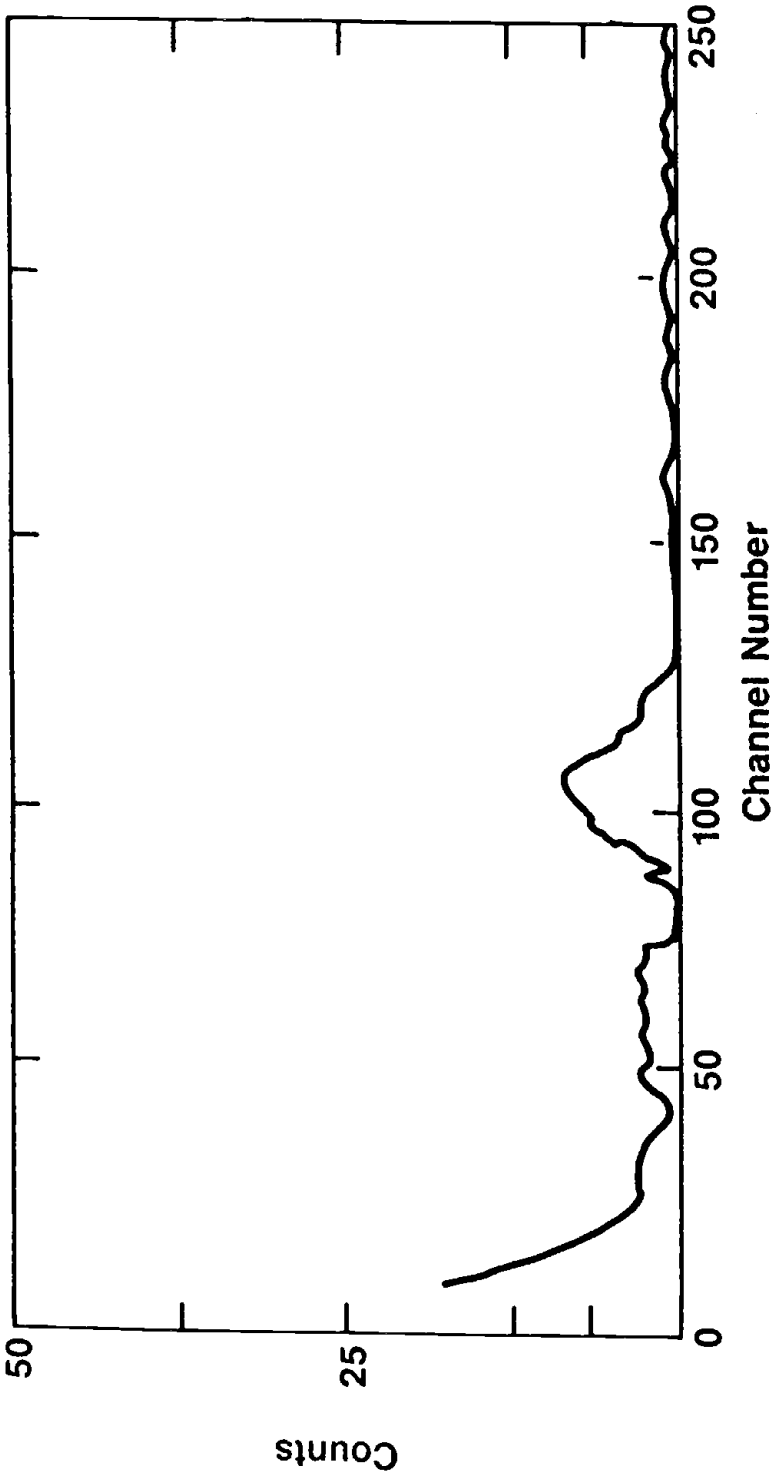


Figure 6. Background spectrum.

secondary extraction than the HDEHP but does not partially extract Pu in the direct soil mode. Soil added to the scintillant does not increase the background significantly but does shift the ROI.

From the background count rate of blank soil (Table 5, 0.16 dpm) the approximate detection limit of 100 pCi/g can be estimated. Assuming a detection limit of 5 (4.66 sigma) times background, the activity of the sample would have to be about 0.8 dpm. At 20% efficiency this is 4 dpm in the sample, or about 0.02 g of sample. The count rates for about 10 mg of the 100 pCi/g standard, 1000 pCi/g RFP soil, and soil on filter are also at least 5 times the background of the blank soil.

## Precision

The precision associated with background, resolution, and efficiency for direct and extracted soil analysis can be seen in Tables 1, 3, and 4 with a summation in Table 5. Standard deviations (1 sigma) in Tables 1 and 3 give an idea of the stability of the instrument and standards and the reproducibility of the final extraction procedure.

The combined instrument and sample stability, as expressed by reproducible counts of the same standard or blank over 2 weeks time, is about 1.4%. Some degradation of standard was noted after 2 weeks. The extraction procedure is more of a factor in efficiency reproducibility than the instrument instability. Lack of temperature control in the basement lab must also be considered. The standard deviation of efficiency for multiple counts of different standards, covering a wide range of concentrations (0.1 to 200 pCi) on different days, was about 4%.

The peak location or energy stability varied by about 10% for the extraction and counting of standards that varied by over the three orders of magnitude in concentration. The percent standard deviation (1 sigma) in resolution, as expressed by FWHM, was 2.2%. The energy stability for a well sealed standard over time was about 2%.

