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**Chemical Treatment of US Department Of Energy High Level and Low Level Waste to Obtain a Pure Radiochemical Fraction For Determination of Californium  $\alpha$ -Decay Content**

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**ABSTRACT**

We have developed a chemical separation technique that allows the radiochemical determination of the californium  $\alpha$ -decay content in Department of Energy (DOE) high level wastes from the Hanford and Savannah River sites. The chemical separation technique uses a series of column extraction chromatography steps that use Eichrom Industries' lanthanide and actinide +3 oxidation state selective Ln-resin<sup>®</sup> and the transuranic selective +4 oxidation state TRU-resin<sup>®</sup> to obtain intermediate product phases in dilute nitric acid. The technique has been demonstrated on three types of authentic DOE high and low level waste samples. We obtain discrimination from Pu  $\alpha$ -activity by a factor of over 200 and from Cm-244  $\alpha$ -activity by a factor approaching 1700. Californium recoveries are measured by addition of a Cf-249 spike and are in the range of 50% to 90% in the synthetic samples and are in the range of 1.4% to 48% for the authentic DOE waste samples.

**INTRODUCTION**

Cf-249,250,251 are transuranic nuclides that are frequently requested in analyses of Savannah River Site (SRS) high level wastes. While none of these radionuclides was produced in large quantities at SRS, Am, Cm, and Cf were made in significant quantities during special Am/Cm production campaigns.<sup>1</sup> Most of the transuranic nuclides up to Cm-246 can be unambiguously measured by direct ICP-MS analysis, but the Cf nuclides present some special difficulties that we describe below. We were required to develop radiochemical measurement capabilities for the Cf isotopes. In this paper we describe the development of an extraction chromatography technique to obtain a fraction of californium separated from plutonium and high activity  $\beta$ -decaying fission and activation products. The californium isotopic content of a sample can usually be measured by  $\alpha$ -PHA spectroscopy if the sample is free of Pu.

In the SRS low level solid waste characterization programs we require that each piece of solid waste material has surface contamination at levels less than 1000 dpm/100cm<sup>2</sup> of  $\beta$ - $\gamma$  activity and less than 200 dpm/100cm<sup>2</sup> of  $\alpha$ -activity.<sup>2,3</sup> For items that meet this requirement, we seek to certify the reportable content of a list of 24 long lived radionuclides that includes the californium isotopes with mass numbers 249 – 251. While these 24 radionuclides are not reportable for every individual piece, it is the objective of the low level solid waste program to keep a tabulated running estimate of total nuclide-specific activity going to the solid waste storage vaults.<sup>3</sup> In general these nuclide-specific activities are calculated from other easily measured quantities such as  $\gamma$ -PHA and total dose-to-Curie calculations. Thus each item of solid waste is measured by one or both techniques, and the nuclide-specific surface contamination is calculated based on a process knowledge of the waste stream whence the item originated. Piece by piece, this method of reporting introduces a large uncertainty, but for an overall estimation of nuclide-specific vault content, it is believed to produce a reliable approximation. As a periodic check on the waste certification program, we run analyses for the list of 24 nuclides on selected pieces of solid waste. These checks are among the prime motivations for developing a Cf-isotopics analysis technique.

For a few samples, analysis of Cf-isotopes by ICP-MS is a better option than by radiochemical means. The isotopes 249 and 251 can be analyzed at the Savannah River Technology Center (SRTC) by direct ICP-MS, but with uncertain detection efficiency. Cf-249 can be easily observed by  $\gamma$ -ray PHA with a sensitivity similar to Am-241,243. Cf-248 and Cf-252 are relatively short-lived (334 d and 2.6 y, respectively) and cannot be analyzed by ICP-MS. Generally, detection efficiencies for transuranics are extrapolated from the measured efficiency in the U-238 region. For Am, Pu, and Cm this extrapolation has been tested at SRTC using reliable standards,<sup>4</sup> but the Cf nuclides are eleven atomic mass units greater than U-238 and standards are not available. The extrapolation of detection efficiency out to the Cf isotopes has not been previously tested. Since each of californium isotopes from Cf-248 to Cf-252 has an  $\alpha$ -decay energy greater than 6-MeV, measurement by alpha detection after chemical separation is a feasible technique with less uncertainty in the efficiencies, provided the Cm-244 and Pu-238 content of the sample is not too large.

The radiochemical analysis scheme that we have developed takes advantage of the fact that  $\text{Pu}^{+4}$  and  $\text{PuO}_2^{2+}$  form anionic complexes in strong mineral acids while  $\text{Am}^{+3}$ ,  $\text{Cm}^{+3}$ , and  $\text{Cf}^{+3}$  do not form anionic complexes under these same conditions and will not readily load onto anion exchange resins.<sup>5</sup> We have observed that  $\text{Am}^{+3}$ ,  $\text{Cm}^{+3}$ , and  $\text{Cf}^{+3}$  species behave similarly to the  $\text{Ln}^{+3}$  fission products and will load with similar characteristics onto Eichrom Industries Ln-resin in dilute nitric acid solutions while  $\text{Pu}^{+4}$  and  $\text{PuO}_2^{2+}$  do not load. Further, we have observed that while all of the  $\text{Ln}^{+3}$  series and  $\text{Ac}^{+3,+4}$  series load onto Eichrom TRU-resin in 1 - 5 M  $\text{HNO}_3$ , it is very difficult to elute  $\text{Pu}^{+4}$  off the column without reduction to  $\text{Pu}^{+3}$ .<sup>(6)</sup> Our method of purification of Cf from Pu uses successive load-elute treatments onto Ln-resin and then onto TRU-resin. We report recoveries of Cf near 100% in laboratory test samples with discrimination against Pu by a factor of 200. The recoveries of Am and Cm vary in our experiments from 20% to 80%.

## EXPERIMENTAL

We ran several preliminary experiments to confirm our hypothesis that Am and Cm would display load-elute characteristics similar to the +3 lanthanides with respect to Eichrom Ln-resin and TRU-resin. In these initial experiments, we loaded 10 – 100 nCi levels of Am-241, Am-243 and Cm-244 and 5 – 20 nCi levels of spiked Eu-152 and Sm-151 onto Ln-resin in a 0.01M  $\text{HNO}_3$  medium. We then eluted with 3M  $\text{HNO}_3$  and loaded the eluate onto TRU-resin. The TRU-resin columns were finally eluted with 0.05M  $\text{HNO}_3$ . The series column technique is shown schematically in Figure 1. In previous experiments we had observed recoveries of 30 – 70% for the lanthanides Pm-147, Sm-151, and Eu-152 using this method.<sup>7</sup>

We noted by  $\gamma$ -PHA that recovery of Am-241 and Am-243 ranged from 60% to 80%. Recovery of total  $\alpha$ -activity was in the range of 40 – 90%, and recovery of total  $\beta$ -activity was in the range of 30 – 80%. These data were consistent with our previous observations regarding the radiochemical behavior of the lanthanides and indicate satisfactory recovery rates for Am and Cm. We extended these experiments to include an examination of Cf and Pu behavior under similar separation conditions.

In our initial quantitative tests with Cf and Pu, we prepared four vials to use a dual sequence of load-elute with the two extraction chromatography resins. Samples 8525 and 8526 were prepared in 0.01M  $\text{HNO}_3$  for the Ln-resin, TRU-resin sequence as described above and as shown in Figure 1, and samples 7790 and 7791 were prepared in 3M  $\text{HNO}_3$  to reverse the load-elute sequence. To sample 8525 we added approximately 12000 dpm of Cf-249 and 567000 dpm of Am-241, and to sample 8526 we added 12000 dpm Cf-249 only. To samples 7790 and 7791 we added the activities shown in Table 1. Note that the Pu contributions to samples 7790 and 7791 include large Pu-241  $\beta$ -decay components. Because of its distinctive  $\beta$ -decay spectrum, Pu-241 is especially valuable in determining the Pu recovery in the presence of Cf.

**Table 1. Spiked activity added to each of test samples 7790 and 7791.**

|                |                     |                                 |                     |                    |                     |
|----------------|---------------------|---------------------------------|---------------------|--------------------|---------------------|
| Sample<br>7790 | Cf-249<br>23400 dpm | Pu-241<br>$4.8 \times 10^5$ dpm | Pu-242<br>27300 dpm | Cm-244<br>7350 dpm | Eu-152<br>22700 dpm |
| Sample<br>7791 | Cf-249<br>5850 dpm  | Pu-241<br>$4.8 \times 10^5$ dpm | Pu-242<br>27300 dpm | Cm-244<br>7350 dpm | Pm-147<br>2000 dpm  |

Samples 7790 and 7791 were loaded onto TRU-resin in 3M HNO<sub>3</sub> and eluted with 0.01M HNO<sub>3</sub>. The eluates from this step were then loaded onto Ln-resin in the 0.01M HNO<sub>3</sub> medium, and the Ln-resin columns were eluted with 3M HNO<sub>3</sub>. The treatment of samples 7790 and 7791 is shown schematically in Figure 2. All four product phases were analyzed by pulse shape discrimination liquid scintillation counting (PSD),<sup>8</sup> by  $\gamma$ -PHA, and by total alpha plate counting.

