LA-SUB-99-26

Separation and Analytical Chemistry of the Actinides

Final Report for Subcontract 493BH0017-3C

January 23, 1997 - June 30, 1998

Submitted by

Dr. Dale D. Ensor
Chemistry Department
Tennessee Technological University
Cookeville, TN 38505

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Abstract

The determination of low levels of actinides from water samples and aqueous waste streams involves a lengthy and complicated process which is characterized by low recoveries and poor precision. The objective of this work was to evaluate the use of a Photon Electron Rejecting Alpha Liquid Scintillation Spectrometer (PERALS®), in combination with extractive scintillators, for the detection of actinides. The results of the application of this method to aqueous samples containing uranium, thorium, plutonium, and americium, both individually and in mixtures showed promising results. Using a commercially available extractant, ALPHAEX®, recoveries of plutonium and americium were > 98.4% in individual samples and in mixtures with activities ranging from 6 pci to 500 pci. The separation of these two elements was acomplished by selective extraction after adjusting the acidity of the aqueous sample. The application of this technique to a raw waste sample showed reasonable recoveries when combined with classical anion exchange separation techniques. Efforts to develop an extractive scintillator using a recently synthesized tetradentate extractant were only moderately successful since solubility problems limit the extractant's efficiency in the scintillator. The application of a curve fitting program, PEAKFIT®, to spectra obtained using the PERALS® spectrometer provided useful isotopic information.

Objectives

1. Complete evaluation of more selective extractants for the PERALS® system.

The extractant, 4,4'-nonanedioyl-*bis*(3-methyl-1-phenyl-2-pyrazolin-5-one) (H_2NDBP), was evaluated in a toluene-based cocktail. Previous work with this tetradentate extractant indicated that it might be useful in the separation of Pu^{+4} from Th^{+4} at high acid concentrations (>0.5M). The H_2NDBP was incorporated into an extractive scintillation cocktail using toluene as the solvent. Initial studies showed that the presence of H_2NDBP did not degrade the pulse-shape spectra and good discrimination between the alpha and beta/gamma was possible. The results for the determination of Th^{+4}, Pu^{+4}, and UO_2^{+2} using this new extractive scintillator are contained in Table I. The efficiency for Pu^{+4} was not as good as predicted from previous extraction studies. It is possible that the extractant was degraded by reacting with the KNO_2 used to adjust the oxidation state of plutonium from +3 to +4. A distinct yellow coloration was apparent in the extractive scintillator after contact with plutonium solutions containing nitrite. This led to poor separation of the pulse-shaped spectrum and lower alpha efficiency.

Table I. Actinide Recoveries Using an Extractive Scintillator With H_2NDBP (1.0×10^{-3}M)

Metal	% Recovery	Acid Strength
Pu^{+4}	90+%	0.5 M HNO_3
Th^{+4}	8%	0.5 M HNO_3
Th^{+4}	98%	0.1 M HNO_3
UO_2^{+2}	0%	0.1 M HNO_3
UO_2^{+2}	98.8%	0.001 M HNO_3

Although the separations of Pu^{+4} and Th^{+4} were not as good as anticipated, the separation of UO_2^{+2} from either Th^{+4} or Pu^{+4} was excellent. This type of separation is more difficult using ALPHAEX® requiring a holdback reagent to complex the +4 ion and allow the UO_2^{+2} to be extracted. The inability to increase the concentration of H_2NDBP in the extractive scintillator limits its usefulness in higher concentrations of nitric acid.

2. Complete testing of curve-fitting procedures in order to improve isotopic information.

PEAKFIT™ is a peak separation and analysis program. Spectra from the PERALS® spectrometer can be easily evaluated using this program. The program has several smoothing options, but the Savitzky-Golay algorithm proved the most useful.

Figure 1 is a spectrum of an unknown sample of Pu-239 that had been spiked with Pu-242. Reasonable resolution between Pu-242 and Pu-239 with energies of 4.86 MeV and 5.15 MeV respectively was obtained. Figure 2 shows the results of PEAKFIT™ on the same sample with a projected isotopic distribution.

