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RAPID DETERMINATION OF PU CONTENT ON FILTERS AND SMEARS USING ALPHA LIQUID SCINTILLATION

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ABSTRACT

RAPID DETERMINATION OF PLUTONIUM CONTENT ON FILTERS AND SMEARS USING ALPHA LIQUID SCINTILLATION TECHNIQUES

This paper 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 (Pu^{239}) 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 utilizing 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) should be possible in less than 2 hours.

EXECUTIVE SUMMARY

Filter and smear samples will be analyzed daily for plutonium (Pu^{239}) content during projected waste retrieval operations at the Radioactive Waste Management Complex (RWMC) of the Idaho National Engineering Laboratory. Monitoring multiple times a day 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. Quick screening for Pu using this technique is not feasible because of extensive sample preparation required. Currently a sample is solubilized by wet ashing and fusion, chemically extracted with organic and ion exchange techniques, precipitated or electroplated as a thin film and counted on a silicon surface barrier detector. Alpha spectra are highly dependent on the purity of the separation. Mass degrades the spectra and interferences from nonradioactive substances may hinder good separation efficiency.

Alpha liquid scintillation (ALS) in conjunction with microwave digestion was investigated as a technique for rapid Pu analyses. Potential advantages are short turnaround time and field use with acceptable accuracy. The technique was tested for the determination of Pu on both soils and air filter samples.

Using a state-of-the-art Photon Electron Rejecting Alpha Liquid Scintillation (PERALS) spectrometer utilizing pulse shape discrimination (PSD). Relatively clean filter samples could be directly counted in an all purpose scintillant. The detector is an oil filled chamber directly coupled to a high sensitivity photomultiplier tube. This counting chamber arrangement with PSD circuitry gives 99.7% counting efficiency and 99.95% rejection of beta and gamma pulses. The scintillant was bis 2-ethylhexyl phosphoric acid (HDEHP), 4-biphenyl-6-phenylbenzoxazole (PBBO), toluene and naphthalene.

Soil samples and smears contaminated with Rocky Flats Plant plutonium waste with a high inert solids content were prepared for analysis by dissolution of the sample in nitric and hydrofluoric acids using a microwave digestion system and teflon pressure vessels. After ionic strength and oxidation state adjustments Pu was extracted into a high molecular weight tertiary amine. This amine was stripped with dilute sulfuric or perchloric acids and then extracted into the extractive scintillant, HDEHP or 1-nonyldecylamine sulfate (NDAS) dissolved with the scintillant and fluor.

Total plutonium content in air filters, smears and soils were successfully determined with this technique. Currently the approximate minimum detectable activity (MDA) for direct counting of air filters is about 100 pCi/g (3.7 Bq/g) for an hour count. With further work a dissolved and extracted sample should have an MDA of less than 1 pCi/g (0.037 Bq/g).

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ACRONYMS

ROI	Regions of Interest
PSD	Pulse Shape Discrimination
RWMC	Radioactive Waste Management Complex
HDEHP	bis 2-ethylhexyl phosphoric acid
PERALS	Photon Electron Rejecting Alpha Liquid Scintillation
ALS	Alpha Liquid Scintillation
PBBO	4-bephenyl-6-phenylbenzoxazole
MDA	Minimum Detectable Activity
DOE	Department of Energy
MCA	Multi Channel Analysis
PHA	Pulse Height Analysis
ORDELA	Oak Ridge Detector Labs
MEV	Million Electron Volts
KEV	Thousand Electron Volts
CAM	Constant Air Monitors
RFP	Rocky Flats Plant
INEL	Idaho National Engineering Laboratory
FWHM	Full Width at Half Max
TSP	Total Suspended Particulate
RPD	Replicate Percent Difference
NDAS	1-nonyldecylamine Sulfate
ERP	Environmental Restoration Program
SDA	Surface Disposal Area
HEPA	High Efficiency Particulate Air
EPA	Environmental Protection Agency
NBS	National Bureau of Standards
SAP	Sampling and Analysis Plan

1. INTRODUCTION

Filter and smear samples will be analyzed multiple times a day for plutonium (Pu^{239}) 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.

Extremely low amounts of TRU alpha-emitting isotopes such as plutonium (Pu) are allowed in a controlled area. Plutonium (Pu-239) is a radioactive isotope which emits primarily alpha particles in the 4-6 MeV range.(1) The Pu of concern here is attached to dust particles and has a gross chemical form usually assumed to be the oxide, PuO_2.(2) The present limit for the classification of a solid as TRU is 100 pCi/g according to the present DOE standard. For decontaminated equipment to be considered radioactive at the INEL, the activity level is 300 pCi/g.(3) The goal with this instrument is the detection of one tenth this amount 30 pCi/g on an air filter or smear,(4) in a rapid manner to allow trend data for contamination levels during retrieval operations.

Current published routine techniques for Pu analysis are time consuming (on the order of days) as both numerous naturally occurring isotopes, such as uranium and thorium daughters, and inert solids must be removed prior to counting to avoid mass and overlapping peak interferences when plated out and counted on a surface barrier detector. Quick screening for Pu using this technique is not feasible because of extensive sample preparation required. With current techniques the sample is solubilized by wet ashing and fusion, chemically extracted with organic and ion exchange techniques, precipitated or electroplated as a thin film and counted on a silicon surface barrier detector.(5) Alpha spectra are highly dependent on the purity of the separation. Mass degrades the spectra and interferences from nonradioactive substances may hinder good separation efficiency.(1)

Current state-of the art alpha liquid scintillation (ALS) instrumentation for counting and/or spectrometry is a Photon Electron Rejecting Alpha Liquid Scintillation (PERALS) Spectrometer.(6) Features include: 0.02 cpm background, 5% resolution, 99.7% counting efficiency and 99.95% rejection of beta and gamma pulses. Counting compares changes in the ratio of counts in a certain region to that of the background and would be useful for example in a direct analysis mode for screening of filters or smears. ALS spectrometry is the generation of a plutonium peak within an alpha spectrum. It is used when the larger amounts of dust and higher thorium levels not normally found in indoor air require sample digestion and extraction of the filters. It gives greater separation between natural and Pu alpha and has a lower detection limit than direct sample counting.

Special sample preparation techniques are important in ALS such as microwave digestion. Microwave digestion quickly reduces solid samples to an extractable form.(7) Microwave digestion in specially designed closed vessel 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.(8) Together with the proper organic extractants ALS techniques both direct and extract give short turnaround time and field use with acceptable accuracy with excellent discrimination against natural background components in the soil.

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.(9) However, 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.(9,10)

This report:

1. Discusses the ALS system and the apparatus, equipment and reagents needed to prepare samples for the system, Section 2

2. Discusses in detail the procedures used to collect and prepare samples, standards and blanks to test the system, Section 3

3. Gives preliminary results of multiple counts of smears, filters and soils, Section 4

4. Outlines laboratory requirements for an integrated plutonium analysis facility, Section 5

5. Concludes with the validity of ALS techniques and recommendations for further work, Section 6.

2. APPARATUS

2.1 PERALS Detector

Until recently adaptation of existing beta detectors was the only way to perform Alpha Liquid Scintillation Spectrometry.(11,12) However, these detector systems did not provide good spectrometric results. To obtain good results an alpha only detector with several features was needed: (a) improved counting chamber design with no air gap, (b) improved pulse shape discriminator (PSD) to separate alpha form beta and gamma pulse continuum, (c) multi channel analysis (MCA) instead of the normal pulse height analysis (PHA) counting of energy regions, (d) elimination of most quenching, (e) lower background through the rejection of afterpulses characteristic of cosmic radiation, and (f) improving the efficiency through rejection of unwanted luminescence.

McDowell(6) has designed a workable ALS instrument called a Photon-Electron Rejecting Alpha Liquid Scintillation Spectrometer (PERALS). Currently this state-of-the-art alpha liquid scintillation design is manufactured exclusively by Oak Ridge Detector Labs (ORDELA). The detector follows the design of McDowell but has an improved electronics module with resolution of 5% (200 KeV) for energies in the Pu region of 5162 KeV and an electronic background of 0.02 cpm. The arrangement of PM tube, sample chamber and specially designed reflector help achieve the improved energy resolution.(6)

Three operational parameters of any counting device are of interest: background, efficiency, and resolution. The background includes electronic and cosmic ray inputs to the final count rate. Efficiency is the percentage of analyte pulses successfully detected by the instrument and converted to the count rate. Resolution is the degree of separation by energy of one group of pulses from another.

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, and those from other alpha emitters in the same region as Pu. The PERALS uses PSD, sample chamber design and extraction chemistry to lessen backgrounds and interferences.

