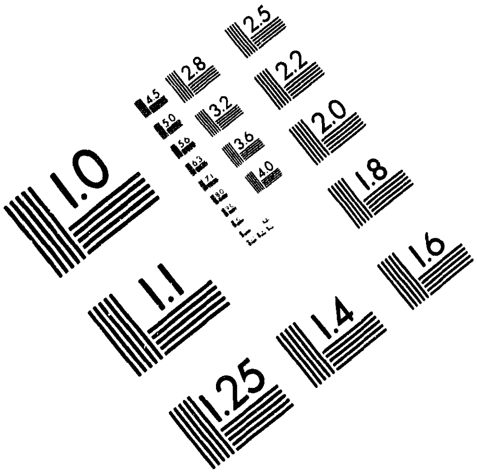

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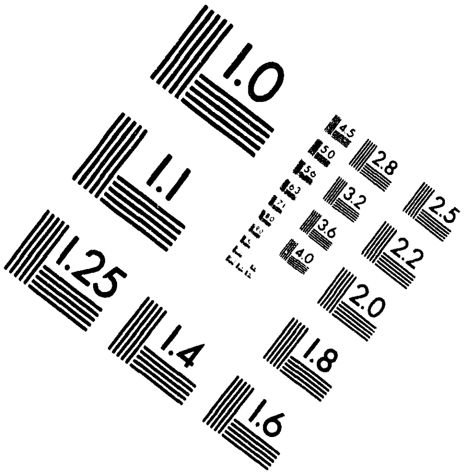

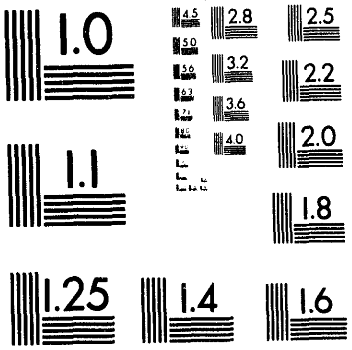

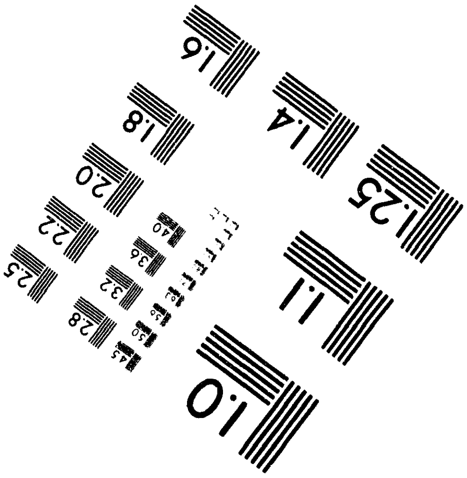

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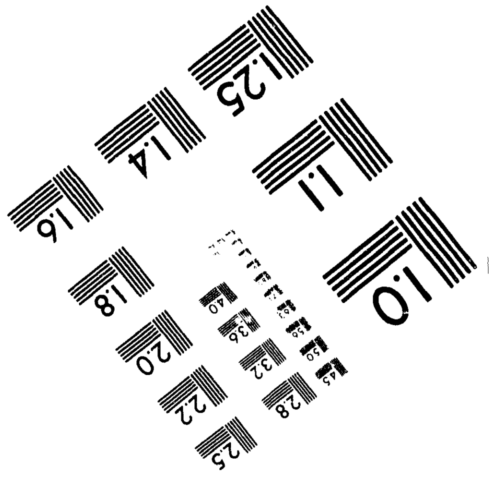

1 of 1

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WSRC-MS-94-0234

MEASUREMENT OF ACTINIDES IN ENVIRONMENTAL SAMPLES BY PERALS (U)

by
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Measurement of Actinides in Environmental Samples by Photo-Electron Rejecting Alpha Liquid Scintillation

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SUMMARY

This work describes the adaptation of extractive scintillation with a Photo-Electron Rejecting Alpha Liquid Scintillation (PERALS) (ORDELA, Inc.) spectrometer to the analysis of actinides in environmental samples from the Savannah River Site (SRS). Environmental quality assurance standards and actual water samples were treated by one of two methods; either a two step direct extraction, or for more complex samples, pretreatment by an extraction chromatographic separation prior to measurement of the alpha activity by PERALS. Accuracy of the method of ±5% was confirmed on a number of sample types at activity levels of a few pCi/L or less. Minimum detectable activities were estimated for counting times up to a week in duration and were as low as 0.003–0.005 pCi/L.