Figure 1 Spectrum of Plutonium Without Any Smoothing or Data Treatment

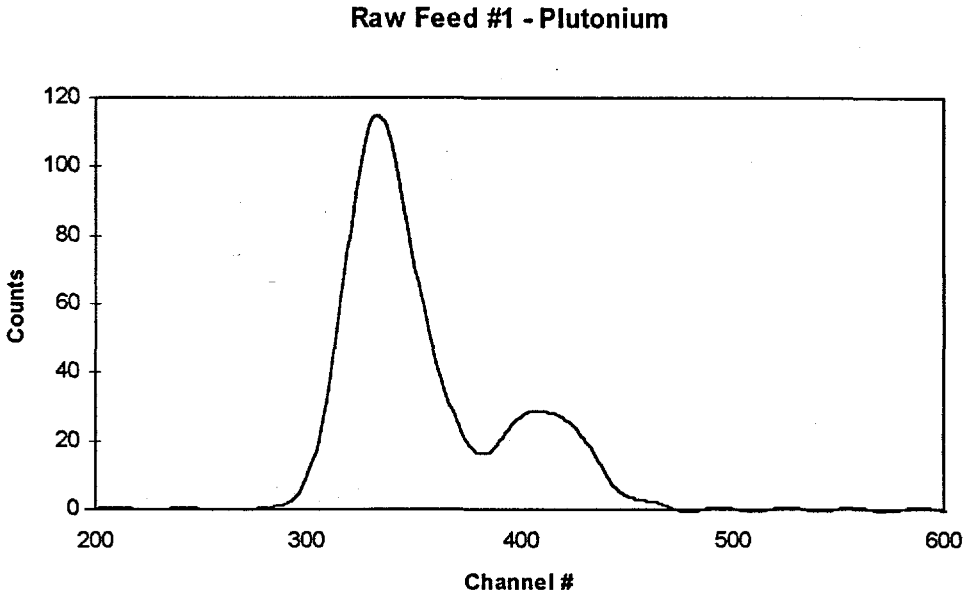
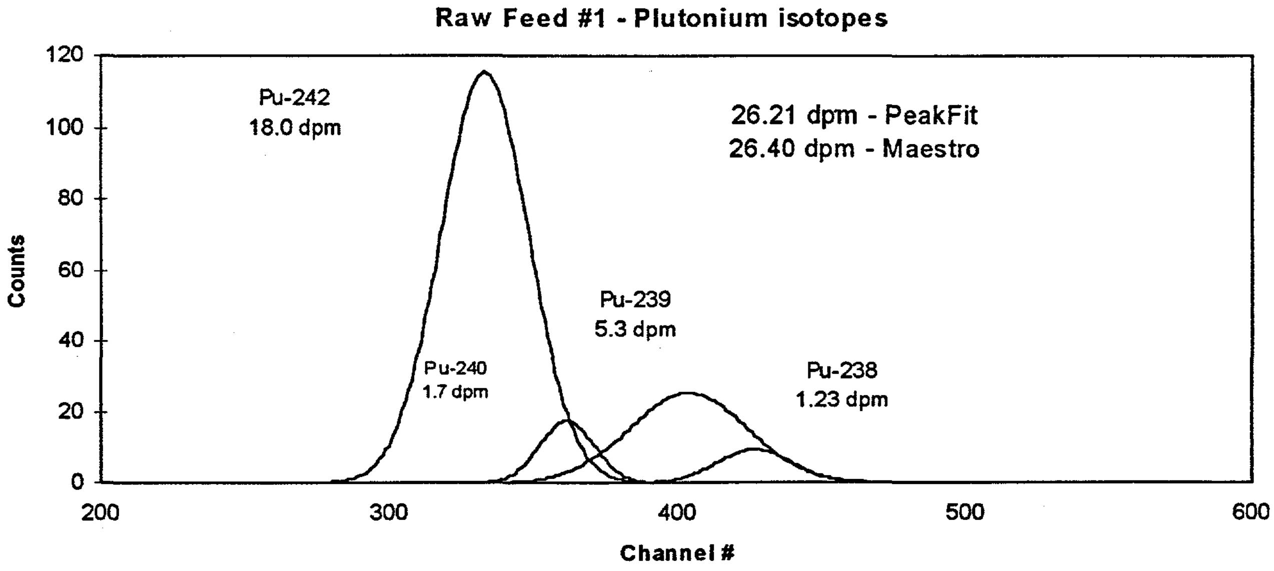


Figure 2 Spectrum of Plutonium Showing Isotopic Data Obtained Using PEAKFIT™



The validity of this type of data treatment could not be checked due to the lack of an isotopic standard. However, the results indicate that, if appropriate standards were used to validate the procedure the isotopic information available from a PERALS® spectrum could be enhanced using the PEAKFIT™ software.