Potassium-40 and naturally occurring radionuclides of the uranium and thorium chains are ubiquitous in soil and give off alpha, beta and gamma radiations. Even the nuclides of interest plutonium (Pu) and americium (Am) have a non-alpha decay component. Radon (Rn), a noble gas and a daughter of both U and Th decay chains, is of concern because of its high specific activity alpha and beta activity and mobility in air. However, isotopes of Rn and their progeny (elements below atomic number 86) are of primary interest in background elimination. Radioactive isotopes of Rn are continually emanating from the earth's surface into the atmosphere. They decay into other radionuclides which attach themselves to dust particles which may be subsequently collected on air samples. Release of Rn is accelerated if there is any disturbance of the earth's surface such as excavations. Rn is also present in construction material buried with the waste such as bricks, concrete, and other mineral products.

Elimination of beta and gamma background is achieved by pulse shape discrimination (PSD).(6) Beta emits 10 times the light of alpha and emit light as prompt fluorescence. Alpha particles give a delayed component of a few hundred nanoseconds. The PERALS has a separate "pulse shape" output to view the separation of the prompt beta and delayed alpha components. The delayed component is electronically treated by PSD to give separate alpha and beta pulses. PSD results in efficient separation of the alpha and beta/gamma peaks thus minimizing background, and improving efficiency and resolution.

Energy resolution, the separation of two alpha peaks, depends on the amount of light per pulse received. Thus an efficient scintillator and 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. These result in light loss, peak broadening and pulse shape distortion.

The background beta and alpha peaks may mask, add to or distort the Pu peak when displayed as a spectrum of energies. The arrangement of sample and PM tube and improved internal electronic gating circuit with PSD, reduces background allowing low concentrations of alpha emitters to be seen and improves resolution so alphas of the natural decay chains and Pu are resolved from each other.

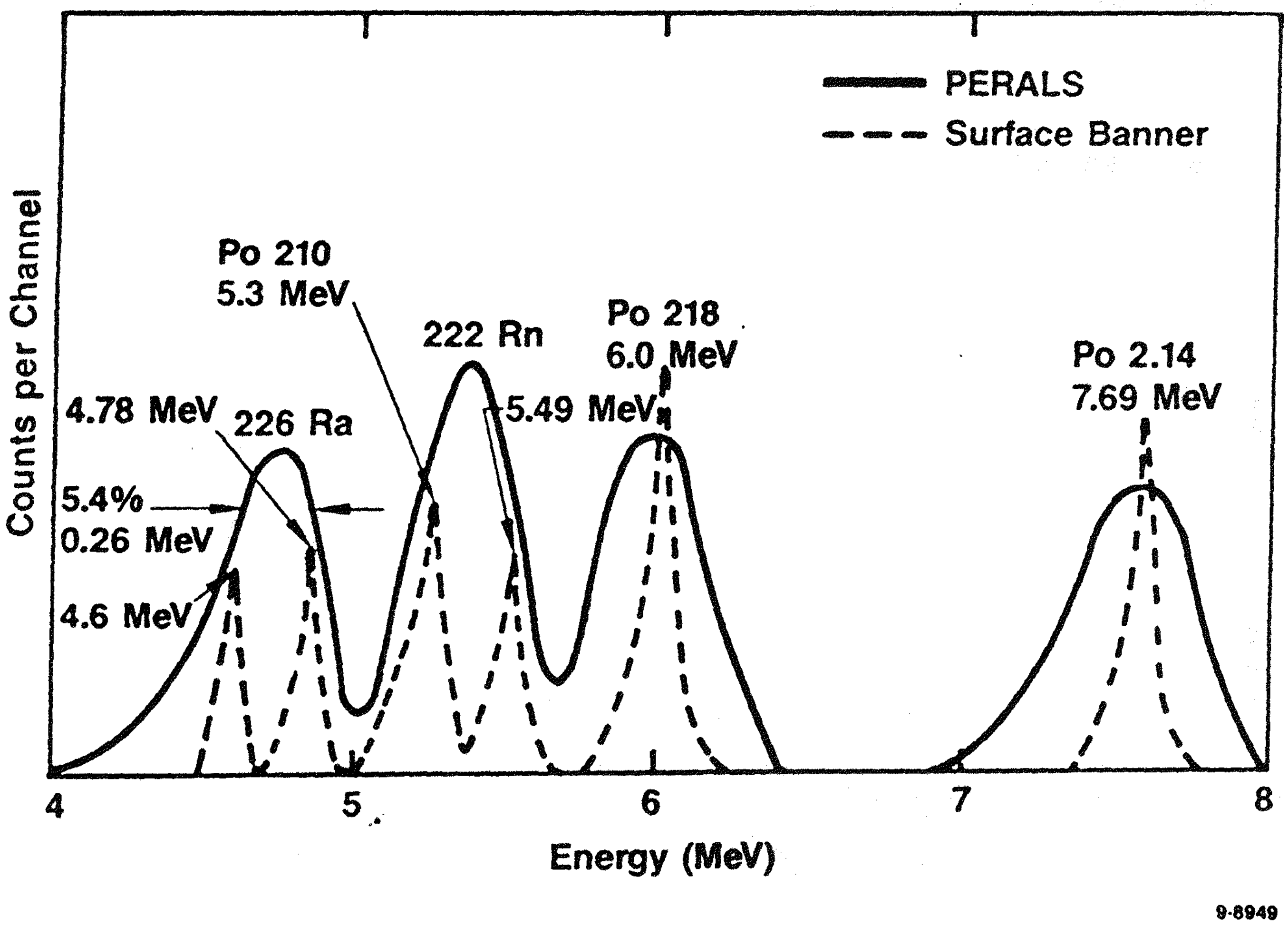
A PERALS spectrum of Radium-226 and its daughters is overlaid on a typical one using silicon surface barrier alpha spectrometry Figure 1. This comparison shows the radium, radon and polonium peaks resolved in both systems. The resolution of 5% for PERALS (250 KEV for Pu) compared to about 20 KEV in the surface barrier spectrum does not allow resolution of. Though the ALS Ra standard is in a different extractive scintillant from that used for Pu the practical outcome of 5% resolution is seen within the 4-7 MEV alpha spectrum. The weak 4.6 MEV radium however is not resolved from the strong 4.78 MEV radium illustrating the the practical limitation of this 5% resolution limit for ALS. Americium -241 and Pu-239 are also seen as one peak on the PERALS system.

2.2 Equipment and Reagents

2.2.1 Equipment

Air sampling equipment includes Hi-Vol or Constant Air Monitoring (CAM) samplers, glass fiber or cellulosic filters, and some type of constant flow control or flow monitoring. Soil and contamination sampling equipment includes smears, shovels, scoops, settling plates, coupons. Analysis

FIGURE 1. SURFACE BARRIER AND PERALS RADIUM-226 SPECTRUM



equipment includes: CEM 81D microwave digestion unit, assorted sizes of separatory funnels (30-500 ml), adjustable hot plates, heat lamps, a balance capable of weighing to 0.1 g, small beakers 10-30 ml., dry argon sparging apparatus, 10 x 75 mm test-tube, cork stoppers, parafilm, and lambda pipettes. Automatic pipettes are useful for addition of reagent acids. For purposes of scintillation cocktail transfer they are calibrated by weight. It is 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 coupled to an IBM PC for peak detection and analysis.

2.2.2 Reagents

Four types of reagents are used in the procedure: (a) mineral acids for sample dissolution and organic stripping, (b) inorganic salts for oxidation state adjustment, (c) large organic amines or phosphates for sample extraction and (d) scintillation grade organic reagents and fluors for cocktail preparations. High purity reagents decrease the probability of various unwanted reactions and introduction of undesirable quenching species such as chloride.

Concentrated hydrochloric acid (HCl), nitric acid (HNO_3), hydrofluoric acid (HF), and hydrogen peroxide (H_2O_2) are used for primary sample dissolution. The HCl and HNO_3 are used to form aqua regia at a 3-1 ratio. Aqua regia dissolves most of the mineral components in soil. HF is mixed 7:3 with the aqua regia to dissolve salacious material. H_2O_2 is added after all material is dissolved to break down any remaining organic matter as the chloride and fluoride are being evaporated from the solution.

Either dilute perchloric or dilute sulfuric acids are used to strip Pu from the primary extractant, the tertiary amine. Sodium sulfate or lithium perchlorate are added to prevent Pu from plating on the wall of the beaker upon evaporation in the volume reduction steps. Sodium nitrite, aluminum nitrate, ferrous sulfate and potassium persulfate are used for ionic strength and oxidation state adjustments.

Tertiary amine nitrate $TANO_3$ is the primary extractant but cannot be incorporated into the scintillator because of the severe quenching caused by the nitrate groups. HDEHP (Di 2-Ethylhexyl Phosphoric acid) or NDAS (1-nonyldecylamine sulfate) are secondary extractants that also are incorporated in the scintillator. The scintillant is prepared from a solvent-toluene, a fluor- PBBO (4-biphenyl-6-phenylbenzoxazole) and an energy transfer agent -napthalene. Generally the maximum amount of fluor that is soluble in the solvent is used. All the scintillants used also contained an extractant. Generally the scintillator contained 0.5% PBBO, 25% napthalene and 0.1-0.3 M extractant. Prepared cocktails were filtered and stored in dark glass containers.