Both orders of the load-elute steps proved compatible with good lanthanide and Cf recovery. Measured total alpha recovery on sample 8525, which was dominated by the Am-241 spike, was determined by PSD to be  $106\% \pm 2\%$ . The PSD program assumes a 90% alpha particle counting efficiency with no beta cross-talk, so a positive bias of up to 10% is not uncommon. Recovery of total  $\alpha$ -activity measured by PSD on sample 8526 was  $107\% \pm 2\%$ . The liquid scintillation spectra of the product phases of 7790 and 7791 are shown in Figure 3. The spectrum of 7790 shows components from Eu-152, Pu-241, and  $\alpha$ -activity from Cm-244 and Cf-249. The spectrum from 7791 indicates components from Pu-241 and  $\alpha$ -activity from Cm-244 and Cf-249. The Pu-241 component in each spectrum demonstrate recoveries of Pu equal to only 0.5% and 0.7%, resulting in little contribution to the total  $\alpha$ -activity in each sample.

The total  $\alpha$ -activities for the product phases of 7790 and 7791 were measured by plate counting, which we consider to be an unbiased measure, though it does not distinguish between Cm-244 and Cf-249. Assuming near zero recovery of Pu  $\alpha$ -activity, the plate data indicates a 40% recovery of the Cm-244 and Cf-249  $\alpha$ -activity in sample 7790 and 72% recovery in sample 7791. A calculation of the individual recoveries using the measured total alpha in the product phases indicates a Cf-249 recovery rate of 85% - 100% and a Cm-244 recovery of 20% - 0% in the two samples, respectively. The  $\gamma$ -PHA data demonstrate a Eu-152 recovery of close to 100%. The PSD data indicate recovery of Pm-147 of greater than 10%, but we are not able to separate the Pu-241 interference in this measurement. Even at near 100% recovery, the Cf-249  $\gamma$ -ray events were below our sensitivity limit for the product phases of samples 7790 and 7791. These  $\gamma$ -ray measurements were made using a side-looking coaxial HPGe detector, which had an efficiency of only about 0.4%.

The four samples discussed above indicated that we could obtain good recovery of Cf and good discrimination against Pu using either sequence of the load-elute cycles. However because we did not distinguish between the Am, Cm, and Cf  $\alpha$ -activities, we did not quantitatively measure the Cf recovery. Our next series of experiments consisting of four samples used the load-elute cycle sequence of the TRU-resin first, followed by the Ln-resin (Figure 2). Two of the four samples contained Cf  $\alpha$ -activity only (37813 and 37814). One of the four samples contained only Cm-244  $\alpha$ -activity (13126), and one contained only  $\alpha$ -activity from Pu-238 and Am-241,243 (13125). Three of the four samples contained  $\beta$ -activity spikes of Pm-147, Sm-151, and Eu-152. This mix of spiked activity provided a good control to measure the individual recoveries of Pu through Cf and also to acquire more data on the radiochemical behavior of the lanthanides in this analytical method. The radionuclide content of each of these four samples is shown in Table 2.

**Table 2 Spiked activity in samples 13125, 13126, 37813, and 37814.**

|              |                       |                       |                       |                       |                       |
|--------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| Sample 13125 | Am-243<br>(24900 dpm) | Pm-147<br>(19000 dpm) | Sm-151<br>(20400 dpm) | Pu-238<br>(10800 dpm) | Am-241<br>(14200 dpm) |
| Sample 13126 | Sm-151<br>(20400 dpm) | Cm-244<br>(7350 dpm)  | Eu-152<br>(12000 dpm) |                       |                       |
| Sample 37813 | Cf-249<br>(23500 dpm) |                       | 3.5 mg Eu<br>carrier  |                       |                       |
| Sample 37814 | Cf-249<br>(23500 dpm) | Pm-147<br>(970 dpm)   | 3.5 mg Eu<br>carrier  |                       |                       |

These four samples were all loaded onto TRU-resin in 3M HNO<sub>3</sub> and followed by elution with 5mL of 0.02M HNO<sub>3</sub>. The 0.02M eluates were then loaded onto Ln-resin and were eluted with 5mL of 2M HNO<sub>3</sub> to obtain the final product phases. All four product phases were counted by  $\gamma$ -PHA and by PSD. From the  $\gamma$ -ray spectra we obtained an 83% recovery of the spiked Eu-152 in sample 13126, and the PSD data demonstrated 50%  $\pm$  10% recovery of the spiked Sm-151 and Pm-147 in the three samples that contained these radioisotopes. These results agreed very well with previous experiments.<sup>7</sup>

The  $\alpha$ -components of the PSD data demonstrated 58% and 53% recovery of the spiked Cf in samples 37813 and 37814 and 79% recovery of the spiked Cm-244 in sample 13126. Each of these PSD recoveries was determined unambiguously since each starting sample contained only a single  $\alpha$ -emitter. The product phase of sample 37813 was measured by  $\gamma$ -PHA after several days of ingrowth of the Am-243/Np-239 equilibrium. Recovery of Am-241,243 was measured to be 35%. PSD measurement of the Am-241,243 recovery was in good agreement with that value if we assume that Pu-238 recovery efficiency was negligible as indicated in the previous experiment.

Figure 4 shows the liquid scintillation spectra obtained for the product phases for the two samples denoted as 13125 and 13126. In 13125 we observe the  $\alpha$ -component that is a composite of Am-241,243 and the  $\beta$ -component that is a composite of Pm-147, Sm-151, and the in-growth of Np-239 from decay of recovered Am-243. In the chemical treatment we obtained good discrimination against pre-existing equilibrium Np-239 and spiked Pu-238. In 13126 we observe the  $\alpha$ -component from Cm-244 and the  $\beta$ -component from Sm-151 and Eu-152, thus demonstrating measurable recovery of all three of these species.

Finally, we describe the results of our most definitive series of experiments. These samples produced  $\gamma$ -PHA measurements of Cf-249 recovery along with  $\alpha$ -PHA spectra of the final product phases. This last set of experiments involved five samples whose initial contents are shown in Table 3. Sample 361 contained only Am, and sample 362 contained only Cm-244. Samples 12485, 12486, and 12487 each contained a mix of  $\alpha$ -activity, and two of them were used to further emphasize the discrimination we obtain against Pu activity.

**Table 3. Spiked activity added to each of test samples  
361, 362, and 12485 - 12487.**

|                 |                       |                                    |                       |                     |
|-----------------|-----------------------|------------------------------------|-----------------------|---------------------|
| Sample<br>361   | Am-243<br>(50000 dpm) | Am-241<br>(56000 dpm)              |                       |                     |
| Sample<br>362   | Cm-244<br>(14700 dpm) |                                    |                       |                     |
| Sample<br>12485 | Cf-249<br>(11700 dpm) | Am-241<br>(14000 dpm)              |                       |                     |
| Sample<br>12486 | Cf-249<br>(11700 dpm) | Pu-238<br>( $1.5 \times 10^5$ dpm) |                       |                     |
| Sample<br>12487 | Cf-249<br>(46800 dpm) | Pu-238<br>( $1.5 \times 10^5$ dpm) | Am-243<br>(25000 dpm) | Ru-106<br>(140 dpm) |

Samples 361 and 362 were loaded onto TRU-resin in a 3M HNO<sub>3</sub> medium and were eluted with 0.02M HNO<sub>3</sub>. The dilute acid eluates were then loaded onto Ln-resin, and eluted with 5mL of 2M HNO<sub>3</sub>. Samples 12485 - 12487 were loaded onto Ln-resin in a 0.01M HNO<sub>3</sub> medium and eluted with 2M HNO<sub>3</sub>. These eluates were then loaded onto TRU-resin, and the TRU-resin columns were eluted with 6mL of 0.01M HNO<sub>3</sub>. The products phases of all five samples were analyzed by several counting methods.

## RESULTS

The results of our last trial again demonstrated good recovery of Cf with very good discrimination against spiked Pu-238. Recovery of Am-241,243 as measured by PSD in product phase 361 was 30%, and recovery of Cm-244 in product phase 362 was 21%. The product phases 12485 - 12487 were measured by PSD,  $\gamma$ -PHA, and for total  $\alpha$ -activity by plate counting and by  $\alpha$ -PHA. For these last three product phases, the measured  $\alpha$ -decay contents determined by plate counting and by PSD are recorded in Table 4 in units of dpm/mL. The  $\alpha$ -decay data show an 8% positive bias of plate counting relative to PSD. To determine recoveries from the total  $\alpha$ -activity measurements it was necessary to obtain nuclide-specific distributions by  $\alpha$ -PHA. The  $\alpha$ -PHA spectra obtained for the last three product phases are shown in Figure 5. These spectra allowed us to assign the measured  $\alpha$ -activity among the specific nuclides Am-241 through Cf-249. From this distribution we determined the total alpha activity among the specific nuclides that is shown in Table 4. Finally the total activities measured by  $\gamma$ -PHA are shown in the last columns of Table 4.

| <b>Table 4. Measured <math>\alpha</math>-activities ( dpm/mL) in samples 12485 - 12487 by PSD and plate counting along with <math>\gamma</math>-PHA results.</b> |       |       |       |
|--|-------|-------|-------|
| Sample   | 12485 | 12486 | 12487 |
| total $\alpha$ -activity (PSD)   | 4560  | 2324  | 14980 |
| total $\alpha$ -activity (plate)   | 4230  | 2110  | 14020 |
| Percent of total $\alpha$ -activity ( $\alpha$ -PHA)   |       |       |       |
| Pu-238   | -     | <2    | <3    |
| Am-241   | 60    | -     | -     |
| Am-243   | -     | -     | 39    |
| Cf-249   | 40    | 100   | 58    |
| $\gamma$ -PHA Counts   |       |       |       |
| Am-241   | 2000  | -     | -     |
| Am-243   | -     | -     | 5000  |
| Cf-249   | 1970  | 2300  | 8300  |