INTRODUCTION

PERALS analysis of alpha emitting radionuclides combines chemical separation by liquid-liquid extraction with activity measurement by liquid scintillation counting. Actinides are extracted from an aqueous solution into an organic phase containing the complexing extractant, an energy transfer reagent and a light emitting fluor. The phases are separated and oxygen is purged from the organic phase to improve energy resolution. Use of an oxygen-free organic phase gives a counting efficiency of nearly 100% and an energy resolution of approximately 5% full width half maximum for 5–6 meV alpha particles. Pulse Shape Discrimination (PSD) significantly reduces the background from photo-electrons produced by ambient gamma-ray activity and eliminates interferences from beta emitters that coextract. PSD electronically selects only pulses produced by alpha particles based on their longer dieaway times which are due to the much higher linear energy transfers in their interactions in the solution.

The original evaluation of the PERALS system for alpha measurements at the SRS concentrated on process support samples at high to moderate alpha activity levels [1]. However the high counting efficiency and relatively low background indicated that the PERALS technique was quite competitive with conventional alpha spectrometry for low level samples as well. The recent emphasis on environmental restoration and strict regulatory requirements for radionuclides in water has stimulated renewed interest in a rapid and simple method for measurement of actinides in water samples. Laboratory studies of the direct extraction of uranium and americium from up to 1 liter water samples with no pretreatment demonstrated minimum detectable activities (MDAs) of less than 0.1 pCi/l for $^{234-238}$U and 10 pCi/l for ^{241}Am [2].

Direct extraction and measurement by PERALS appears eminently suitable for rapid surveys of large numbers of water samples for actinides at these activity levels.

However there are a number of problems inherent in using a direct extraction for determining the actinide content of a large water sample. First the complexing extractant for the actinides used routinely (and in this work) is Bis (2-diethylhexyl) phosphoric acid (HDEHP). At the acidity range required for the coextraction of actinides in the +3 oxidation state (Am and Cm) with this reagent the extraction behavior of plutonium is very erratic at best due to the hydrolysis of the plutonium ions in solution. In addition, ^{238}Pu and ^{241}Am have alpha energies that are nearly identical and unresolvable by alpha spectrometric methods. Thus chemical separation of plutonium and americium is required before measurement if unambiguous values are desired.

Iron in the form of Fe^{+3} and possibly other transition metals also coextract into the organic phase giving colored organic phases which interfere with or "quench" the light transfer process in the sample. This is not a problem for most river or surface water stream samples, but is for some samples from monitoring wells and seepage basins. The quenching results in degraded energy resolution and shifts the pulse height spectrum of the alpha peaks toward lower energy. In the case of environmental samples with very low count rates it results in a very practical problem for quantitative analysis of determining where the energy regions are for the peak integration.

In samples where natural uranium and thorium or their progeny are present the single extraction of all the actinides does not allow one to rule out the presence of man-made activities such as plutonium and americium. This is due to the low resolution of the PERALS alpha spectra. In particular, the 5.5 meV alpha from ^{228}Th in natural thorium directly overlaps with the energy for ^{239}Pu and progeny of ^{228}Th with numerous alpha particle energies grow into the sample with a 3 day half-life

This work addresses these problems with a procedure designed around the PERALS technique that is considerably simpler and less time-consuming than conventional alpha spectrometry, . The objectives were to integrate the PERALS into methods currently in use at the Savannah River Site (SRS) for the analysis of low level samples. Specifically we wished to demonstrate the PERALS applicability on environmental quality assurance standards and representative water samples from SRS.

PERALS PROCEDURE

The classical procedure in use at SRS for low level actinides in water includes evaporation and wet ashing of the sample, chemical separation by liquid-liquid extraction followed by ion-exchange and electroplating of the sample prior to measurement. Alpha spectra are then acquired with a semiconductor detector in a vacuum chamber. For this work the standard sample treatment of wet oxidation was retained and merged with a modified version of McDowell's procedure for total alpha measurements in environmental materials [3]. Water samples were acidified with nitric acid and evaporated to near dryness overnight in Teflon (TM E.I. du Pont de Nemours & Co.) beakers. The use of Teflon instead of Pyrex improved the reproducibility of the recoveries of the actinides considerably and eliminated an occasional low energy background observed in the counting spectra. Samples were oxidized repeatedly with small amounts of concentrated nitric acid and 30% hydrogen peroxide in a Teflon beaker. The evaporation was repeated to incipient dryness. In a few cases 10-15 milligrams of potassium bromate was added before the final evaporation to complete the destruction of an organic residue. The sample was then dissolved in a small volume (5 to 10 mL) of dilute nitric acid (at least 0.8 M in concentration).