3. PROCEDURE

The sampling and analysis plan (SAP)(4) outlines general requirements for quality assurance in ALS development experiments. These requirements include sampling procedures, sample control, document management, equipment, calibration, analytical procedures, data reduction and safety. This procedure describes the ALS analytical scheme and the experimental compliance with the SAP. A preliminary performance evaluation of the ALS system, microwave digestion and organic extraction as an analytical tool for both directly analyzed and digested/extracted samples that will be generated in a contamination control verification plan is given in Section 4 the discussion/ results section.

3.1 Safety

The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined: however, each chemical compound should be treated as a potential health hazard. The laboratory maintains a current awareness file of OSHA regulations regarding safe handling of chemicals. Material Safety Data sheets are also on file.

The Standard Practice Safety manual, an internal document, contains general safety principles applicable to this procedure. These meet the safety considerations outlined in the Sampling Analysis Plan.(4) Those of interest are in the safe handling of chemicals and performing radiochemical operations are: "Hazard Review Committee" 18.2.2.6, "Chemical Lab Inventory" 18.2.2.10, "Chemical Spill Control" 18.2.2.11, "Laboratory Protective Clothing Use" 18.2.2.13, and "Radioactive Material Handling" 18.2.3.3. Safety glasses are always worn in the lab. Normal safety precautions when handling acids and reagents should be exercised.

3.2 Sample Collection, Preservation and Handling

Proper sample collection techniques will be critical in both daily monitoring efforts and soil assays. The sample collection will be integrated with other monitoring devices such as constant air monitoring (CAM). Three types of samples will be collected: air filter samples, swipes or smears of equipment surfaces and soil samples from settling plates or directly of the retrieved soil.

Low concentrations of Pu in air may be sampled by standard Total Suspended Particulate (TSP) Hi-Volume samplers. A smaller sized filter with a quantity of soil (<1 g) may be sampled using a 1 cfm pump in conjunction with the operation of a Constant Air Monitor (CAM). The CAM filter paper itself can be counted directly or the collected material dissolved, extracted, then counted by ALS.(4) For quantitative results the air flow rate at start up and shut down, filter pressure drop, and total elapsed time should be recorded. Humidity conditions during the sampling and the total weight of the filter and collected matter should be recorded for each sample.

Contamination on surfaces has been routinely assessed by smearing a 100 cm^2 area with a 47 mm filter paper. Masses collected in this manner are less than 50 milligrams. Again this filter paper itself can be counted directly or the collected material dissolved, extracted, then counted by ALS.(4) Selection of filter paper will be critical as many papers will not become translucent in the scintillant. Other standard smear media has an adhesive backing and would not be compatible for direct counting.

Airborne dust can also be determined indirectly through settling plates or coupons. An open chamber is placed in the desired area and dust is allowed to settle within the chamber which is protected from side air currents. This collected dust may be scraped directly into the scintillant or the entire surface washed, collected material dissolved, extracted, then counted by ALS.(4) The proposed laboratory facility, Section 5 will have provision for immediate analysis upon collection.

3.3 Direct Sample Preparation

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 soil or matter is in the sample it will require that the sample be digested which is discussed in the next section.

A filter disc, smear, or portions thereof are folded and pushed with a lambda pipette into the counting test-tube so it takes up no more space than the volume of one ml scintillation solution. One ml of an all purpose scintillant such as HDEHP is added to the 10 x 75 mm pyrex culture tube. 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 should become transparent and seem to disappear. The test-tube is corked and sealed with parafilm, wiped clean and placed in the sample holder. The 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.

3.4 Sample Digestion

Sample dissolution concentrates the sample, removes interferences, and provides an optimum solution geometry and composition for good alpha energy resolution. Dissolution of solid samples can be accomplished by wet ashing in nitric and hydrochloric acids using hydrofluoric acid or some type of fusion to break down silicates. For ALS a microwave digestion system with teflon pressure vessels was used to contain the HF, reduce dissolution time and avoid the sulfate system required in fusions.

The sample (soil, smear or filter) is weighed to 0.1 ± mg on an analytical balance and placed in a 120 ml high temperature teflon vessel. A 7:3 mixture of aqua regia and hydrofluoric acid is added. For this size sample 5 ml of nitric, 3 ml of hydrofluoric and 2 ml of hydrochloric make a suitable initial mixture.

The cap is tightened on the vessel to a prescribed torque using a calibrated capping station. This allows the acid mixture to become pressurized to 120 psi. At this pressure the temperature of the solution reaches 150^{o}C and the HF remains in solution longer than in an open system. The microwave is operated for 5 minutes at full power (650 watts) then 10 minutes 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 ion and oxidize minute traces of organic matter. The vessels are capped to hand tightness and the microwave is operated for 10 minutes at full power and 15 minutes at 50% power. These times are for 6 vessels and should be adjusted for a different number of vessels or different size samples.

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 molar nitric acid and 3 molar total nitrate.

Larger samples can be handled but 8-10 ml of 7:3 aqua regia for each gram of sample should be added and more than one volume reduction step should be performed to remove residual chloride, fluoride and organic matter. Digestion should be continued until no particles can be observed.

3.5 Sample Extraction

The dissolved sample is extracted into an an aqueous immiscible scintillator. The main concern in the extraction step is the removal of Th and 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.

Before extraction Pu must be converted to an extractable oxidation state. Pu is primarily in the +6 state after nitric acid digestion. It is brought to the +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 with the tertiary amine with little time delay or it 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 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 acid solution is transferred to a 30 ml separatory funnel and shaken with the amine for several minutes by an automatic shaker. Aqueous and organic layers are allowed to separate. Distribution coefficients (ratio of concentration in organic to that of aqueous) for this system is 4000 for Pu+4, 1 for U+6 1 and 0.01 for Fe+3. The aqueous phase is drained and the organic washed twice with small portions of of 0.7 M nitric acid to remove any residual uranium. The organic phase should now contain Pu and nothing else. It cannot be used in an extractive scintillator however since the nitrate form of the amine is highly quenched.

The Pu therefore, must be stripped from the amine 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.

Either the sulfate or perchloric acid will strip Pu. The sulfuric acid is not as rapid as the perchloric since phase separation is slower. The perchloric acid does require some special ventilation or a trap for the small amount of fumes produced. The type of acid determines the final extractive scintillant. An extractive scintillant containing HDEHP was used for perchloric acid, NDAS for the sulfuric. 2 ethylhexanol should be added to the trioctylamine nitrate ($TANO_3$) as a diluent to aid stripping into 1 N sulfuric acids.

Acidity of the stripped solution is reduced by heating. This also reduces sample volume and destroys any residual organic. 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. Conversion to a suitable oxidation state is not necessary when extracting from the sulfate system. $K_2S_2O_8$ 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. In both system the acid concentration must be reduced for proper extraction and to remove any residual organic form the first separation. Each extraction step in both the primary and secondary extractions requires shaking vigorously for at least 1 minute with an automatic Burrel wrist action shaker.

3.6 Standard and Blank Preparation

In complying with the SAP, multiple tests needed to be performed and several different types of prepared samples needed to be analyzed. It is helpful to define the types of tests and preparations needed to develop and then test different aspects of the ALS procedure. Some of these definitions will be used to discuss performance quality of the ALS system itself in Section 4 for both directly analyzed and digested/extracted samples given.

Stock standards are used to prepare secondary standard solutions called working or calibration standards. Stock standards used here were prepared from an NBS traceable Pu salt dissolved in 5% nitric acid.(2) All transfers are made with calibrated Class A pipettes. The transfers are verified by counting on a calibrated surface barrier detector. For this procedure a 78.5 pCi/ml stock standard of Pu-239 in 5% nitric acid and water was used.

A calibration standard is a solution prepared from stock standards for daily calibration verification. Preparation of these is recorded in the lab notebook. These standards are extracts of the stock standard in the extractive scintillator (HDEHP or NDAS) that is used in sample analysis. A weighed amount of the stock standard is pipetted into a small 10 ml vial. It is diluted or neutralized to the proper pH with distilled water and sodium carbonate. The oxidation state is adjusted with 5% potassium persulfate before being shaken with the extractive scintillator.

The laboratory control standard is similar to the calibration standard but different concentrations are used. Standards were used to test resolution, energy calibration and efficiency of the system. The efficiency of the instrument and the extraction to make the standard should be $\geq$99%. Standards of 5 times background give less than 1% counting uncertainty when counted by ALS for one hour. Lower concentrations were prepared to establish the detection limit of the instrument and minimum count time for a specified level of counting uncertainty.

Standards are counted each day. Standards were used to assess: recovery efficiency of the last extraction, energy stability over time of the scintillator formulation and the detector, and efficiency degradation due to the presence of varying amounts of any residual quenchants. These standards ranged from the detection limit of 0.1 pCi/sample to 240 pCi/ml, 0.2 dpm to 500 dpm respectively.