We have made three calculations of nuclide-specific recoveries. The results of these calculations are shown in Table 5. In the first measurement we show recoveries measured from the fitted total alpha activity. The recoveries for Cf-249 were determined by subtracting the  $\gamma$ -PHA values for Am-241,243 from the total alpha content and assigning that result to the Cf-249  $\alpha$ -activity. In the second measurement we show the recoveries that we were able to measure from the  $\gamma$ -PHA data. In product phase 12487 we used the measure of ingrown Np-239 along with Am-243 to determine the Am-243 content. Finally our overall recoveries of each element were determined as an average for all measured values obtained from all three product phases. For samples 12485, 12486, and 12487, we adopted an Am recovery of  $110\% \pm 20\%$ , a Pu recovery of  $<2\%$ , and a Cf recovery of  $90\% \pm 20\%$ .

| <b>Table 5. Measured recoveries of Am, Pu, and Cf.</b> |                 |                 |                 |
|--|-----------------|-----------------|-----------------|
| Sample   | 12485           | 12486           | 12487           |
| Recovery by Fitted $\alpha$ -PHA                       |                 |                 |                 |
| Am-241   | 108%            |                 |                 |
| Am-243   |                 |                 | 137%            |
| Pu-238   |                 | <2%             | <2%             |
| Cf-249   | 86%             | 108%            | 112%            |
| Recovery by $\gamma$ -PHA                              |                 |                 |                 |
| Am-241   | 85%             |                 |                 |
| Am-243   |                 |                 | 120%            |
| Cf-249   | $110\% \pm 7\%$ | $101\% \pm 3\%$ | $99\% \pm 26\%$ |

It is clear that order of selection of resin matters for Am and Cm, but is not so important for Cf. For samples 361 and 362, where we loaded onto the TRU-resin first, we obtained 30% recovery of Am and 21% recovery of Cm. For 12485, 12486, and 12487, where we loaded onto the Ln-resin first, we obtained essentially 100% recovery of Am-241,243. These data are consistent with the recoveries on all previous samples. Using TRU-resin first our Am and Cm recoveries varied from about 10% up to about 80%, while the Cf-249 recoveries were never lower than 53%. Using Ln-resin first we obtained near 100% recovery of all three of Am, Cm, and Cf. In all of our experiments we obtained very good discrimination against Pu activity and variable but measurable recoveries of the lanthanides Pm-147, Sm-151, and Eu-152.

### Analysis of Actual Samples

We next extended our method to the separation and analysis of a set of actual dissolved solid waste samples. Our goal was to identify the Cf-isotopes in our separated product phases. These authentic samples contained many more interfering radionuclides in addition to the actinides. We ran radiochemical counting diagnostics on each intermediate product phase in order to identify and remove interfering species. We proposed to use selective ion-exchange and extraction chromatography to remove Cs-137 and Sr-90 that were expected to be at levels very much higher than the Cf isotopes.

To test our method to measure Cf-isotopes, we prepared five samples from three aqueous dissolutions of environmental restoration tri-*n*-butylphosphate (TBP) extraction samples. These samples originated from spent organic solvent from the SRS chemical separations processes. The samples were previously measured to contain  $2 \times 10^6$  dpm/mL Cs-137, 40000 dpm/mL Sr-90,  $6 \times 10^6$  dpm/mL Pu-238,  $2 \times 10^6$  dpm/mL Pu-241, and Cm-244 at up to  $10^8$  dpm/mL, and so they represented a rigorous challenge to our abilities to remove interfering activity. The samples were labeled 118517, 117649, and 119289. We also included two spiked standard addition duplicates that contained 23,400 dpm of Cf-249 and that were assigned sample numbers 118517.sp and 119289.sp.

We also analyzed an SRS solid waste sample (128238) and five Hanford samples that were assigned sample numbers 129080 through 129087 (not inclusive of all values). This set of six samples included one spiked standard addition sample that contained 46800 dpm of Cf-249. All thirteen of the authentic samples were treated to obtain Pu in the +4 oxidation state and were loaded onto EiChrom Industries TEVA-resin® in 3M HNO<sub>3</sub> to remove anionic Pu and Np complexes. The TEVA-resin load eluate, cleaned of Pu, was loaded onto TRU-resin in the same 3M HNO<sub>3</sub> medium, and the TRU columns were eluted with 5mL of 0.01M HNO<sub>3</sub>. This TRU-resin eluate was then loaded onto Ln-resin with four 1 mL rinses of 0.01M HNO<sub>3</sub>, and the Ln-resin columns were then eluted with 5mL of 2M HNO<sub>3</sub>. These chemical pre-treatments were designed to remove Pu first and then to take advantage of the preferred order of TRU-resin and Ln-resin extraction and elution.

The chemical treatments for samples 118517, 119289, and for the two standard addition samples 118517.sp and 119289.sp diverged from that of the remaining eight samples. These four intermediate product phases each had very large  $\alpha$ -activity components as well as residual activity from Cs-137 and Sr-90/Y-90 as determined by LSC spectra. To each of these samples we added about 0.25 gram of Bio-Rad AMP-1 Cs-removal resin. In 2M HNO<sub>3</sub>, this resin removes more than 99% of the Cs-137 activity.<sup>9</sup> We stirred the resin-slurry mixtures and added each to separate EiChrom Sr-spec® Sr-selective ion chromatography columns. We added four 1 mL rinses of 3M HNO<sub>3</sub> to each column and then eluted into product vials. These product phases were essentially free of all Cs-137 and Sr-90 but contained a large component of 64-hr Y-90. The high energy Y-90  $\beta$ -decay events always produce large positive biases in the  $\alpha$ -activity channels of PSD analyses, but after decaying for 36 days, the product phases were free of this interference. The overall dilution factor in these samples was 11.4:1. The other eight intermediate sample phases required only removal of Cs-137 after eluting from the Ln-resin and had an overall dilution factor of 5:1.



We obtained LSC and PSD analyses for all twelve final product phases. Selected liquid scintillation spectra are shown in Figure 7. Several product phases also contain product  $\beta$ -decay activity from Sm-151, which we reported in the Sm-151 analytical paper of reference 7. We used radiochemical diagnostic tests to demonstrate that all observed  $\alpha$ -activity in the product phases was from either Cf or Cm.  $\gamma$ -PHA tests demonstrated that each product phase was pure of Am-241,243. The LSC spectra indicate a null content for a Pu-241  $\beta$ -decay component. The Cf-249 recovery was measured in the three spiked aliquots by both PSD analysis and  $\gamma$ -PHA. From these measured recoveries we were able to measure Cf activity or determine upper limits of Cf content in all of the samples.

The following results were obtained for samples 118517, 117649, 119289, and the two spiked samples 118517.sp and 119289.sp. After elution from the Ln-resin and subsequent removal of Cs-137 and Sr-90/Y-90 and after allowing 36 days for decay of the Y-90 component, we obtained the product phase liquid scintillation spectrum of sample 119289.sp that is shown in Figure 7(a). This LSC spectrum shows a large alpha component that we believe comes from Cm-244. A comparison of the PSD analysis of this product phase to that of the unspiked sample 119289 yields a recovery of spiked Cf-249 of 37%. The  $\gamma$ -PHA analysis of the two samples gives a recovery of 35%, a result in very good agreement with the PSD measurement. We performed one additional treatment of passing these five product phases through TEVA-spec resin to remove any possible trace Pu, and obtained spiked Cf-249 PSD recoveries of 19% in product phase 119289.sp and of 1.4% in product phase 118517.sp.

In the unspiked product phases of environmental restoration TBP samples 118517, 117649, 119289, we observed PSD alpha activities ranging from  $< 6$  dpm/mL to 5220 dpm/mL as shown in Table 6. We note that for sample 119289 the 5200 dpm/mL of  $\alpha$ -activity yields a recovery of  $< 0.06\%$  for Cm-244. The measured Cf activity for this sample will have a high upper limit because of the large  $\alpha$ -decay content in the product phase, but the discrimination against Cm in the separation procedure was excellent.

**Table 6. Measured alpha decay component in the product phases of the original environmental restoration TBP samples.**

| Original Sample | $\alpha$ -activity of product phase (dpm/mL) | Dilution Factor | Recovery        | Reported [Cf] (dpm/mL) |
|-----------------|--|-----------------|-----------------|------------------------|
| 118517.sp       | 64.0   | 11.4            | 1.4% $\pm$ 0.3% |                        |
| 118517          | 35.0   | 11.4            |                 | 28000 $\pm$ 7000       |
| 119289          | 5220   | 11.4            |                 | $< 3 \times 10^5$      |
| 119289.sp       | 5608   | 11.4            | 19% $\pm$ 4%    |                        |
| 117649          | $< 6$  | 5               |                 | $< 80$                 |

We used the 19% Cf spike recovery measured in sample 119289.sp to calculate an upper limit of  $3 \times 10^5$  dpm/mL for the Cf content of sample 119289. For sample 118517 we use the measured 1.4%  $\pm$  0.3% Cf spike recovery in 118517.sp to estimate a Cf activity of 28000  $\pm$  7000 dpm/mL for this sample. For sample 117649 we used the recovery of 36% measured on 119289.sp after decay of the Y-90 component and a dilution factor of 5:1 to report an upper limit of less than 80 dpm/mL. We are not able to check the accuracy of these measurements against an alternative method or against a theoretical calculation, but ICP-MS analysis of the product phases demonstrates that each sample is free of Pu and Cm isotopes at the level of  $< 0.03$  ppb.