Variations in extraction procedure are more of a factor in any energy shifts than the instrument instability. Energy shifts between soil types for both extracted and direct analysis can be seen in comparing ROI reproducibility in Table 5 and the spectra of the standard soil and the RFP soil on a filter Figures 3 and 4. The location of the peak for the spiked RWMC soil is not shifted noticeably from that of the standard, but there is a shift when comparing the direct RFP soil on filter sample. The primary peak activity for the RFP soil on filter was located in the 10–20 channel ROI, whereas the standard and standard soil peak is around channel 100.

Background stability can be seen when comparing the ROI of either extractant in the standard blank (scintillant only) to soil blank (soil and scintillant) in Tables 4 and 5. In HDEHP the shift is 7% from 9.4 to 8.7 in the low channels near the continuum and 12% from 105 to 92 in the Pu ROI (5100 keV). For

NDAS the shift is 4% in the higher background beta continuum region and 24% in the Pu ROI.

Considerable shifting of the peak is apparent when comparing direct soil and extracted soil analysis (Table 3). Rocky Flats soil and filters caused a greater energy shift than the directly prepared RWMC soil standard. The Pu on the standard soil is in a more extractable form than that of the aged RFP soil; thus some Pu was detected in true solution rather than from a soil particle. The clarity of the sample in direct analysis was critical and made a great difference in the peak location and the overall counting efficiency. After sparging, some samples settled more rapidly than others. Their clearing up gave rise to much of the variation between replicate counts.

A general idea of background stability can be seen in Tables 4 and 5 with the use of replicate background counts and uncertainties within a single count. Background can be influenced by instrument stability and chemical stability, and it is a factor in analysis precision. The uncertainties for the replicate blanks are the standard deviations (1 sigma) of multiple counts. The background spectrum lacked well defined peaks (Figure 6). The width of the ROIs for most of the background counts, the low count rates, and the energy shifting do not allow identification of specific contaminant isotope contributions to background activity. The counting uncertainties are higher than when activity is actually present (Table 5). High standard deviation of replicate runs and high blank count rates could have been from the poor location of the spectrometer in a known high-radon-background basement lab.

Digestion and a single extraction into the final scintillator gives most of the advantages not found in a directly counted sample, such as improved resolution and efficiency and background elimination, but it saves time by eliminating subsequent stripping and extraction steps. This was tried with several dissolution systems and extractive scintillators with some success. The primary problem was incomplete extraction and extraction of iron, making the solution highly colored. Getting the aqueous sample into the proper state, by adjusting pH and ionic strength without precipitating out calcium, was also a problem without the preliminary extraction. The time saved is significant and for some applications may be feasible, especially if some other organic extractant could be found. The ideal extractant needs to be selective for removing Pu from a nitrate or sulphate system, rejecting thorium, uranium, and iron, and not containing chloride, nitrate, or other quenchant groups. The tertiary amine nitrate now used is selective but is itself highly quenched due to the nitrate group.

Multiple extractions should give lower backgrounds, less energy shifting, and increased resolution. Possible interferences while extracting the aqueous solution from the digested sample into the organic amine or extractive scintillator, in order of importance are: (1) incomplete extraction of Pu, (2) extraction of unwanted ions, and (3) inability to strip the Pu from the first extractant into the aqueous solution. Some of the causes of these interferences are: incorrect Pu oxidation state, incorrect pH, insufficient ionic strength, impure

extractants, and nonextractable Pu complexes in the aqueous solution. The spectral separation of Pu from an interfering alpha emitter such as thorium is shown in Figure 2. Thorium should not be a problem in direct analysis unless present in great amount and allowed to ingrow, as some thorium daughters will add to the Pu peak. Multiple extractions chemically remove thorium and uranium and eliminate alpha interference problems.

## CONCLUSIONS

An ALS system called PERALS has been investigated for use in obtaining alpha radiation levels during the TRU waste retrieval. By directly analyzing lightly soiled filters, the ALS system can detect concentrations as low as 100 pCi/g Pu within 1 hr of receiving the sample. For heavily soiled filters or soil samples, a minimum detectable activity of 1 pCi/g can be obtained in 2 hr including the time to dissolve and extract the sample. Direct counting of filters gave efficiencies of about 20%. Alpha resolution of about 5% was sufficient to separate the Pu peak from the primary Th peaks.

Areas of future work include: improving extraction efficiency and reproducibility, determining detection limits in the presence of uranium and varying amounts of thorium, and decreasing the preparation time and complexities. Instrumental improvements such as better photomultiplier tubes, better light couplings, and better electronics are possible, though interferences in the instrumentation and counting area have been reduced to a considerable extent.

The largest gains can be made by improving the overall efficiency for the entire analytical scheme. Future work would involve spiking at various points during dissolution and extracting to pinpoint critical procedural parameters where losses are occurring. Noninstrumental interferences can hinder the separation of alpha and beta pulses and the resolution of alpha peaks. Chemistry improvements in the selection of fluors and scintillants, and elimination of quenching and interferences through organic extraction, are currently under investigation. The inherent advantages of near 100% counting efficiency make ALS a viable method for rapid Pu analysis and screening in conjunction with traditional analysis methods.

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