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 microns) followed by a 200 mesh screen (75 microns). 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 Pu-239 stock solution. These slurries were mixed thoroughly and dried, ground, resieved then mixed in a special dual cylinder mixer. Enough Pu-239 spike was added to each fraction so that the activity concentration of each fraction 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 microns. 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 micron Pu particles. This area was decontaminated in 1969 and covered with an asphalt pad.(13) The estimated Pu-239 concentration was 1000 pCi/g.

The RFP soil was dried and sieved to determine particle size distribution. The finest particle size range, that less than 45 micron 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 were 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 provide another way to test the method particularly the contribution of natural background alphas and reagent impurities to the peak. Blank soil is soil known to be Pu free, in our case subsurface soil from a basement excavation presumably having no Pu fallout. This was treated exactly the same throughout laboratory analytical procedures as the sample. This soil was counted directly or was dissolved extracted and counted. Differences between the matrix standards and blanks help determine the minimum detectable activity and how well the ALS system and chemistry is distinguishing Pu alpha from those alpha naturally in the soil.

The calibration blank, standard, and method blanks can help in spotting reagent and apparatus contamination and interferences. The calibration blank is the extractive scintillator used for the final extraction (HDEHP or NDAS) sparged and run as a sample. It contains none of the impurities that might be present in a method or standard blank and is the lowest background achievable. The standard blank is prepared in the same way as the standard without the addition of any Pu and indicates any other influences to the standard. The method blank is distilled water that has been through the entire dissolution and extraction process.

Differences in background between blanks help locate contamination and interference problems. The closer the background count rates for each blank the better the procedure. The matrix background is the sum of all the contributions to background, the instrument electronics, scintillant, reagents, glassware, handling and soil.

The Pu and Am concentration of the standard and blank soil was determined by the Rocky Flats Plant, Golden Co., UNC Geotech, Grand Junction, CO and the INEL, using 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 and assumed a 10 to one ratio of Am to Pu their results in pCi/g were Pu 970 and Am 97 and Pu 1010 Am 101 respectively. UNC used alpha spec for Pu and obtained Pu 1001 and Am 87 for the bulk soil.

3.7 Sample Counting

Following sample preparation samples must be purged of dissolved oxygen and dried before insertion in the oil filled counting chamber. In direct filter analysis occluded air on the filter must also be removed. This is done by argon gas sparging the sample containing scintillant in the counting test-tube for 2-3 minutes before counting. 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. Sparging removes oxygen and water quenchants and increases alpha resolution.

After sparging the test-tube was corked and sealed with parafilm. A sample thus prepared may last for several weeks but slow evaporation of the scintillant still occurs. The test-tube is wiped free of hand prints and placed in the oil bath of the counting holder. The light tight cap is turned, the high voltage activated and counting on the ALS spectrometer begun.

All the ALS spectrum and results to date are kept in a looseleaf notebook by type of spectrum and spectrum date. Data from each spectrum is compiled on Lotus Spread Sheets which lists: sample ID, sample analysis date, count rate, peak parameters, matrix standard recoveries, spike recoveries, duplicate precision, blank and standard count rates at several regions of interest (ROI), and standard full width at half max (FWHM) or peak resolution. Detailed operational parameters for digestion and extraction of samples, standards and blanks is described in the numbered lab notebook. Detailed operational parameters for the ALS instrument and its electronic performance are in instrument notebooks. Procedures for Pu analysis and microwave digestion are also maintained in separate notebooks.

3.8 Calibration

Two types of calibration are necessary in the ALS system, energy and amplitude. The energy calibration is needed for proper peak identification and the amplitude in quantitating the peak. Both give indication of quenching and other interference problems that might effect the results. Energy calibration is done by extracting Pu from the standard aqueous solution into the same scintillant and in the same manner as the sample. The peak energy of the sample should match that of the standard. Instrument and extraction efficiency are maintained by checking standards daily for consistency and near 100% counting efficiency. Commercial standards for this type of instrumentation have only recently become available and have been ordered.

When direct 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. Counting the standard spiked soil and adding blank soil to a prepared standard were two methods to verify calibration in this situation. Results for direct counting of various types of blanks, prepared calibration standards and standard spiked soil are given in Section 4.

3.9 Calculations

The concentration of Pu in directly counted smear samples is calculated by dividing the counts per minute by the fractional efficiency and the collected mass if the smear has been preweighed. The result is given in pCi/g, for smears and soils. If an unweighed smear is used for the standard 100 cm^2 swipe the counts are divided by the fractional efficiency and the result is give in pCi/sample. For an air sample the total volume of air is calculated from the flow rate and corrected for changes in pressure and temperature throughout the sampling period. The activity is divided by this air volume and reported as pCi/cm^3. The constant air monitor result (CAM) is concerned with total air sampled. The concentration in soil or dust is concerned with total mass sampled. The total suspended particulate (TSP) obtained through Hi-Vol measurements can be used to obtain the mass of the soil sampled if the CAM filter cannot be preweighed. In calculating the activity concentration in air from collection or deposition plates a correction factor for settling rate needs to be made to make the transition from the activity concentration on the collected soil in pCi/g to some value for either surface area pCi/cm^2 or air pCi/cm^3.

All values are reported with the statistical counting uncertainty. This is roughly the difference of the peak from a perfect gaussian shape. At a minimum the count time must be sufficient to bring this uncertainty below 50%. This value is calculated from the peak area and uses a 1.65 sigma unit confidence level.

$$\text{PERCENT UNCERTAINTY} = (1.65)(S_g)/\text{AREA})*100$$

$S_g = [G+(N/2)(N/2)(1/K)(B_1+B_2)]^{0.5}$
G = gross counts in the peak
N = number of channels in the peak
K = number of endpoints, 4
B_1 = averaged height of background on the left
B_2 = averaged height of background on the right
AREA = Total counts in the ROI minus the background area

A laboratory duplicate is two aliquots of the same sample that are treated exactly the same throughout laboratory analytical procedures. For each set of duplicates a replicate percent difference (RPD) is calculated:

$$\text{RPD} = (D_1-D_2)/(D_1+D_2)*200$$

D_1= first result
D_2= second duplicate result

The standard control limit set by the EPA for standard trace metals analysis is for RPD to be less than 25%.

Several laboratory spikes were performed. This is the addition of known amounts of Pu to a known volume of sample to test for any matrix affects. For each spike a percent recovery (%R) is calculated:

$$\%R = (SSR-SR)/SA\ (100)$$

SSR = spiked sample result
SR = sample result
SA = spiked added

Recoveries between 75 and 125 indicate that the matrix is not interfering by enhancing or detracting from the determined concentrations of analytes.

Closeness of laboratory duplicate and spike results indicate the precision and matrix affects associated with the laboratory operations but not sample collection, preservation or storage. The quality of these latter operations can be assessed by collecting duplicate samples or spiking samples at the source. Quality assurance measures for sampling include special container or coupon washing, verification of contamination free filters and smears, proper sample packaging and preservation, chain of custody control and prompt analysis.

Following are the results obtained to date, reviewed as to efficiency, background and resolution. The optimum desirable is 99.7% efficiency, 5% resolution and background less than 0.02 cpm for the entire process (dissolution, extraction, counting) of a soil sample. Problems encountered and further work necessary are also discussed. Precision for duplicate standards, soil standards, blanks, soil blanks samples and soil samples are discussed in the results Section 4. Though there were severe time constraints some spike testing was accomplished with results also in Section 4. The efficiency of counting, extractions and separations should be near 100% so no efficiency calculation is necessary. The various standards and blanks help determine where losses are occurring.

4. 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, background and resolution. The optimum for each of these have been discussed in section 2 and are: 99.7% efficiency, 5% resolution and background less than 0.02 cpm. Achieving these for the entire process (dissolution, extraction, counting) of a soil sample and the associated precision for duplicate standards, soil standards, blanks, soil blanks and soil spikes, problems encountered and further work necessary are discussed below.

Background includes electronic noise, cosmic rays and chemical impurity contributions to the final count rate. Efficiency is the percentage of analyte pulses successfully detected by the instrument and converted to the count rate, and the percentage of the analyte extracted. Resolution is the degree of separation by energy 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.

4.1 Resolution

Energy resolution (the separation of two alpha peaks by energy, and 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.