For the majority of samples that were known not to contain thorium and/or significant amounts of iron a two stage extraction proved to be a simple solution to the problems. A first extraction from 0.8 M nitric acid separated U and Pu into the organic phase. After the organic phase was removed the aqueous phase was adjusted to 2.5 to 3.0 pH by addition of a formate buffer solution. The second PERALS extraction was then performed to remove americium and curium. The extractive scintillator mixture contained 120 g/L of HDEHP, 180 g/L of scintillation grade naphthalene and 4.0 g of 2-(4'-biphenylyl-6-phenyl-benzoxazole) (PBBO) dissolved in spectroscopic grade p-xylene. This is twice the concentration of HDEHP recommended in reference 3. It was found in repeated experiments that the higher HDEHP concentration was necessary for

the complete recovery of ^{241}Am. Extractions were performed as previously described [1] with 1.0 mL (out of the 1.5 mL of extractant equilibrated) recovered for counting.
Tests of the two step extraction on water samples with known actinide activities showed recoveries of >95% with a precision of 2-3%.

For samples containing thorium and/or significant amounts of iron the actinides were rapidly removed as a group on a TRU·Spec (TM Eichrom Industries, Inc.) resin column. The resin has a combination of two highly specific actinide extractants, octyl(phenyl)-N,N-diisobutylcaramoylmethyl phosphine oxide (CMPO) and tributyl phosphate (TBP) supported on an inert polymer substrate. The column effectively removes actinides in the +3,+4 and +6 oxidation states from aqueous solutions that are 0.5 M to 5 M in nitric acid [5]. The actinides can then be eluted as a group or separated individually. Neptunium is generally in the +5 oxidation state under these conditions and is not extracted by CMPO/TBP. However the iron reduction step has the added benefit of reducing neptunium to the +4 state which is retained on the column.

The sample acidity was adjusted to 2M in nitric acid and 0.5 M in aluminum nitrate. Iron was reduced to the +2 oxidation state with ascorbic acid to prevent its retention on the column during the loading step and the sample was loaded at a flow rate of 1-2 mL/min using reduced pressure. The column was rinsed with several column volumes of 1 M nitric acid. Individual actinides were eluted as per reference 5. Americium eluted first in 4 M hydrochloric acid, followed by thorium in 1 M hydrochloric acid, plutonium is next eluted in 0.5 M hydrochloric acid/0.1 M ascorbic acid, neptunium can then be eluted with 0.5 M hydrochloric acid/0.1 M hydrofluoric acid and finally uranium is removed by 0.1 M ammonium oxalate. An individual sample took about 30 minutes to complete the column separations. Each fraction was wet oxidized with nitric acid and potassium bromate, evaporated to near dryness and the residue redissolved for PERALS extraction. Uranium, thorium and plutonium were extracted from 0.8 M nitric acid; americium and curium were extracted from a formate buffer solution at pH 2.5-3.0.

Oxygen was purged from the organic phases by sparging the samples with about 1 mL/min of argon. The tubes were then sealed and counted. Samples were measured for times ranging from a few hours to a week and were stable for at least two weeks. Numerous tests of this procedure were performed with acidified surface water samples from a number of sources. They were "spiked" by adding known amounts of ^{235}U, ^{238}Pu and ^{241}Am. before processing. Recoveries from the column separations were 88±5% for americium, 96±5% for plutonium and 94±3% for uranium.

Samples were processed in duplicate and agreed to within 5 % or less and, as typical for very low level samples, the precision was generally limited by counting statistics. A sample spiked with known amounts of activity and a reagent blank using deionized water were also processed simultaneously.