The actinide region of the ICP-MS spectra of product phases 118517, 119289, 119289.sp and 118517.sp are shown in Figure 8. Note that each of the unspiked samples demonstrates that the product phases are free of Cf-isotopes at a level of approximately 0.03 ppb. Unfortunately, applying the Cf recovery efficiency of 19%, the dilution factor of 11.4, and the specific activities still yields upper limits of content for each of the Cf-248,250,252 isotopes that are larger than the LLD of  $3 \times 10^5$  as measured by the  $\alpha$ -activity. These measurements reinforce the requirement that an  $\alpha$ -decay radiochemical procedure is required to determine Cf and Cf-isotopes. An important feature of the ICP-MS spectra of Figure 8 is that we are able to observe mass 249 in 119289.sp from the spiked Cf-249. This represents measurement of Cf-249 at a level of approximately 0.04 ppb. The peaks at mass 238 and 254 represent U-238 and U-238 oxide ( $\text{UO}^+$ ) peaks formed in the argon plasma of the ICP-MS instrument. We observe these species at the parts per billion level in all actinide ICP-MS spectra of samples that have been pretreated with reagent grade  $\text{HNO}_3$ .<sup>4,10</sup> Due to this natural uranium impurity in reagent grade  $\text{HNO}_3$ , all ICP-MS sample treatment at SRS is done with high purity  $\text{HNO}_3$  in which the uranium content is well below the instrumental detection limit.

For the remaining five Hanford samples and the single SRS E-Area vault sample, we obtained product phases that were free of non-Cf  $\alpha$ -decay interference with a much shorter treatment. Our product phases were obtained immediately after elution from the Ln-resin followed by Cs-removal. The overall dilution factor for these six samples plus the one spiked standard was 5:1. An example liquid scintillation spectrum is shown in Figure 7(b). As stated above, these product phases also contained Sm-151 activity. We reported Sm-151 content in these with very good precision in these particular samples in reference 7. Comparing the PSD analyses of the product phase 129080.sp with that of 129080 gives a recovery efficiency of spiked Cf-249 equal to  $48.2\% \pm 0.3\%$ . Similarly, the  $\gamma$ -PHA analysis yielded a Cf spike recovery equal to  $47\% \pm 2\%$ , which was in very good agreement with the PSD result. The PSD alpha activities in these product phases are listed in Table 7. The reported Cf contents range from 420 dpm/mL to 10500 dpm/mL.

Table 7. Measured  $\alpha$ -decay component in the product phases of the original Hanford and SRS solid waste samples.

| Original Sample | $\alpha$ -content product phase (dpm/mL) | Dilution Factor | Recovery           | Reported [Cf] (dpm/mL) |
|-----------------|--|-----------------|--------------------|------------------------|
| 129280.sp       | 4952                                     | 5               | $48.2\% \pm 0.3\%$ |                        |
| 129280          | 444                                      | 5               |                    | $4610 \pm 110$         |
| 129283          | 1008                                     | 5               |                    | $10500 \pm 200$        |
| 129284          | 426                                      | 5               |                    | $4400 \pm 100$         |
| 129285          | 529                                      | 5               |                    | $5500 \pm 100$         |
| 129287          | 430                                      | 5               |                    | $4460 \pm 110$         |
| 128238          | 40                                       | 5               |                    | $410 \pm 50$           |

The reported values of Cf  $\alpha$ -activity in the nine authentic waste samples of this section are strongly dependent upon the assumption of good discrimination against Am, Cm-244, and Pu activity. We believe that discrimination against Pu contamination is very good as evidenced by the  $\beta$ -decay components of the liquid scintillation spectra as well as the ICP-MS spectra of Figure 8. The  $\gamma$ -PHA results for the nine authentic samples and three spiked duplicates all indicate good discrimination against Am-241 and Am-243/Np-239. The ICP-MS spectra of Figure 8 confirm the absence of significant amounts of Am-241,243 and Cm-245,246. Because of its high specific activity, ICP-MS data for Cm-244 are not conclusive, but the absence of Cm-245 and Cm-246 in the mass spectrum argues for good discrimination against significant amounts of Cm-244 in the samples. This is confirmed by the total  $\alpha$ -activity observed in the product phases of sample 119289 and its spiked partner 119289.sp.

An important question resulting from this work is why does the order of loading onto the two resins TRU-resin and Ln-resin influence the recovery of Am and Cm? We are able to offer an explanation that is consistent with the mechanism of extraction of both resins and the TEVA-resin, but we do not pursue our hypothesis in this paper. TEVA-resin extracts anionic complexes of Pu using a quaternary amine cation. This extraction is able to load both Pu and Np because they form negatively charged nitrate complexes in all three oxidation states of III, IV, and VI. Cm(III), Am(III), and Cf(III) and the lanthanides do not form anion complexes. Pu and Np are able to bind electron pair donating nitrate ion more strongly.<sup>5</sup> Ward and Welch relate this to the greater ability of the Pu and Np 5f orbitals to hybridize with the 7s and 6d orbitals.<sup>11</sup>

TRU-resin extracts neutral actinide and lanthanide complexes from 2 - 4 M HNO<sub>3</sub> into the organic phase with a mixture of organic phosphate and phosphine oxide extractants. Pu and Np bind so strongly that they are not stripped off in the dilute nitric acid (0.01M HNO<sub>3</sub>) rinses that are used in this procedure. Ln-resin extracts cation complexes of trivalent actinides and lanthanides from dilute acid into the organic phase with the weak acid di-2-ethylhexyl phosphate (DEHP). All but Pu are stripped into the aqueous phase by conversion of the phosphate back to its acid form (HDEHP) in 2 - 4 M HNO<sub>3</sub>.

We believe the order of extraction of Am and Cm onto the TRU-resin and Ln-resin could be related to the form in which they are stripped from the TRU-resin by dilute HNO<sub>3</sub>. If the order of loading truly matters, it must be that Am and Cm come off of the TRU-resin in a form in which they will not load onto the Ln-resin while Cf comes off in a form in which it does load onto Ln-resin. Conversely all three must come off of the Ln-resin in concentrated HNO<sub>3</sub> in a form in which they readily load and then are stripped from TRU-resin. A very simple mechanism that would explain both behaviors would be that the mixed phosphate and phosphine TRU extractants load the Am, Cm, and Cf specifically as neutral tri-nitrate complexes {eg., Am(NO<sub>3</sub>)<sub>3</sub>}. The dilute acid strip removes Am and Cm as the same neutral complex. Alternately Cf must come off of the TRU-resin as the charged cation [Cf(NO<sub>3</sub>)<sub>n</sub>]<sup>(3-n)+</sup>, which readily loads onto Ln-resin.

With this mechanism, reversing the order of the extractions would yield nearly equal recovery of all three species. That is, all three load onto the Ln-resin in dilute HNO<sub>3</sub> as the cation complexes similar to [Am(NO<sub>3</sub>)<sub>n</sub>]<sup>(3-n)+</sup>. They subsequently get stripped from the resin with the 2 - 4 M HNO<sub>3</sub> flush as the neutral complexes Am(NO<sub>3</sub>)<sub>3</sub>, which are then ideally ready for loading onto the TRU-resin. With this order the form in which they come off of the TRU-resin would not affect their relative recovery.

## Conclusion

We have developed, tested, and demonstrated procedures that allow the radiochemical determination of californium  $\alpha$ -decay content in DOE high level waste. The radiochemical separation technique is based on a series of column extractions that uses EiChrom Industries +3 selective Ln-resin and +4 selective TRU-resin to separate +3 actinides and lanthanides from +4 actinides. We then use liquid scintillation counting as a test to guide the separation further on a sample by sample basis to eliminate interference from other radionuclides present. The technique has been demonstrated on three types of authentic DOE high level and low level waste samples. We obtain discrimination from Pu  $\alpha$ -activity by a factor of over 200 and from Cm-244  $\alpha$ -activity by up to a factor of 1700.

The product phases are measured by liquid scintillation spectroscopy and by pulse shape discrimination liquid scintillation spectroscopy (PSD) to determine Cf  $\alpha$ -decay activity or lower limits of detection. Recovery of Cf is determined from duplicate samples that contain spiked Cf-249. Cf-249 recovery can be determined by PSD and by  $\gamma$ -PHA. In our development samples, Cf recoveries have ranged from 50% to 90%. In the real DOE waste samples, recoveries have ranged from 1.4% up to 48%. These have yielded detection limits as low as 80 dpm/mL for the authentic samples and have enabled us to measure values of Cf isotopes. The  $\alpha$ -activities for Cf measurements were in the range of 420 dpm/mL up to 28000 dpm/mL. In addition to the radiochemical measurements we have demonstrated the observation of spiked Cf-249 by ICP-MS in one sample at the level of 0.04 ppb in the product phase. The ICP-MS spectra have assisted in the diagnostic testing to certify the samples to be pure of Pu isotopes and of Cm isotopes.

## Figure Captions

1. Load-Elute sequence using Ln-resin followed by TRU-resin to obtain intermediate product phase in dilute  $\text{HNO}_3$ .
2. Load-Elute sequence using TRU-resin followed by Ln-resin to obtain intermediate product phase in (2-4) M  $\text{HNO}_3$ .
3. Liquid scintillation counting spectra of test samples 7790 and 7791 as described in the text.
4. Liquid scintillation counting spectra of test samples 13125 and 13126 as described in the text.
5.  $\alpha$ -PHA spectra of product phases test samples 12485 - 12487.
6. Illustration of chemical treatment for the authentic high level and low level waste samples as described in text.
7. (a) Liquid scintillation counting spectrum of SRS sample 119289 product phase that contains a large  $\alpha$ -decay component of Cm-244 plus Cf-249. The spectrum demonstrates this product phase is quite free of  $\beta$ -decay activity.  
  