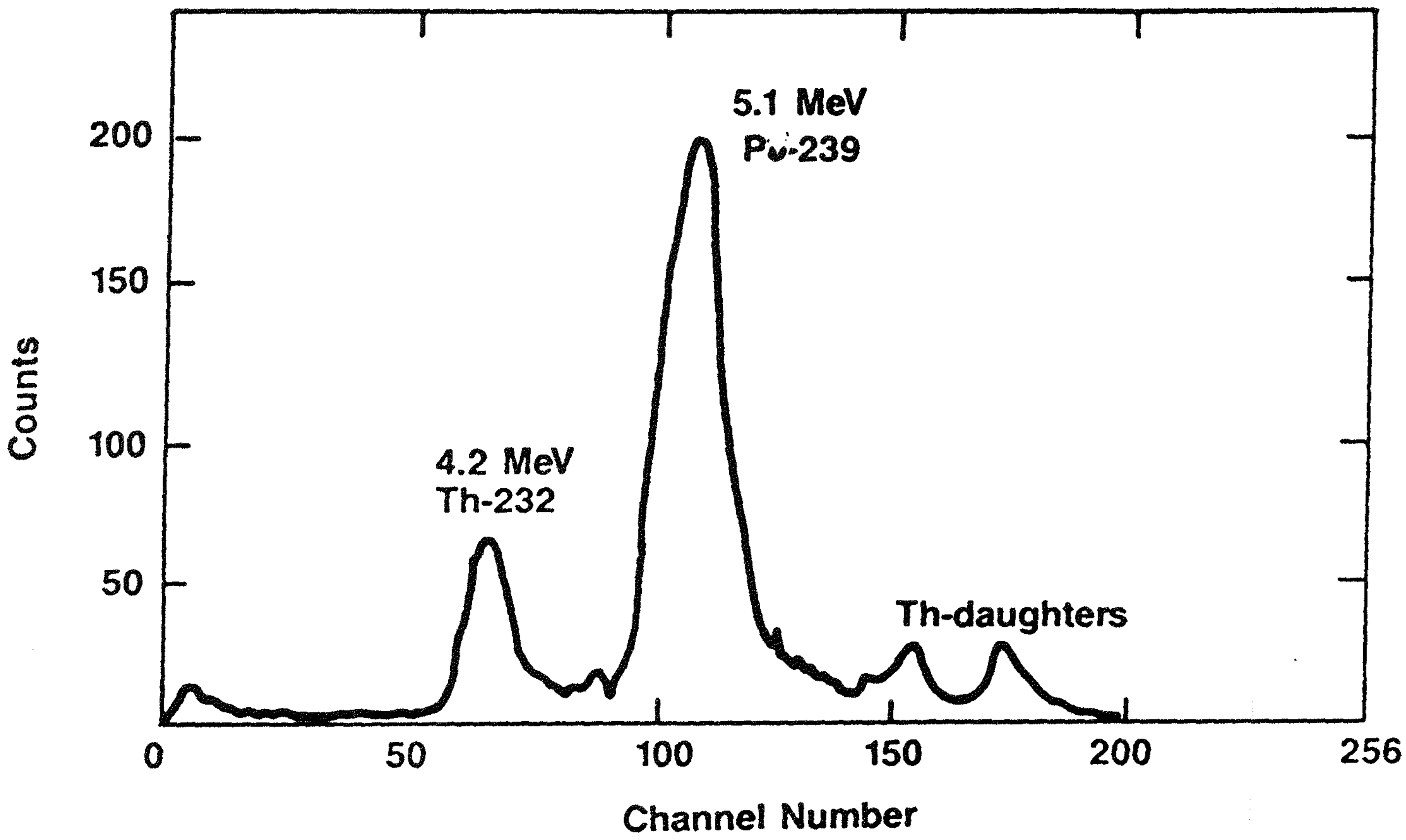
Figure 1 shows a PERALS alpha spectrum for Radium-226 and its daughters overlaid with a surface barrier spectrum.(9) The radium, radon and polonium peaks are resolved in both systems. The weak 4.6 MEV radium, however, is not resolved from the strong 4.78 MEV radium illustrating the the practical limitations 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. With the plutonium -239 peak well resolved from the thorium for this standard of 100 pCi/g, at least 100 pCi/g sensitivity can be achieved.

Table 1 gives resolution for prepared Pu standards. The full width at half max (FWHM) and the region of interest (ROI) width were both used as measurements of resolution. Most peaks had resolutions under 10%. We 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 30-50%. A slight increase in the beta continuum region channel 5-10 was also noted. Spike recovery was 90%.

FIGURE 2. PLUTONIUM AND THORIUM STANDARD SPECTRUM



9-7846

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

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.

4.2 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 encountered 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. Table 3 gives the efficiency for prepared standards. At the current efficiency of about 20-25% 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 rate of 50 milligrams of sample is 2.2 dpm, or over ten times the background of 0.15 dpm and therefore is well within the 100 pCi/g sensitivity.

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

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

Table 3. Plutonium Efficency 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

FIGURE 3. DIRECT PU SOIL SPECTRUM

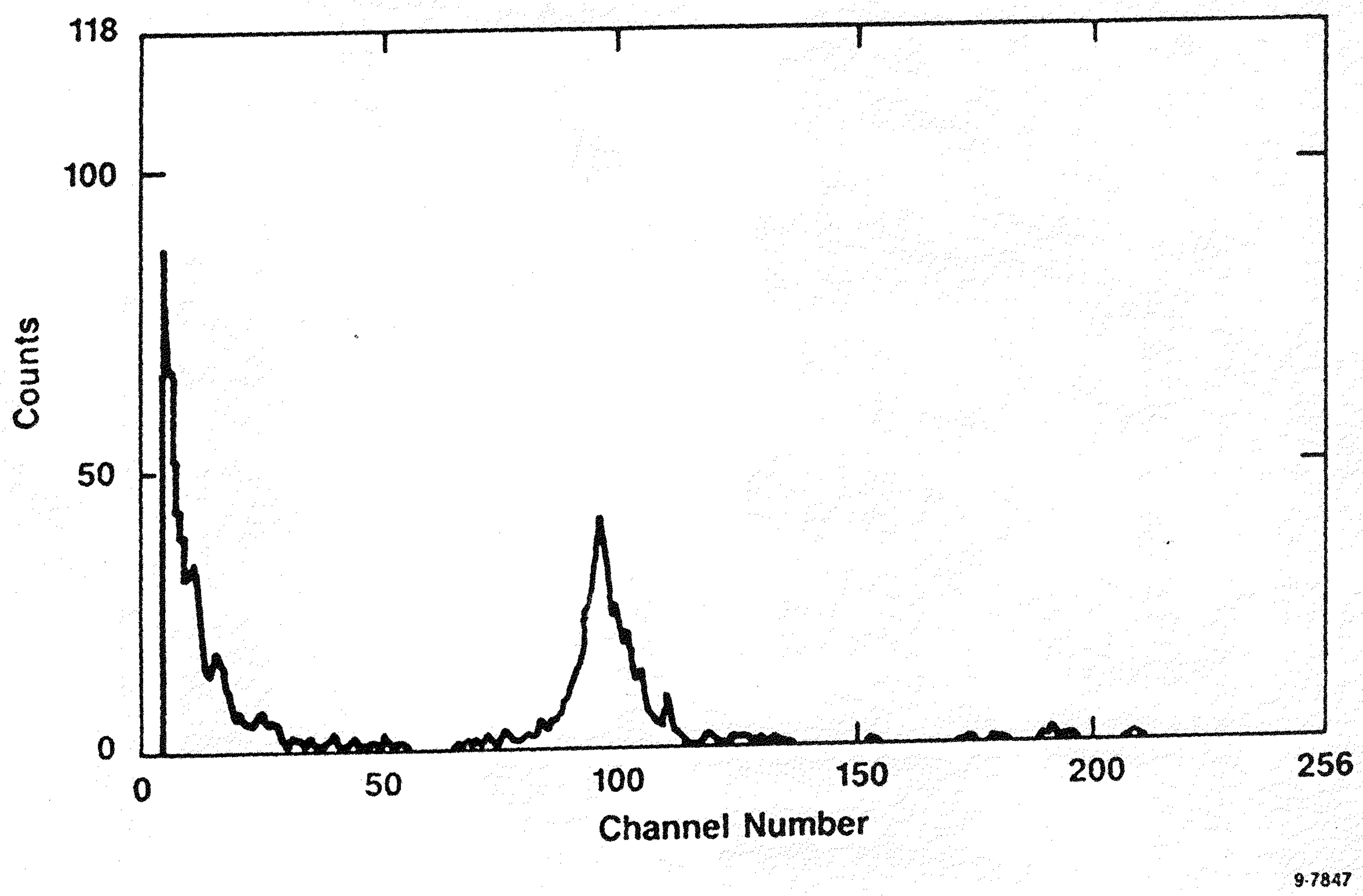
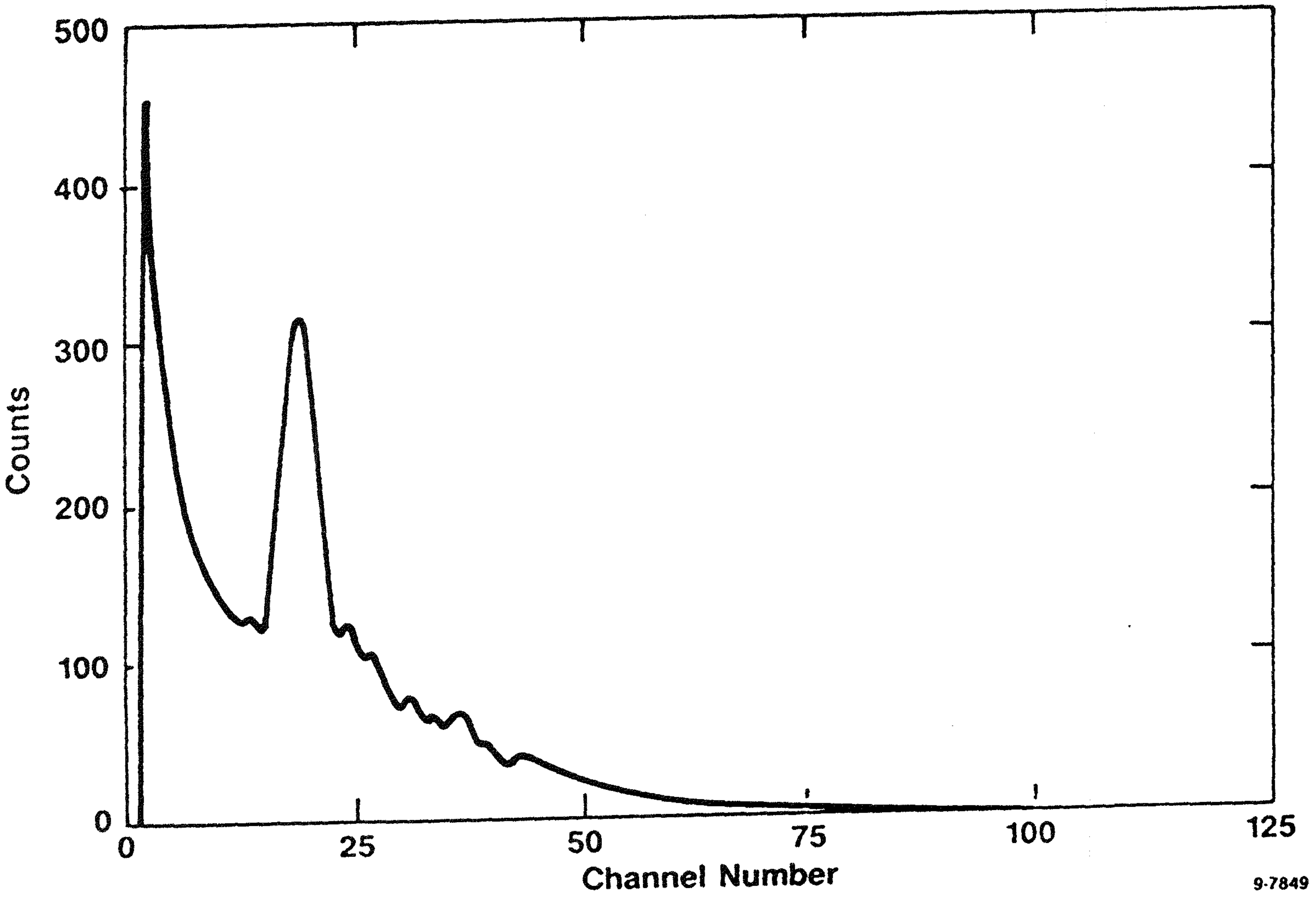