In occasional samples from the two stage extraction where little or no activity above background was detected, color quenching presented a problem. Since the quenching was known to shift the energy gain this introduced an uncertainty in the location of the regions in the spectra to be integrated for each nuclide. To resolve this difficulty the samples were reopened after counting and 10-20 microliters of PERALS extractant containing about 5 pCi each of ^{235}U and ^{238}Pu were added to the 1.0 mL sample. The counting tubes were sparged again with argon to remove oxygen and homogenize the activity then resealed and recounted. Spectra from the spiked samples were used to check and if necessary, adjust the energy alignment.

RESULTS

Environmental Standards

Quality Assurance samples from the Environmental Protection Agency Nuclear Radiation Assessment Division (NRAD) and the Department of Energy Environmental Measurements Laboratory (EML) were processed to prove the accuracy of the PERALS method. Samples of 50 to 100 mL were treated by the previously described procedures. PERALS measurements of uranium were made in an Environmental Protection Agency sample NRAD-RADQA 7/24/92 Multiple determinations gave a value of 4.1±0.23 pCi/L which was formally reported with the other SRS values by the Environmental Monitoring Section. The reference value was 4 pCi/L and the consensus of all participating laboratories was 3.97 pCi/L.

PERALS extractions were used to measure the ^{241}Am concentration in EML Quality Assurance Program (QAP) water sample XXXVII by the two step extraction method. The average value from PERALS reported was 7.3±1.6 pCi/L with an EML value of 5.54 pCi/L and a reported mean of 5.89 pCi/L from all the laboratories reporting data. Actinides from several EML samples were also separated on TRU·Spec columns and each fraction was PERALS extracted and counted. Values for uranium, plutonium and americium from EML QAP XXXVIII are shown in Table 1. The fractions were counted from 4 to 8 hours each and agreed with the EML values within 2 standard deviations (STD) based solely upon counting statistics. Figure 1 shows the spectrum from an 8 hour count of the Pu fraction with a concentration of 13.2 pCi/L ^{238}Pu and 22.4 pCi/L ^{239}Pu..

Table 1

Nuclide	PERALS (pCi/L +/- 2 STD)	EML Value (pCi/L)
^{234}U	4.35 +/- 0.65	4.08
^{238}U	3.92 +/- 0.32	3.97
^{238}Pu + ^{239}Pu	32.20 +/- 3.8	35.6
^{241}Am	14.30 +/- 2.2	11.9

Tims Branch Analyses

Water samples taken in the Tims Branch Creek, downstream from a uranium processing facility, have historically had detectable uranium at concentrations of a few parts per billion [4]. These samples originally were analyzed by total alpha counting which did not provide information on the isotopic composition and could not be converted to elemental concentrations. More recently with the regulatory concerns with elemental uranium concentrations due to its chemical toxicity, analyses had been performed by laser induced fluorescence which directly provides the elemental content. PERALS extractions gave both the simplicity of alpha measurement and the isotopic information required for calculating an elemental concentration. In addition the isotopic enrichment of the uranium was immediately apparent in the PERALS spectrum.

The PERALS spectrum in Figure 2 is from the extraction of a commercial elemental uranium standard routinely used for calibration of elemental analyses by atomic emission. The absence of the higher energy peak for ^{234}U indicates that the standard is depleted in the lighter isotopes ^{234,235}U. Uranium samples with natural isotopic composition of 99.27% ^{238}U, 0.72U a% ^{235}U & 0.0055% ^{234}U by weight have alpha spectra with approximately equal contributions from ^{238}U and ^{234}U with a small contribution from ^{235}U due to their respective halflives. Figure 3 is a PERALS spectrum from an EML QAP sample containing uranium at a concentration of 12 ppb. Samples containing uranium enriched in the lighter isotopes have alpha spectra that are dominated by the peak from ^{234}U In Figure 4 a PERALS spectrum from a sample of National Institute of Standards and Technology Standard Reference Material 100 is shown which contains 10.19 weight % ^{235}U and 0.07 weight % ^{234}U which contributes more than 90% of the alpha activity. The high specific alpha activity of ^{234}U makes the PERALS spectra a very sensitive monitor of the enrichment of the uranium in the sample.

Repeated analyses of Tims Branch samples showed the uranium in them to be of natural isotopic composition. Conversion of the alpha activities into elemental concentrations using the isotopic information gave a concentrations ranging from 1.5 to 5.5 ppb. This range was much greater than the precision of the PERALS technique and was assumed to represent variations in the sample concentrations.