3. **Complete testing of commercially available resins in order to concentrate and separate isotopes.**
4. **Complete studies on applying PERALS® to plutonium process waste.**

The final two objectives were combined due to lack of time at LANL. The testing of commercially available resins was performed using raw feeds obtained from Gordon Jarvinen. The only information about these solutions was the total alpha activity. No information concerning chemical composition or isotopes present was available.

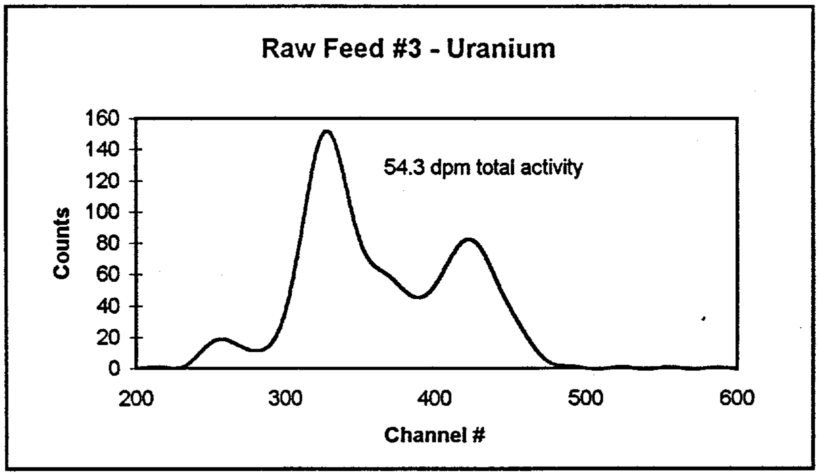
Separation of Americium and Plutonium using Tru-spec

A 3 M nitric acid solution was spiked with Pu-239 (599.45 dpm) and Am-241 (59.018 dpm). Ascorbic acid was added to reduce the plutonium and the solution was loaded onto a Tru-spec column. The americium was eluted first with 0.01 M nitric acid (approx. 20 ml) and the plutonium was then eluted with 0.1 M nitric acid (approx. 20 ml). The fractions were twice heated to near dryness with concentrated nitric acid and hydrogen peroxide. The plutonium residue was dissolved in 1 M nitric acid. Ascorbic acid was then added, followed by sodium nitrite, and the plutonium fraction was extracted with ALPHAEX®. The resulting sample contained 49.3 cpm which represented an 8% recovery of the plutonium spike. The americium residue was then made up in 0.1 M sodium nitrate. The pH was adjusted to 2.5 and the fraction was extracted with ALPHAEX®. The spectra resulting from this extraction showed two peaks instead of the expected single peak for Am-241. The spectra was analyzed by PEAKFIT™ and the other unidentified peak was assumed to be plutonium.. There were 46.15 dpm americium and 16.33 dpm plutonium detected. The total activity in Maestro was found to be 62.5 dpm, while in PEAKFIT™ the total activity was calculated to be 62.48 dpm. The aqueous phase from this extraction was extracted a second time to recover more americium. The second sample also contained two peaks which were assigned to americium and plutonium. In PEAKFIT™, 3.6 dpm americium and 4.9 dpm plutonium were detected. The total recovery for americium was 84.3%, and for plutonium 12.4%. The poor recover of the plutonium spike was a result of not being able to strip the plutonium off the Tru-spec column. Further work with know samples needs to be carried out to identify the reasons for the poor recoveries with this column.