(b) Liquid scintillation counting spectrum of Hanford samples 129284 product phase that contains observable Sm-151  $\beta$ -decay activity and a trace of Cf  $\alpha$ -decay activity.
8. ICP-MS actinide spectra of the product phases of samples 119289, 119289.sp, 118517, and 118517.sp.

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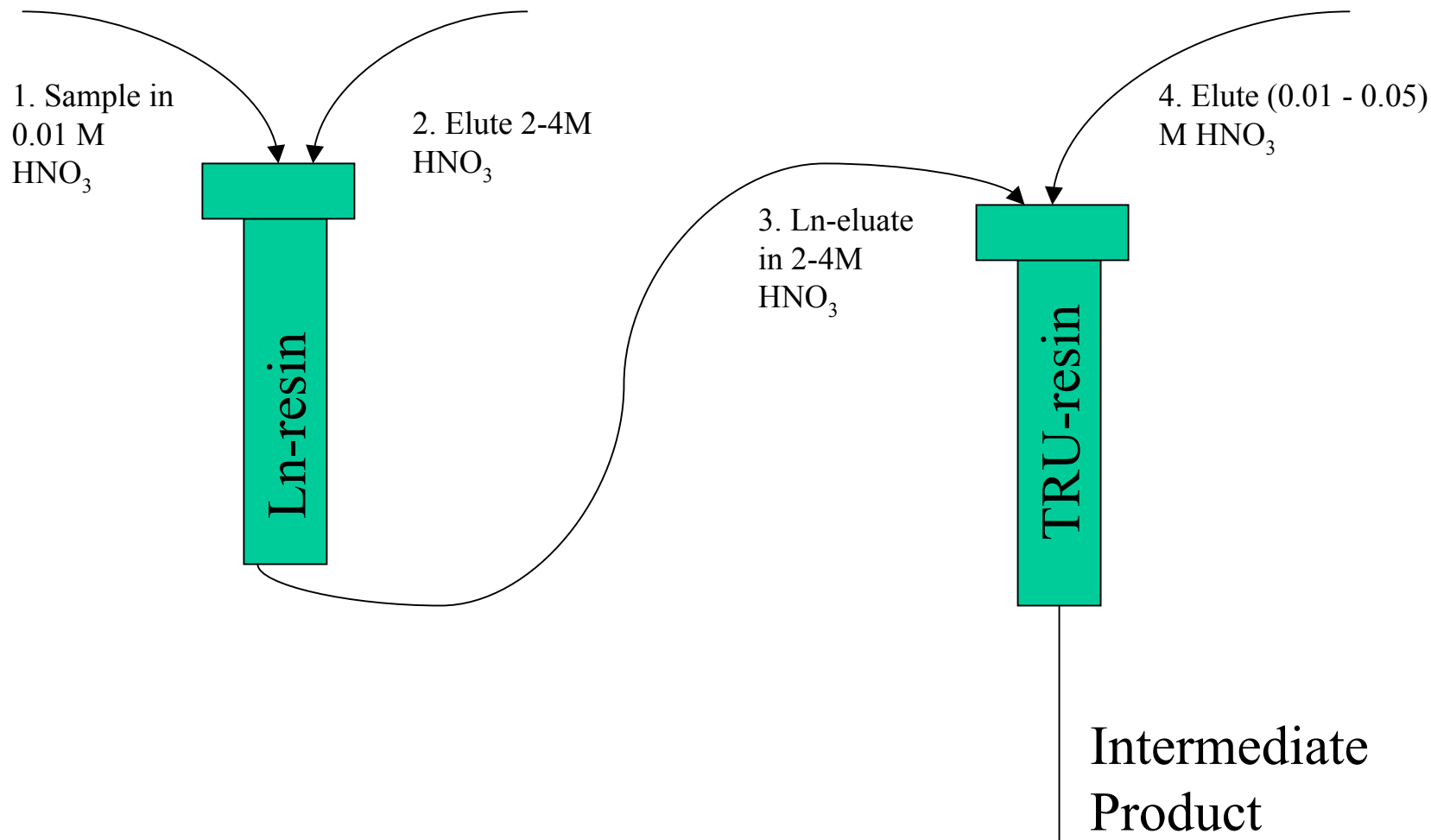


Figure 1. Load-Elute sequence using Ln-resin followed by TRU-resin to obtain intermediate product phase in dilute  $\text{HNO}_3$ .

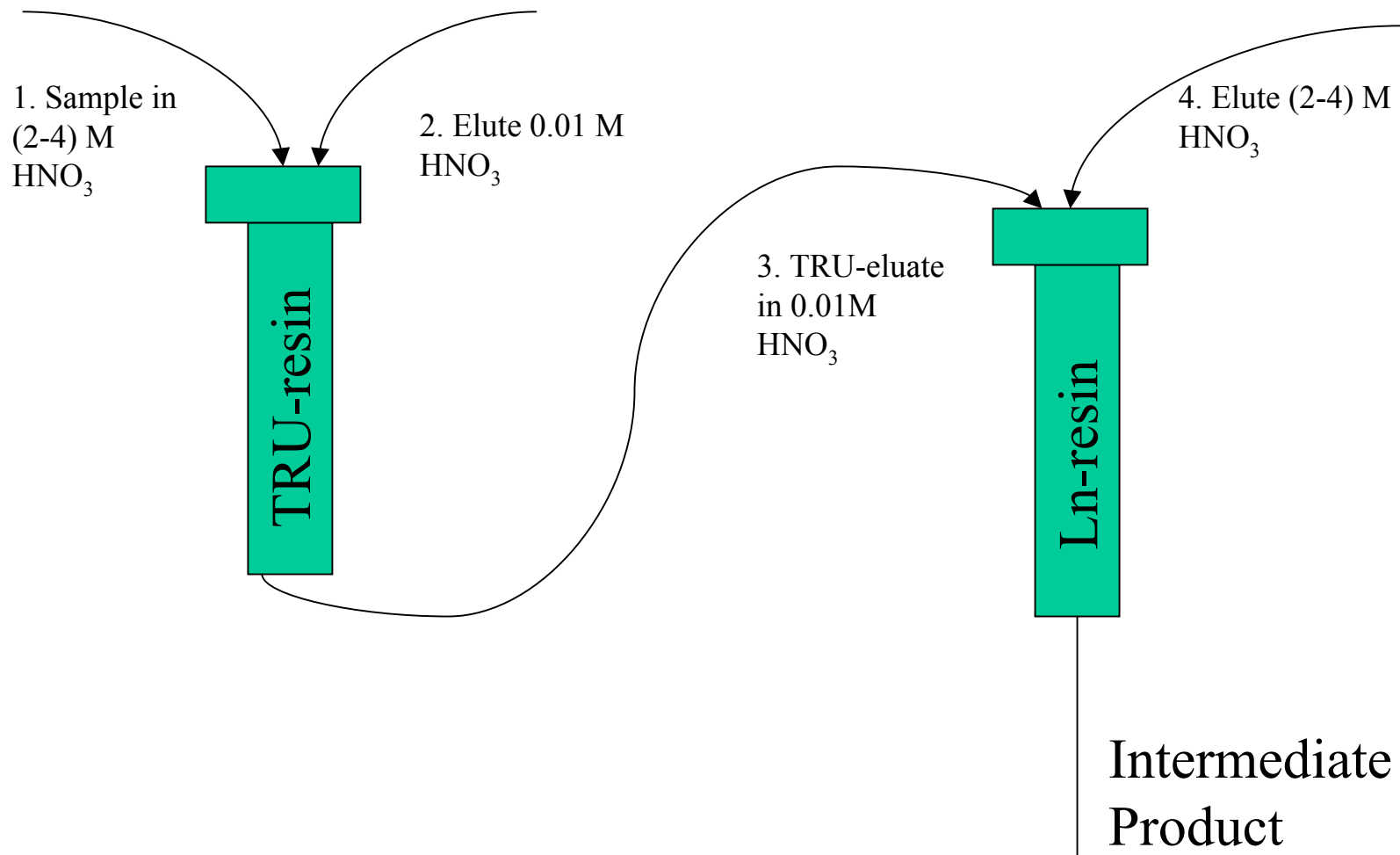
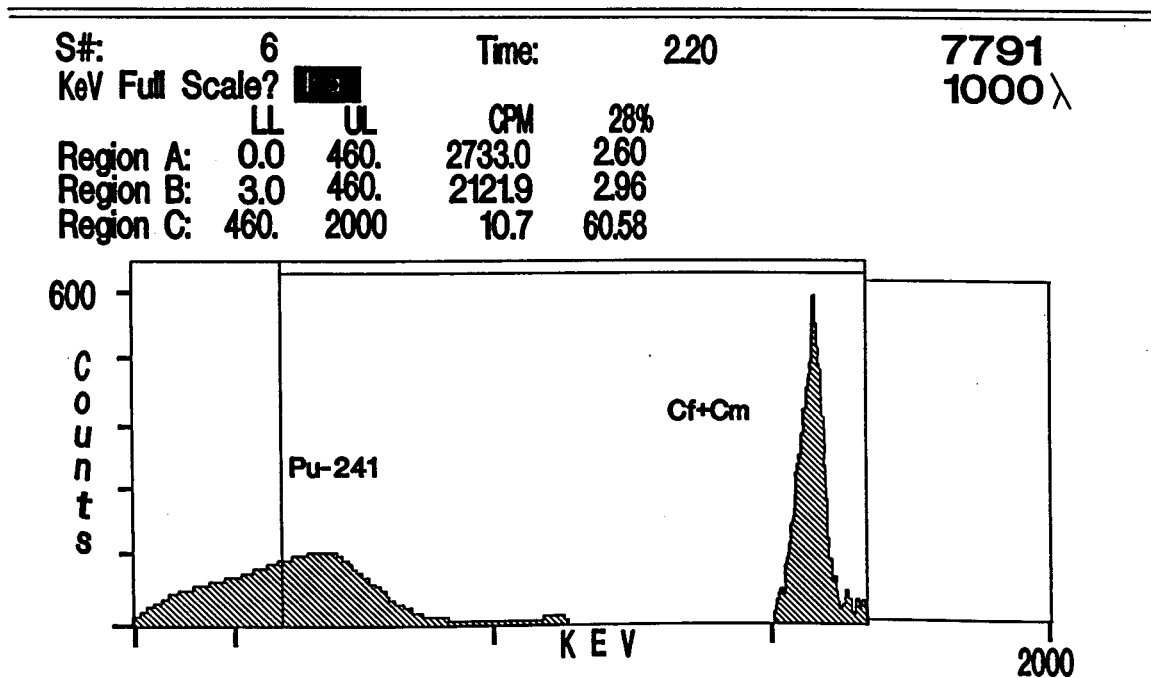
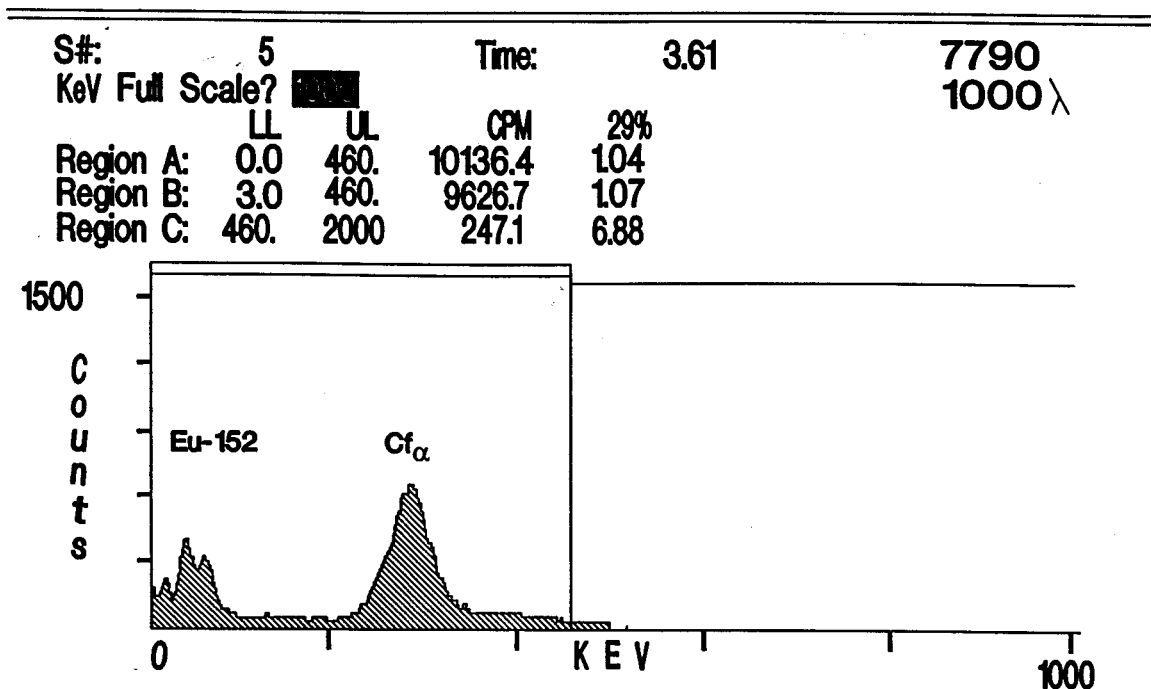