Fourmile Creek

A number of water samples were taken from Fourmile Creek downstream from chemical separation areas at SRS. Most of them did not show detectable activity above the 0.003–0.005 pCi/L level. One sample had traces of ^{241}Am (0.004±0.002 pCi/L) and ^{244}Cm (0.003±0.002 pCi/L) but these activities represented just a few counts above background in a one week count time.

PERALS Sensitivity

Many of the samples analyzed did not have significant activity above the small background of the reagent blanks of deionized water measured on the PERALS. Minimum Detectable Activities (MDAs) were calculated for these one liter blank samples for counting times up to a week in length (Figure 5). The differences for the various nuclides were due to slightly higher backgrounds at lower alpha energies and to the slightly different peak widths of the spectral regions integrated for a given isotope. The sensitivity of a 24 hour PERALS count for the actinides was approximately 0.01 pCi/L which is sufficient for many applications. These MDAs for a one week count (10^4 minutes) are within a factor of two of those routinely obtained with electroplated sources measured on semiconductor alpha detectors. Semiconductor alpha spectrometry has a lower detector background but the PERALS method has higher chemical recoveries and detector efficiency. Moreover the PERALS precision is considerably better than conventional alpha spectrometry. Spiking each sample with an internal tracer activity (such as ^{242}Pu for plutonium) for measurement of chemical recovery was unnecessary. The one limitation of the PERALS, the low resolution of the its spectra, was not a problem in identifying the isotopic composition of the individual fractions measured.

CONCLUSIONS

The PERALS technique has consistently been useful in the analysis of a number of unusual or nonroutine samples and has shown itself to be very flexible and robust. It can eliminate much of the complex chemical separation and electroplating steps in current procedures and is much less sensitive to the technique and training of the analyst. Many times samples have been analyzed by the PERALS method when manpower and effort required for conventional alpha spectrometry was considered prohibitive.

In the future we plan to explore dual parameter analysis of the PERALS spectra to further reduce the counting background. We would also like to extend the analysis to different sample matrices in particular soil and sediments. In a first experiment with soils, actinides were leached from a relatively large (27 gram) sample of EML QAP soil containing from 100 to 1000 pCi/kg of uranium, thorium, plutonium and americium by the procedure described in reference 6. After column separation the analysis of the fractions by PERALS showed quantitative retention of all the actinides present on the single TRU·Spec column. Due to the coloading of other impurities leached from the sample pure chromatographic separations were not obtained but a higher capacity or second column will hopefully produce clean fractions. This technique offers a viable alternative with distinct advantages over conventional alpha spectrometry.