FIGURE 4. DIRECT RFP SOIL ON FILTER SPECTRUM



higher channel regions, with less quenching and count rates about 3 times the soil background. Referring to count rates for RFP and blank soil (Table 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 90-110) 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 as 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 multiple giving a detectable peak in 1 hour of counting for one gram of a 1 pCi/g sample. This is about 0.55 count per minute, 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 as shown on Figure 5. The RFP soil had a higher counting uncertainty and gave a wider peak. 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 possible (counting wall losses only) 99.7%. The main problem in efficiency was in the extraction rather than counting. Some standards were either not in the

TABLE 4. Summary of Background

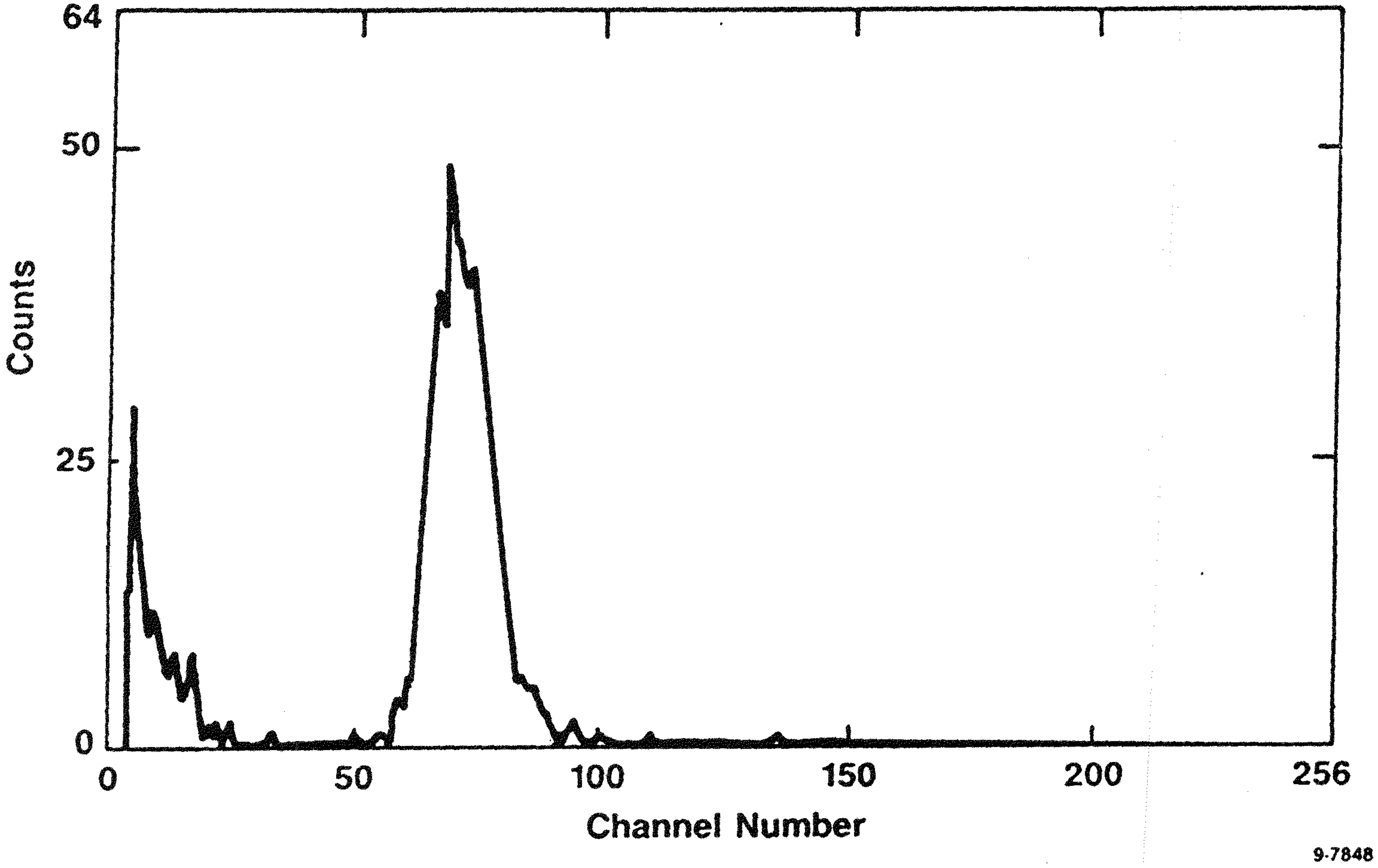
Background Type	Extractive Scintillant	Total DPM in ROI	ROI Centroid	Energy Shift Percent
Standard	HDEHP	1.69 ± 0.90	9.4	
Soil	HDEHP	1.34 ± 0.74	8.7	7
Method	HDEHP	1.58 ± 0.6	5.7	39
Standard	NDAS	0.92 ± 0.90	4.9	
Soil	NDAS	1.16 ± 0.71	4.7	4
Method	NDAS	0.71 ± 0.12	5.8	21
Standard	HDEHP	0.08 ± 0.04	105	
Soil	HDEHP	0.15 ± 0.02	92	12
Method	HDEHP	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

9-7845

TABLE 5. ALS DUPLICATE ANALYSIS

Method	DPM in RO1	Relative Percent Deviation	Primary Peak Channel	RPD Peak Location
Standard	0.14±0.02		108	
Blank	0.15±0.02	7	109	0.9
Soil Blank	0.16±0.10		62	
Direct	0.18±0.18	12	77	22
RFP Soil	2.10±0.38		13	
Direct	1.14±0.21	39	14	7
RFP Filter	4.30±0.30		9	
Direct	3.63±0.33	17	17	61
Standard Soil	0.97±0.12		98	
Direct	0.73±0.04	28	102	4
Standard	192.6±9.4		103	
Extraction	193.8±12.8	0.6	92	11
RFP Soil	83±2.1		72	
Extraction	88±1.1	6	98	15
Standard Soil	28±0.84		82	
Extraction	39±0.4	31	83	0.6

FIGURE 5. EXTRACTED RFP SOIL SPECTRA



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.