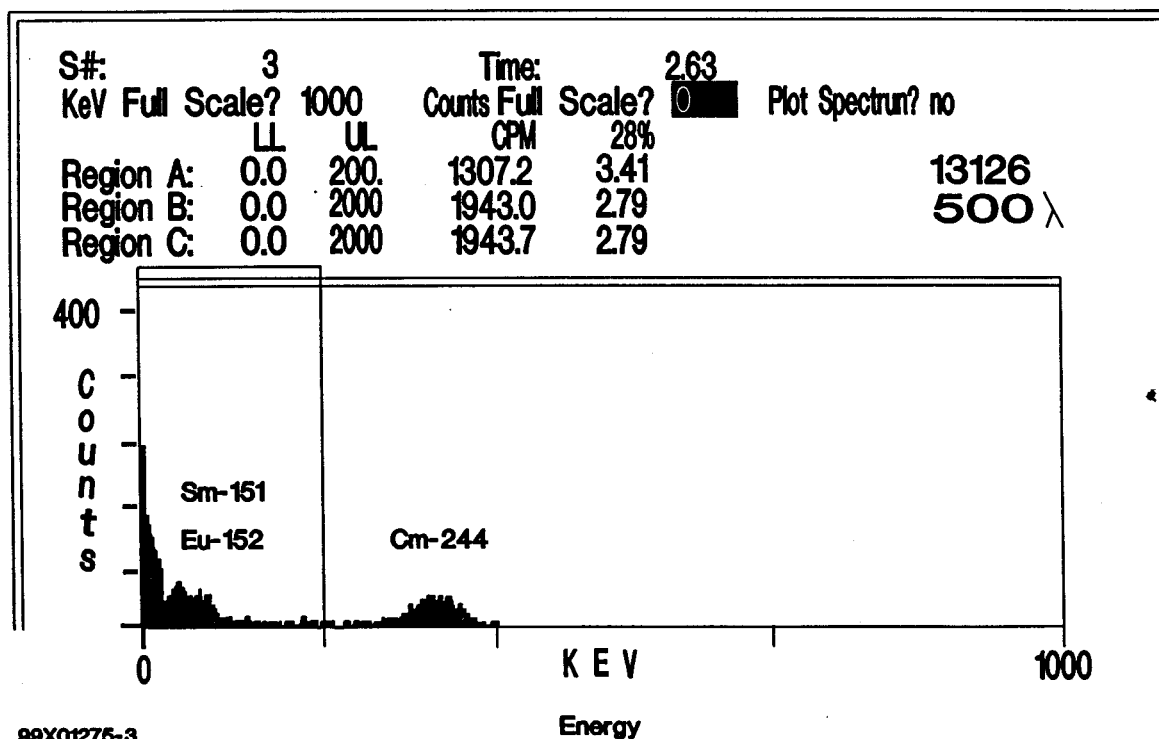
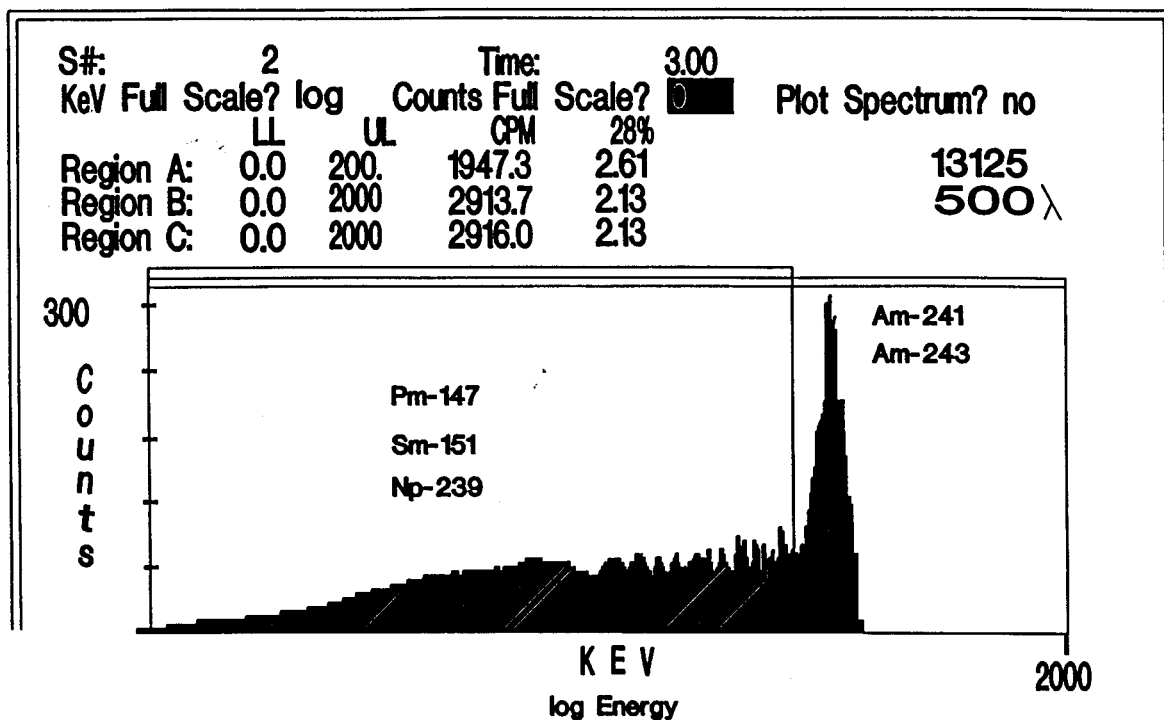
Figure 2. Load-Elute sequence using TRU-resin followed by Ln-resin to obtain intermediate product phase in (2-4) M  $\text{HNO}_3$ .