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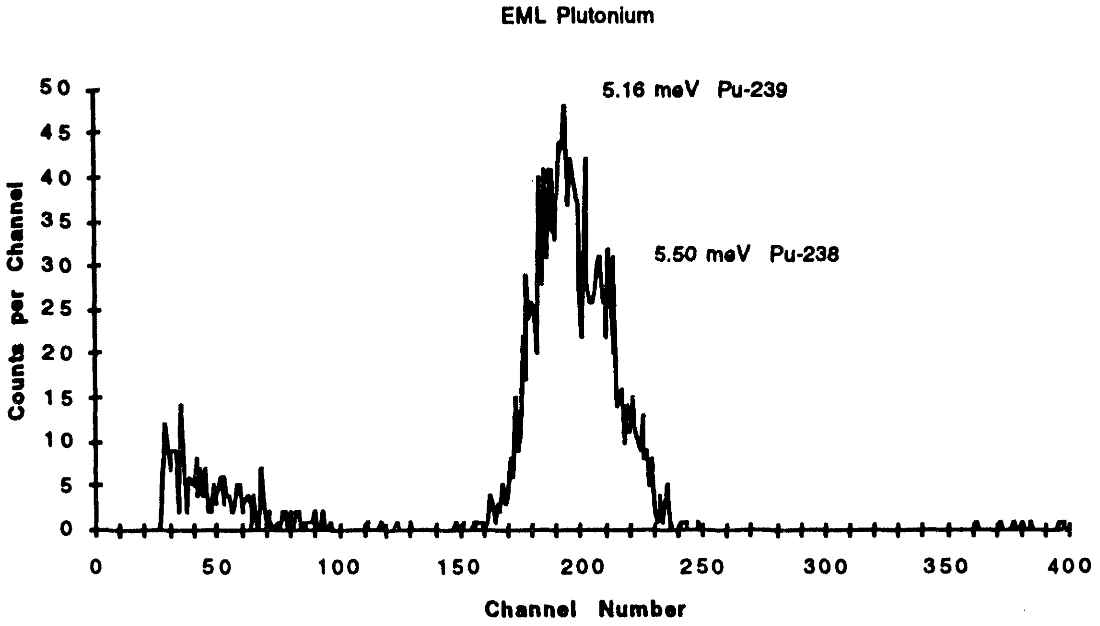
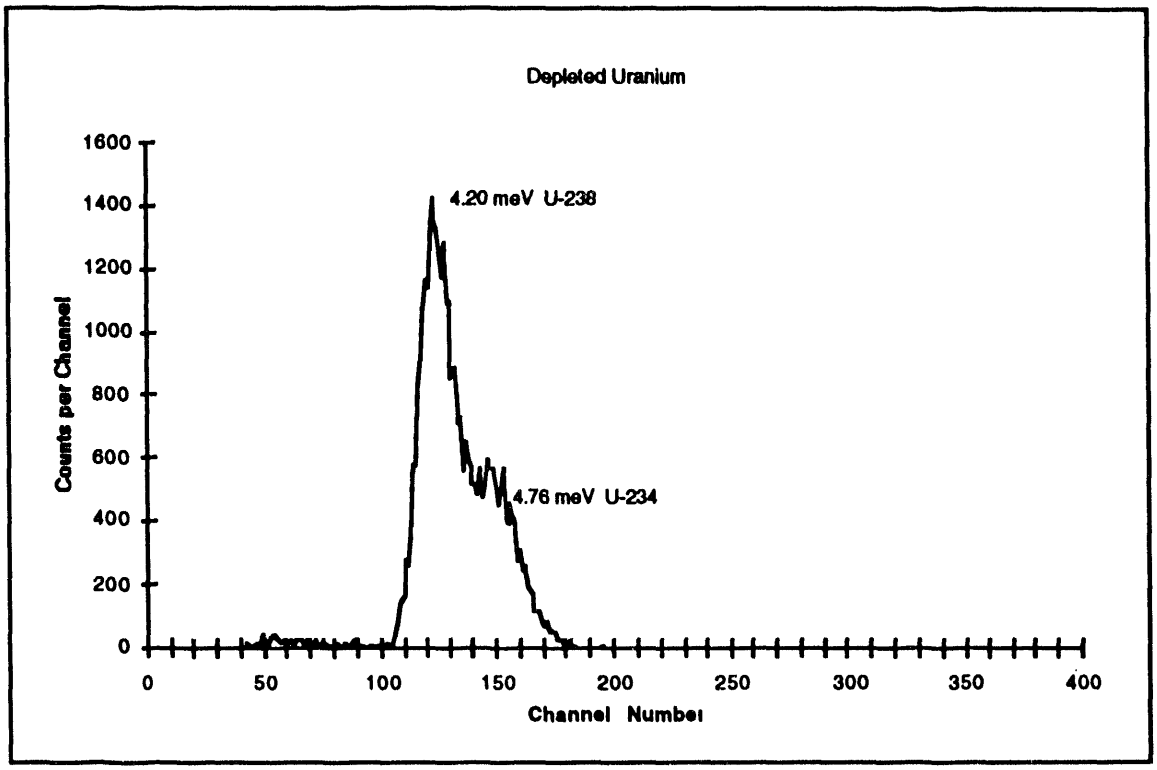
FIGURE 1



EML Plutonium
5.16 meV Pu-239
5.50 meV Pu-238
Counts per Channel
0
5
10
15
20
25
30
35
40
45
50
0
50
100
150
200
250
300
350
400
Channel Number

FIGURE 2



Depleted Uranium
1600
1400
1200
1000
800
600
400
200
0
Counts per Channel
4.20 meV U-238
4.76 meV U-234
0
50
100
150
200
250
300
350
400
Channel Number