Analysis of Raw Feed #3 using Eichrom resins

Raw Feed #3 was chosen to be analyzed by Eichrom resins and PERALS® because it had the highest activity of the waste samples provided. The alpha activity was 937.187 pCi/L. The sample had a volume of approximately 200 ml, which gave a total activity of 187.4 pCi in the sample and the entire sample was used for analysis. After acidification, the sample was evaporated to near dryness on a hot plate. The residue was dissolved in 10 ml 3M HNO_3 containing aluminum nitrate. Ascorbic acid and ferrous sulfate were added to reduce the plutonium and any neptunium that might be present. The solution was then loaded onto a U/Teva column with eluant fed directly into a Tru-spec column. The Np/Th fraction was eluted from the U/Teva column with the addition of 5M HCl/.5M oxalic acid. The uranium fraction was eluted from the U/Teva with 0.01 M HCl The americium fraction was eluted from the Tru-spec column with 4M HCl. The plutonium fraction was eluted from the Tru-spec by addition of 0.1M HNO_3. The fractions were repeatedly evaporated to near dryness with the addition of conc. HNO_3 and H_2O_2. The Th/Np fraction was made up in 1M HNO_3 and extracted with ALPHAEX®. There was no activity detected above background in this sample. The amercium residue was made up in 0.1M $NaNO_3$ and the pH adjusted to 2.6and extracted with ALPHAEX®. After one extraction an activity of 51.18 dpm americium was detected. A second extraction yielded an additional 33.83 dpm of activity. The total americium detected was 85.01 dpm. The plutonium residue was dissolved in 1M HNO_3 . Ascorbic acid was added, followed by sodium nitrite to ensure plutonium was in the +4 oxidation state. The plutonium faction was extracted with ALPHAEX® and 34.08 dpm activity was detected. The uranium residue was made up in 10^{-4}M HNO_3 and extracted. There are 3 clear peaks present in the untreated spectrum(see Figure 3).

Figure 3 The Untreated Spectrum of the Uranium Fraction



The spectrum was treated using PEAKFIT™ with four peaks being detected (see Figure 4). The three peaks on the right are thought to be isotopes of uranium and are labeled as such. The identity of the small peak on the far left is unknown. One possible explanation for the peak at lower energy is the presence of small particulate matter which would scatter the emitted light and cause this spurious peak. This low energy peak in the uranium fraction also appeared in the spectrum of another waste sample. The energies of the uranium isotopes and their respective channel numbers were used to estimate the alpha energy of the unknown peak. This calculation resulted in an energy of 3.763 MeV which does not correspond to a possible nuclide. Time did not allow the further investigation of this spurious peak.

The aqueous phase of the uranium fraction was then extracted a second time and an additional 7.02 dpm of uranium was recovered. The sum of 82 pCi of alpha activity was detected in the various fractions of Raw Feed #3; this is summarized in Table II. The low recovery was attributed to the inability to effectively strip the isotopes from the Eichrom resins.

Table II Analysis of Raw Feed #3 Using Eichrom Resins

Estimated total activity in Raw Feed #3: 211 pCi

Am Fraction
  1st extraction: 23.26 pCi detected
  2nd extraction: 15.38 pCi detected

Total Am detected: 38.64 pCi

Th/Np Fraction
  no activity detected

Pu Fraction
  Total Pu detected: 15.50 pCi

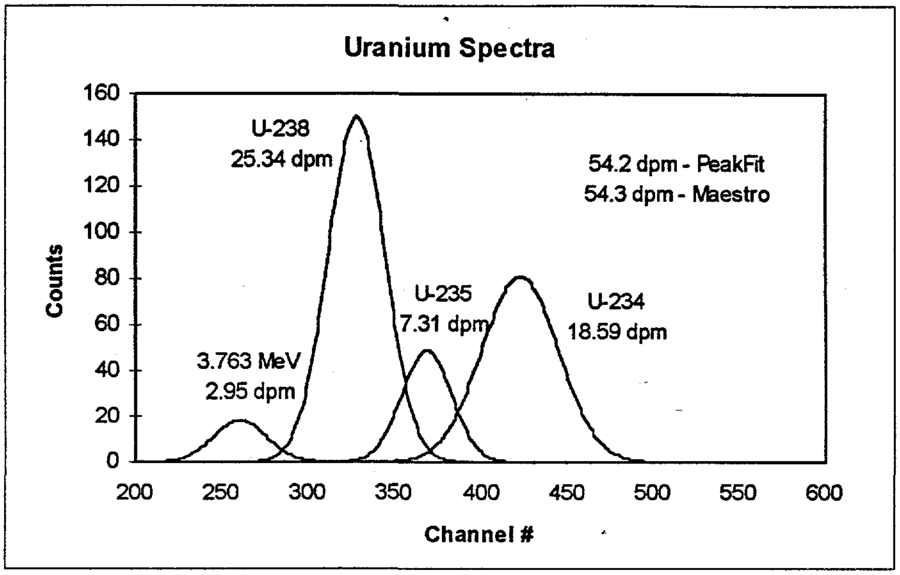
U Fraction
  1st extraction: 24.68 pCi detected
  2nd extraction: 3.19 pCi detected