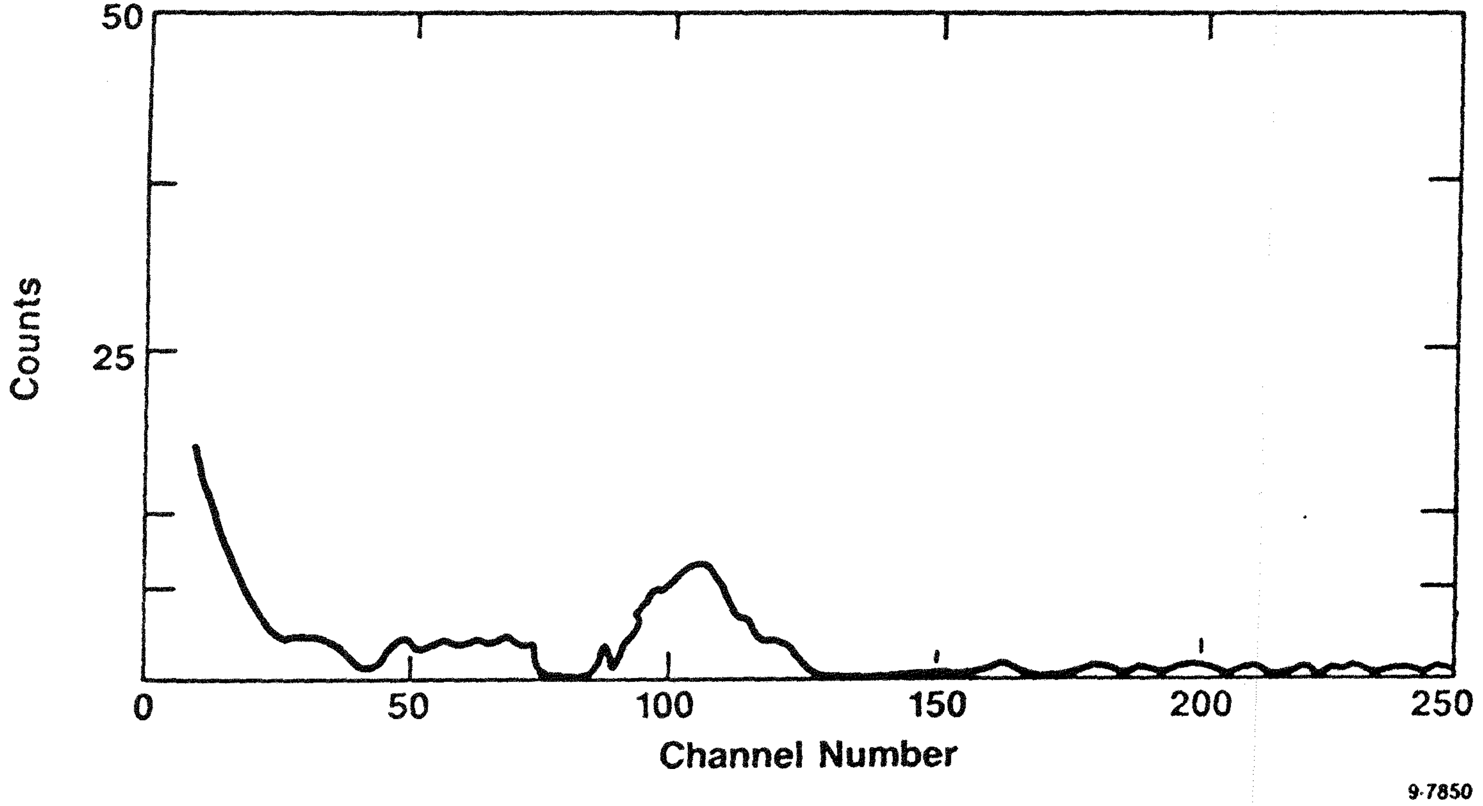
4.3 Background

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 potassium-40, 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 and that of the instrument. Elimination of beta and gamma background is achieved by pulse shape discrimination (PSD). Decreasing alpha background requires clean reagents, and a low radon working area. Currently the method blanks give a background 4-10 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 give an indication of 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 blank 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 and containing possible thorium peaks, the other further down field where Pu peaks should be located. The primary channel is the center of the peak where largest number of counts were 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 ROI's.

FIGURE 6. BACKGROUND SPECTRUM



Background varies more at different regions of interest than with different types of blanks. This seems to indicate 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- 1.7 dpm than in the region of interest for Pu in a clean sample, 0.04-.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 secondary extraction than the HDEHP but does not partially extract Pu in the direct soil mode. Soil added to 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 grams of sample. The count rates for about 10 mg of the 100 pCi/g standard and 1000 pCi/g RFP soil and soil on filter are also at least 5 times the background of the blank soil as shown on Table 5.

4.4 Precision

The precision associated with background, resolution and efficiency for direct and extracted soil analysis can be seen in Tables 1, 3, 4 with a summation in Table 5. Standard deviations (1 sigma) in Table 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 used must also be considered. The standard deviation for multiple counts of different standards on different days over a wide range of concentrations (0.1-200 pCi) for efficiency was about 4%.

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

Variations in extraction procedure is 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 Std soil and the RFP soil on a filter Figure 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 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 Table 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 percent 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 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 and cleared up thus giving 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, chemical stability and 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 ROI's for most of the background counts, the low count rates, and the energy shifting do not allow specific contaminant isotope contributions to background activity to be identified. 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 for 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, background elimination but 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, reject thorium, uranium and iron, and not contain 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. Interferences during extraction, of the aqueous solution from the digested sample into the organic amine or extractive scintillator, that may occur in order of importance are: (a) incomplete extraction of Pu, (b) extraction of unwanted ions and (c) inability to strip the Pu from the first extractant into the aqueous solution. Some of the causes of these interferences are: incorrect oxidation state of Pu, incorrect pH, insufficient ionic strength, impure extractants, and presence of non extractable Pu complexes in the aqueous solution. The spectral separation of Pu from an interfering alpha emitter such as thorium are 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.

4.5 Quality Assurance/Quality Control

This work was part of background experiments to support the contamination control subsystem of the Environmental Restoration Project (ERP).$^{(4)}$ The feasibility of retrieval of buried TRU waste from the subsurface disposal area (SDA) at the INEL depends upon adequate contamination control of Pu. The sampling and analysis plan (SAP) discusses eight areas of experimental investigation. This QA/QC section further details implementation in the area of improvements upon existing technology for measuring of airborne and surface Pu contamination. Rapid monitoring of Pu and discrimination against natural background are two key objectives for ALS development. Many of the SAP requirements such as sampling procedures, sample control document management, equipment, calibration, analytical procedures, data reduction and safety have been discussed. Data quality, quality assurance and procedures to assess data precision are discussed below.

Quality control check samples contain a known concentration of Pu prepared by someone other than the analyst. The Rocky Flats soil and the RWMC standard obtained in previous studies were used as check samples. In future work in house, EPA, round robin and NITS (NBS). Samples were sent to the UNC lab at Grand Junction for cross check using conventional alpha spectrometry. Currently there are few researchers doing ALS but as the technique becomes more common having check samples done by different labs using the same method will become possible.

The ALS spectrometer has been calibrated and maintained under the SAP guidelines and a longer term quality control program will be developed. Method blanks and Pu standards were run daily. The use of a Pu tracer is not necessary if the proper checks normal to any metals analysis are followed. The matrix standard should indicate if any gross interferences are occurring both negatively and positively. Recoveries of 95% should be normal though have not been routinely achieved yet. The Pu matrix standard was run periodically to test modifications to improve extraction efficiency. Samples and standards were counted for at least 10 minutes whereas blanks and background checks has to be counted at least 6 hours and often overnight to obtain reasonable counting statistics.

Results of duplicates, standards, blanks, have been given in previous tables. The calculation of the detection limit is described under the calculation section. The influence of on Pu of interfering substances such thorium are shown in the spectrum Figure 2. The thorium is separated in the extraction process, and is not a problem when present unless allowed to ingrow, as some of its daughters will add to the Pu peak.