FIGURE 3

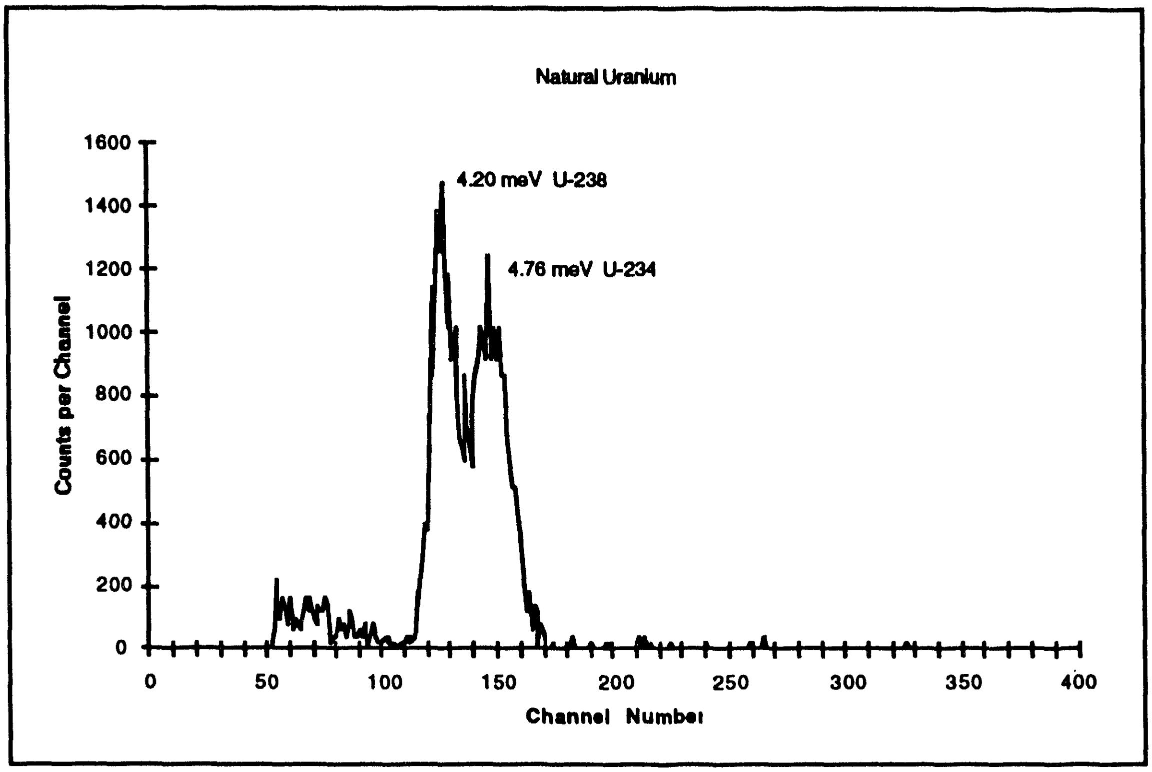

Natural Uranium
4.20 meV U-238
4.76 meV U-234
Counts per Channel
1600
1400
1200
1000
800
600
400
200
0
0
50
100
150
200
250
300
350
400
Channel Number