  Total U detected: 27.87 pCi

Results for Raw Feed #3 aliquot with approximately 211 pCi alpha activity
  Detected Am: 38.64 pCi
  Detected Pu: 15.50 pCi
  Detected U: 27.87 pCi

Total activity detected in sample: 82.01 pCi (38.87% recovery)

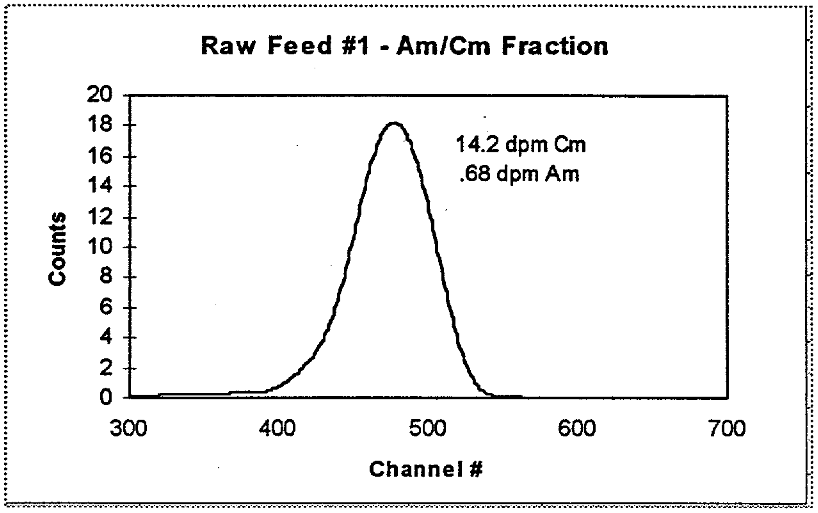
Figure 4 The Uranium Spectrum Fitted Using PEAKFIT™



Analysis of Raw Feed #1 Using Anion Exchange Columns

A second sample of waste water identified as Raw Feed #1 was treated using standard anion exchange procedures. The total alpha activity of this waste sample was 118 pCi/L. A 100 ml portion of the sample was acidified and spiked with Pu-242 (21.86 dpm) and Cm-244 (20.92 dpm) to monitor recovery of plutonium and americium . Sodium nitrite was added to adjust the oxidation state of Plutonium, and iron was added to serve as a carrier. The solution was boiled and NH_4OH added to precipitate the metals as hydroxides. After allowing the precipitate to settle, the liquid was removed and the precipitate was dissolved in conc. HCl (approx. 10 ml), and the solution was loaded onto an anion exchange column. The americium, curium, and thorium were not retained on the column and were collected, evaporated, and the residue dissolved in 8M HNO_3. This solution was placed on a second column. The americium/curium were not retained on the second column and this fraction was evaporated and dissolved in 0.1M $NaNO_3$. After extraction with ALPHAEX® an activity of 14.88 dpm was detected for this americium/curium fraction. The spectrum showed only one peak with an asymmetric shape. The spectrum was treated using PEAKFIT™, making the assumption that the asymmetric shape on the lower energy side of the peak was caused by americium (see Figure 5) since this is where the americium should appear. An activity of 0.68 dpm was obtained.