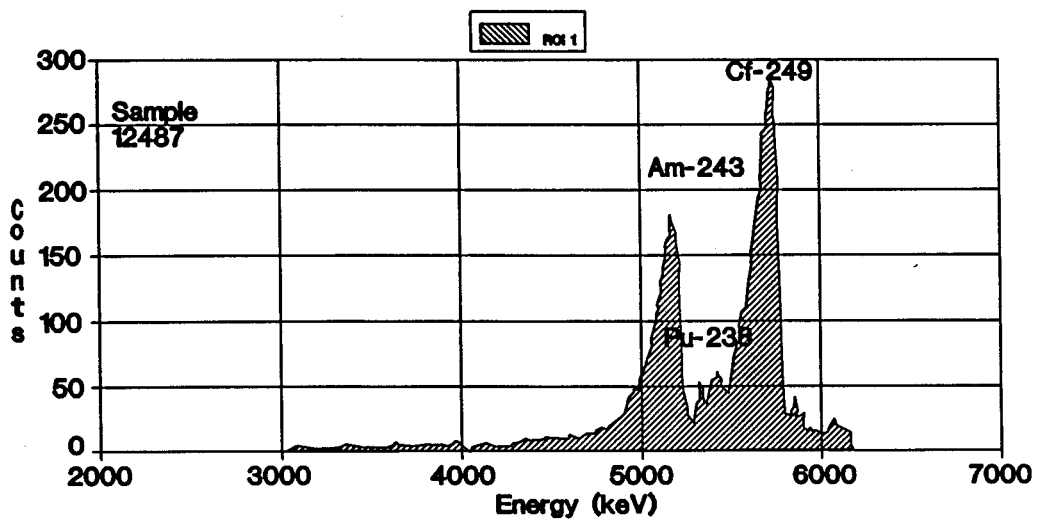
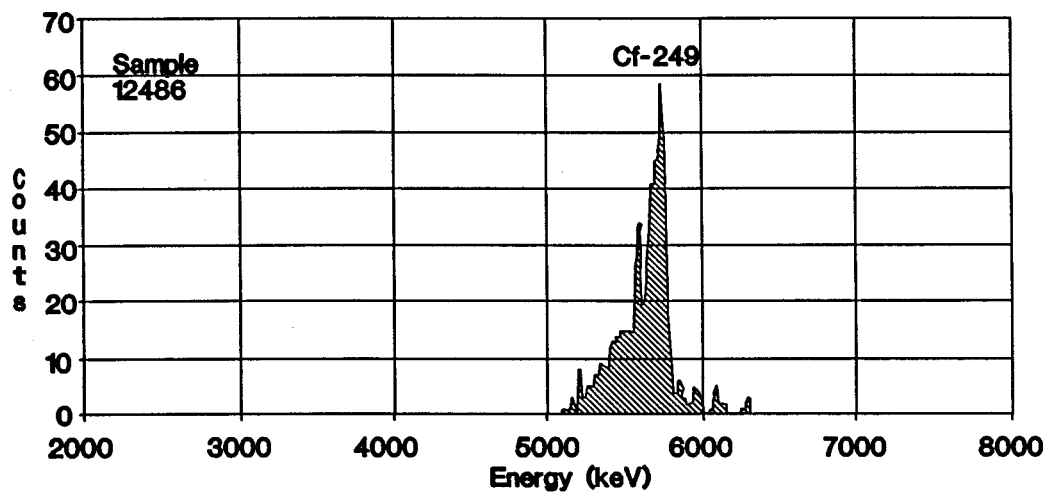
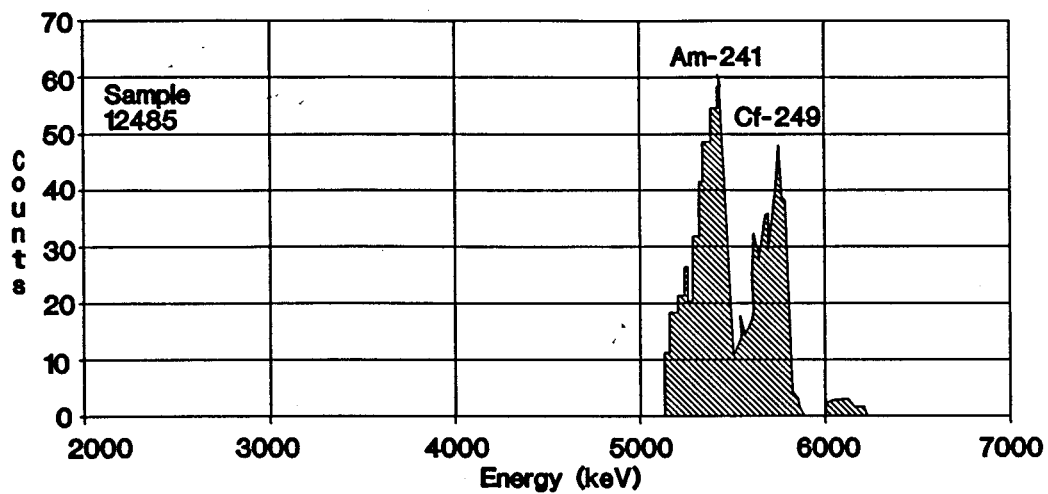
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3. Liquid scintillation counting spectra of test samples 7790 and 7791 as described in the text.



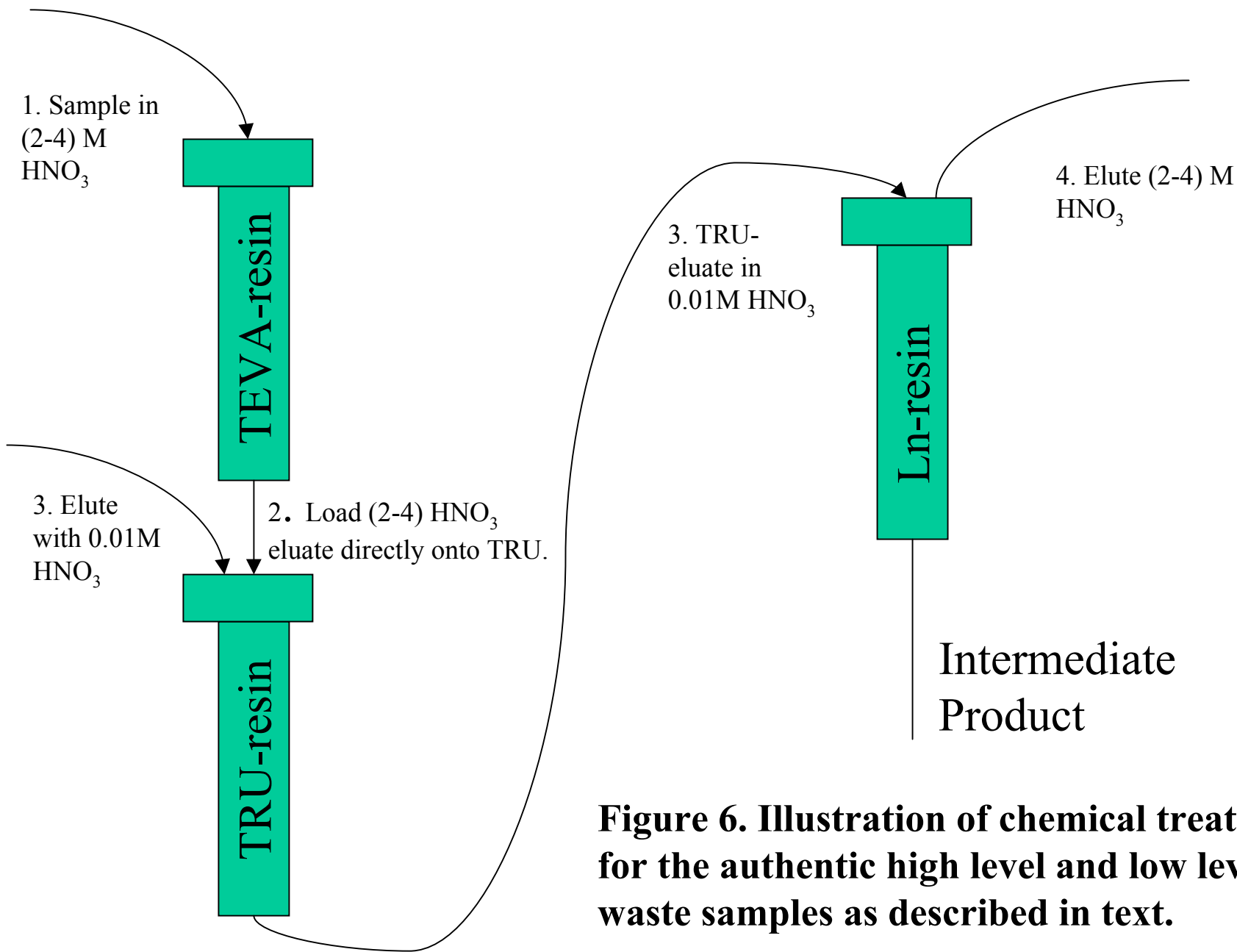


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4. Liquid scintillation counting spectra of test samples 13125 and 13126 as described in the text.