FIGURE 4

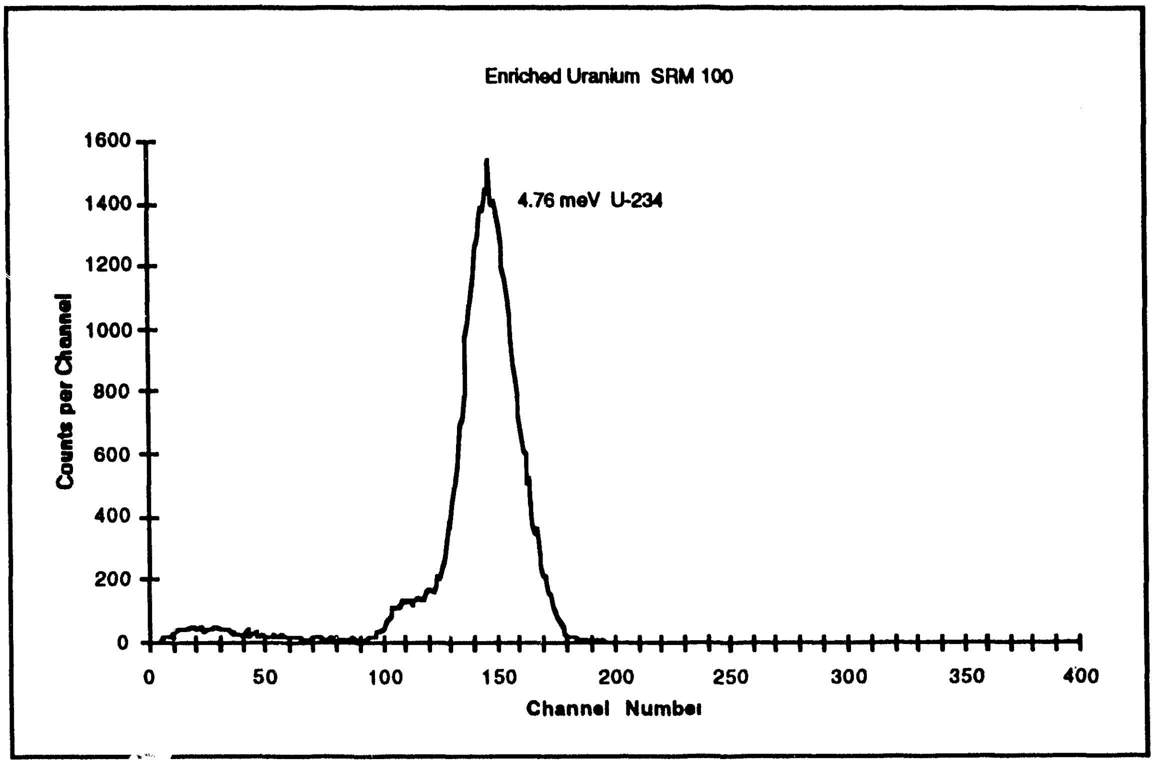
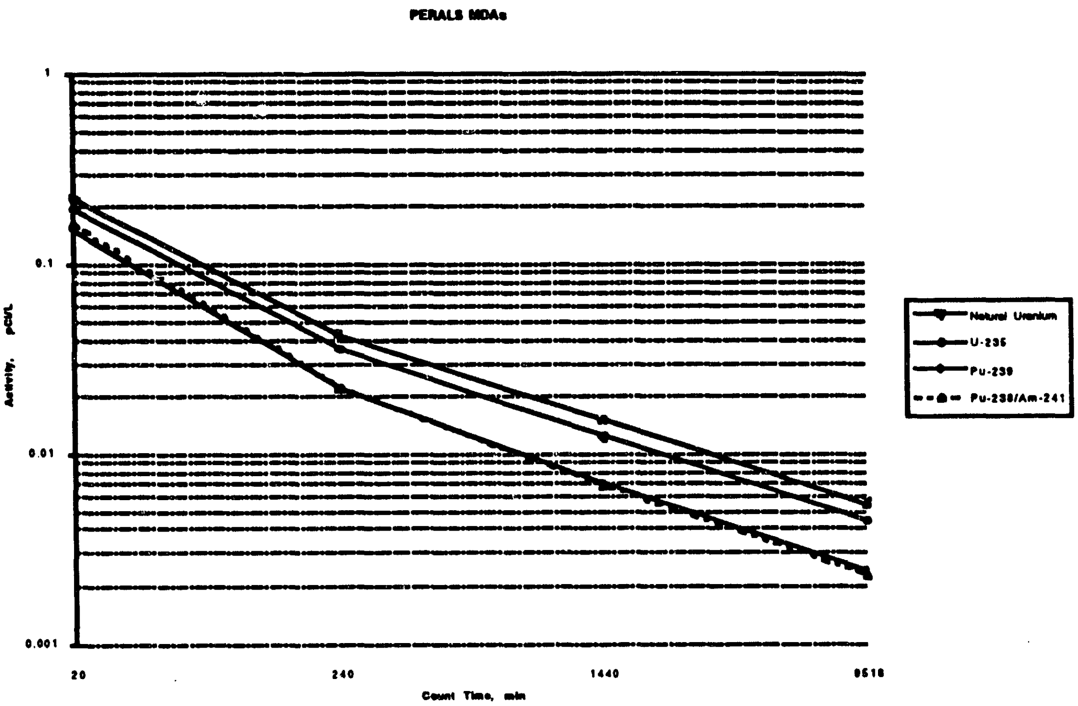

Enriched Uranium SRM 100
4.76 meV U-234
Counts per Channel
0
200
400
600
800
1000
1200
1400
1600
Channel Numbe
0
50
100
150
200
250
300
350
400

FIGURE 5


PERALS MDAs
1
0.1
0.01
0.001
Activity, pCi/L
20
240
1440
8516
Count Time, min
Natural Uranium
U-235
Pu-239
Pu-238/Am-241

DATE
FILMED
6/30/94

END