5. LABORATORY REQUIREMENTS

Laboratory requirements for sample analysis to support the TRU Waste Retrieval effort are described in this section. The following guidelines have been used in determining laboratory requirements:

1. All fallout plates, alpha CAM filters, soil samples, and smear samples will be analyzed on site.

2. Analyses will be performed using ALS, gamma spectroscopy, and alpha surface barrier detectors.

3. Handling of samples and sampling devices will require contamination control within the laboratory and

4. Radioactive releases to the environs will be limited to environmental levels.

5. Sample preparation will require chemical separations for some sample types.

6. Capability must exist to pass-through samples, tools, etc. from the inner building and the sorting building directly to the lab.

7. The laboratory should be modular for ease of construction, speed of construction, potential expansion, and attachment to inner building and sorting building.

Given the listed guidelines a preliminary floor plan, Figure 7, which would satisfy the above criteria was sketched. Vendor literature for both modular interior furniture designs and an entire modular facility was reviewed. The experience of the new central laboratory, CFA-633 was considered. TOTALAB a modular design laboratory building company that designed and built that lab could supply two 12 x 35 ft modular units. When attached this would provide a total floor space of approximately 750 ft^2 which would be the minimum possible for the required purposes.

This floor plan is divided into two inner connected areas separated by a full wall. The area which would be nearest the inner and sorting buildings is used for sample receiving and preparation. The other half of the building is used for sample counting and data analysis. Flow of work and contamination control were considered as the lab was laid out. This configuration allows for samples to be brought into the laboratory in the least heavy traffic area and moved on into the facility once contamination control measures have been taken. The survey station between labs helps to assure contamination stays in the sample preparation area and does not spread to the counting/office area. The sample receiving/storage area will allow for chain of custody locked storage.

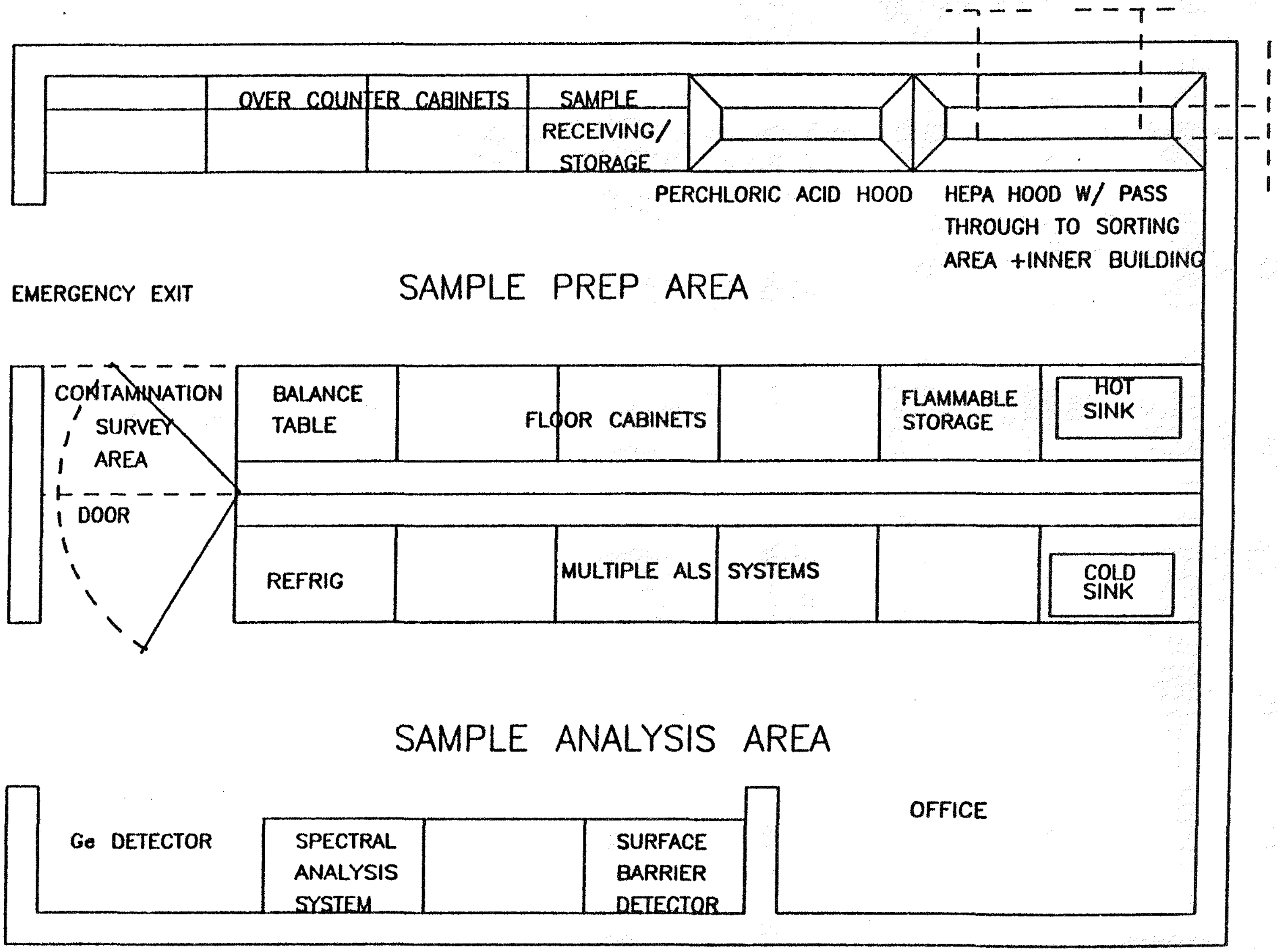


FIGURE 7. PROPOSED LAYOUT FOR SAMPLE ANALYSIS LAB

One hood will be equipped with two pass-through ports so that contaminated or potentially contaminated samples, sample containers, CAM heads, and other miscellaneous small equipment could be moved between the working areas and the laboratory while maintaining good radiological control. The hood will be equipped with HEPA filtration to prevent the release of contaminated dust. A second hood would be for acid digestion, solvent handling and potential perchloric acid use. This hood cannot be HEPA filtered, would have water wash down, and would be for but would be for environmental low activity work only. Work restrictions would be followed to ensure that only limited quantities of radioactive materials would be discharged from the unfiltered stack. Both hoods need stainless steel ducting, electrical and water hook ups, should be class A and have the required face velocity of 125 lfm.

Two stainless steel sinks are necessary. One sink would be used for noncontaminated work such as routine glassware cleaning and general laboratory operations with the drain plumbed to the sanitary waste lines. This sink would have hot, cold and deionized water taps. The other sink would be for any contaminated waste work. The drain for this sink could be plumbed to a holding tank.

Other facility features shown are primarily bench top space with storage both below and above the cabinets. The bench tops surfaces must be be easily cleanable and acid resistant possibly an epoxy composite. Non-bench area is for floor placement of counting equipment (detectors and analyzers), other required equipment such as shielded caves and data stations, and office space. Layout of this space must be custom designed around the instruments and data systems chosen.

6.0. CONCLUSIONS

An ALS system called PERALS has been investigated for use in obtaining alpha radiation levels during the ERP demonstration retrieval project. By directly analyzing lightly soiled filters the ALS system can detect concentrations as low as 100 pCi/g Pu within one hour of receiving the sample. For heavily soiled filters or soil samples a minimum detectable activity of 1 pCi/g should be possible in 2 hours including the time to dissolve and extract the sample. It is estimated that 12 samples per normal work day could be processed (simultaneously processing and counting). Direct counting of filter 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:

1. Improving extraction efficiency and reproducibility.

2. Determining detection limits in the presence of uranium and varying amounts of thorium.

3. Decreasing the preparation time and complexity.

4. Determining optimal extraction parameters, extractive scintillant cocktail stability, and useful lifetime of prepared samples.

5. Testing of INEL soils contaminated with chlorinated hydrocarbons that may be associated with the plutonium.

6. Writing detailed analytical procedures and training personnel.

7. Developing a fully auditable certified analysis program.

8. Improving analysis of spectra techniques such as incorporating the use of derivative and maximum-likelihood-analysis and digital fourier techniques to enhance resolution.

The largest gains can be made in improvement of the overall efficiency for the entire analytical scheme. Future work would involve spiking at various points during dissolution and extraction to pinpoint critical procedural parameters where losses are occurring. Non-instrumental 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 all are currently under investigation.

Liquid scintillation techniques allow both detection and quantization of non-penetrating alpha and beta radiation. Though traditionally a beta analysis method, alpha liquid scintillation analysis methods are a viable option for certain alpha nuclide analytical problems. The development of alpha scintillation techniques has, to some extent, overcome the past problems of high background (beta and gamma interference) and poor resolution.

The former time consuming techniques for TRU material analysis, particularly Pu-239, are being modified to decrease the preparation time needed while still using conventional analysis. Some of these techniques may also be of use in conjunction with current ALS procedures. ALS is currently being standardized and reviewed for EPA radium in water analysis. The inherent advantages of near 100% counting efficiency make ALS a viable method for rapid analysis and screening for Pu contamination control verification during TRU retrieval operations.

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