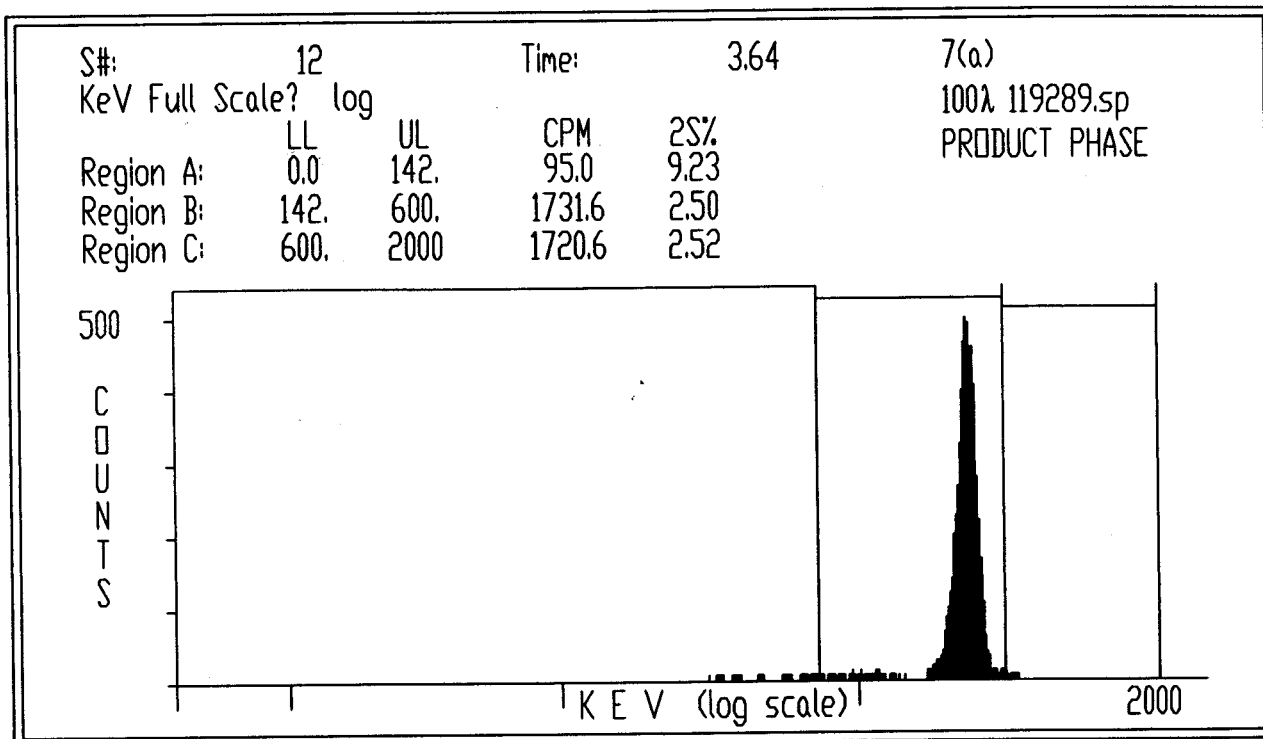


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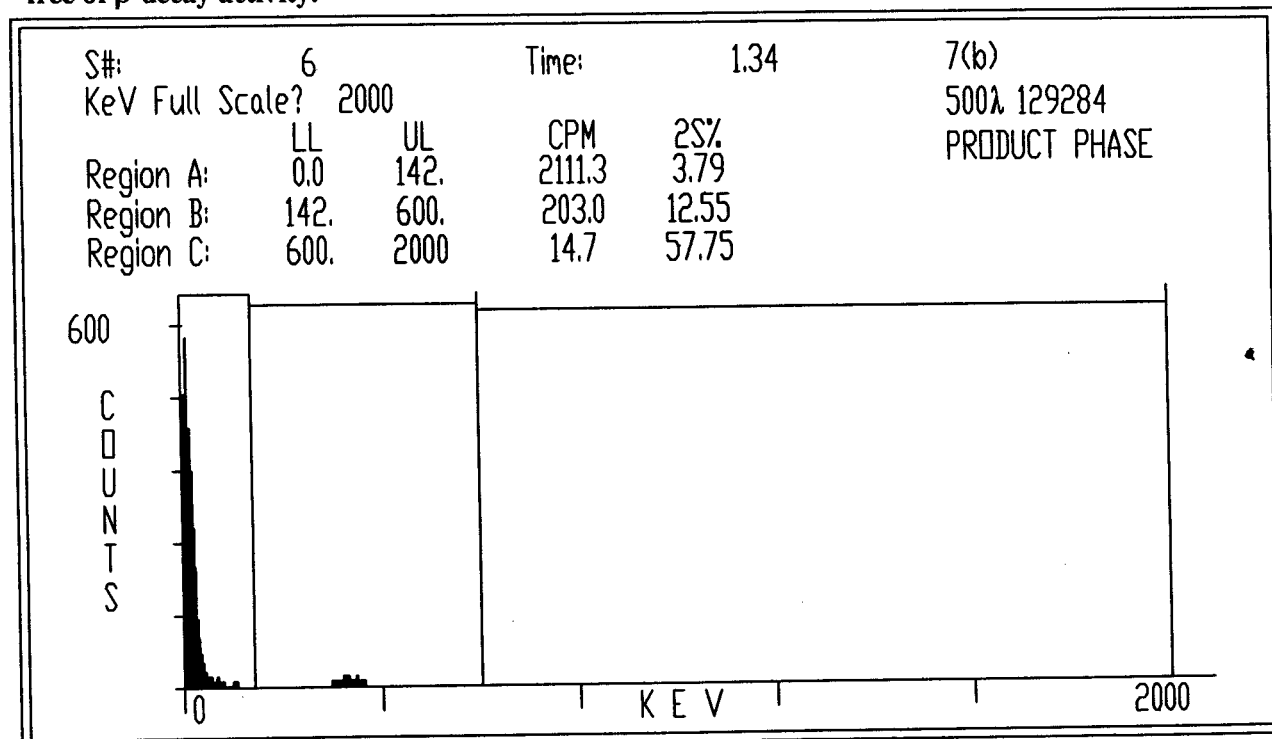
5.  $\alpha$ -PHA spectra of product phases test samples 12485 - 12487.



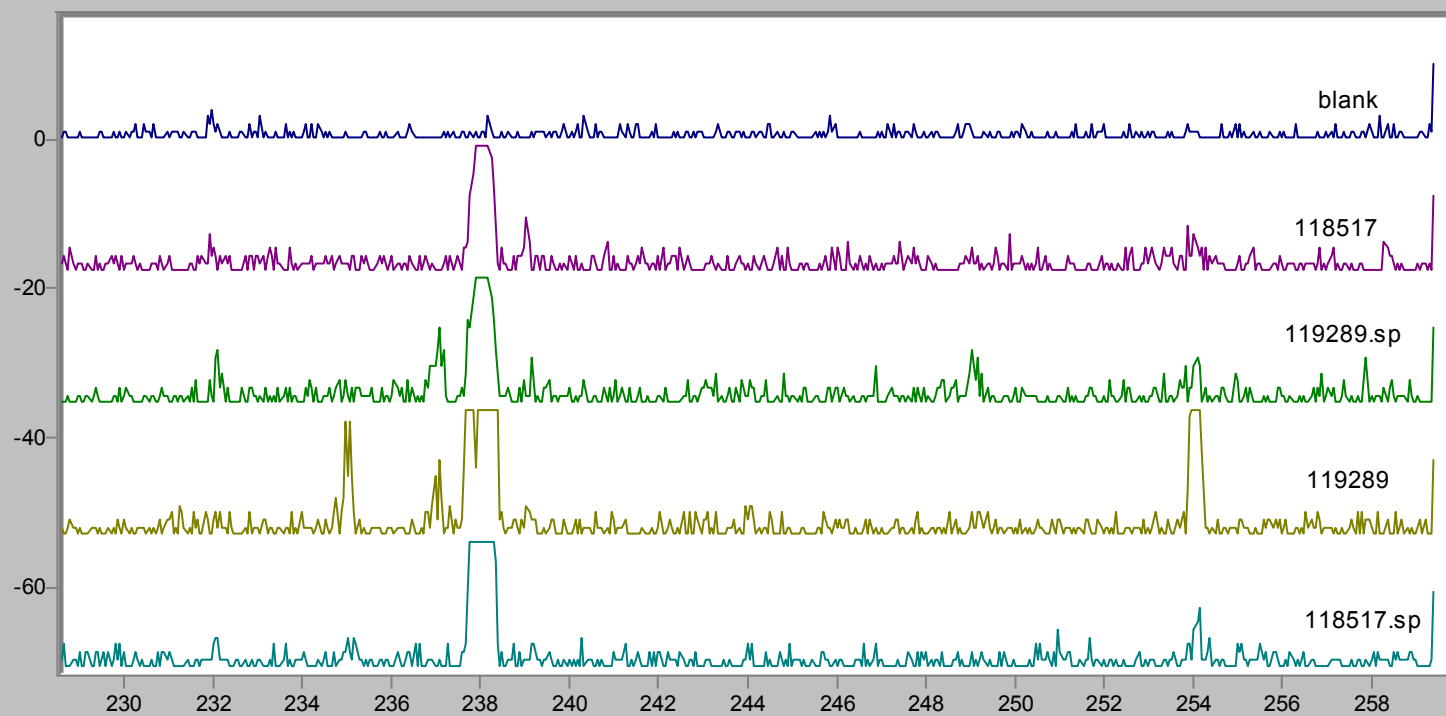
**Figure 6. Illustration of chemical treatment for the authentic high level and low level waste samples as described in text.**



7. (a) Liquid scintillation counting spectrum of SRS sample 119289 product phases that contains a large  $\alpha$ -decay component of Cm-244 plus Cf-249. The spectrum demonstrates this product phase is quite free of  $\beta$ -decay activity.



- (b) Liquid scintillation counting spectrum of Hanford samples 129284 product phase that contains observable Sm-151  $\beta$ -decay activity and a trace of Cf  $\alpha$ -decay activity.



Counts / Mass (m/z)

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