Figure 5 PEAKFIT™ Analysis of the Americium/Curium Fraction

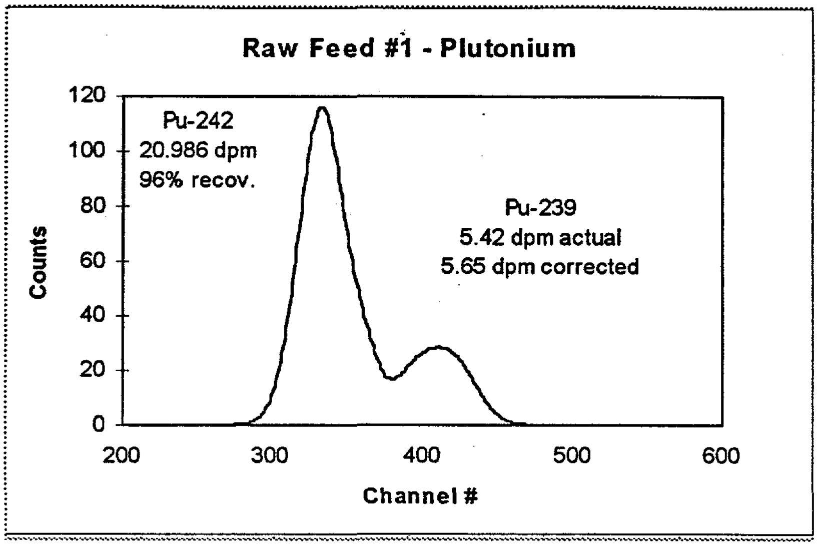


A second extraction of this fraction was performed and 3.91 dpm of activity was is detected. The spectrum was treated by PEAKFIT™ and an additional 3.81 dpm of curium and 0.10 dpm of americium were obtained. The total activity of curium detected, combining the two extractions, was 18.03 dpm. This represented a recovery of 86.2% based on an original curium spike of 20.92 dpm. The total americium detected was 0.78 dpm and based on the recovery of curium yielded 0.90 dpm of americium in the original sample.

The thorium was eluted from the second column using 0.75M HNO_3 and evaporated to dryness. The residue was dissolved in 10^{-4}M HNO_3 and extracted with ALPHAEX®. No alpha activity was apparent after 24 hours of counting.

The plutonium was eluted from the first column by the addition of HCl/HI (10/1). Concentrated HNO_3 was added and the fraction was evaporated; the residue was dissolved in 1M HNO_3. Two peaks were evident (see Figure 6) in the PERALS® spectrum. The activity of Pu-242 was 20.986 dpm which represented a recovery of 96%. The activity detected under the second peak was 5.42 dpm, and, adjusted for recovery, represents 5.65 dpm of Pu-239.

Figure 6   Plutonium Fraction From Anion Exchange Column



The uranium was eluted from the first column by addition of 0.1M HCl. Concentrated HNO_3 was added, Tte fraction was evaporated to dryness,and the residue was dissolved in 10^{-4}M HNO_3. The resulting solution was extracted using ALPHAEX®. Two peaks were seen in the PERALS® spectrum (see Figure 7). The total uranium activity was 13.6 dpm. The small peak to the left of the large peak was also observed in the uranium spectra from the analysis of Raw Feed #3. The source of this peak has not been established, but is probably a result of treating these raw feed samples, since uranium standards do not show this peak. The total activity detected in Raw Feed #1 was 9.16 pCi. This represented a recovery of 77.6% based on the alpha activity of 11.8 pCi reported to be in the 100 ml aliquot treated. Table III contains a summary of the alpha activity found in Raw Feed #1.

Summary

The combination of extractive scintillation cocktails and the PERALS® spectrometer has been shown to be an effective method of detecting alpha-emitting actinides in aqueous solutions at very low concentrations. The sample preparation and counting time is significantly less than for current procedures. The use of the extractive cocktail ALPHAEX® and pH control can be used to selectively separate and assay solutions containing americium and plutonium with recoveries approaching 100%. The major drawback of liquid scintillation counting is the lack of isotopic information that can be obtained due to the poor energy resolution of the process. The isotopic information can be enhanced using a PEAKFIT™ program, with results obtained indicating that it could resolve two overlapping peaks. The accuracy of this must be tested with known mixtures of isotopes. The extractive technology currently being used with the PERALS® system does not make use of the latest separation advances. The incorporation of new extractants, such as H_2NDBP, into the scintillation cocktail can provide more efficient separation schemes for the actinides. This study performed only limited tests of the application of this technique to waste samples. The results were promising, but, since the waste samples were not well-characterized, the accuracy of the treatment used in this study cannot be evaluated. Further work to evaluate the accuracy of the PEAKFIT™ program, including the testing of new more selective extractants and well characterized waste samples, need to be done in order to make a final analysis of the capablilities of the PEARLS® technique.

Figure 7 Uranium Fraction From Anion Exchange Column

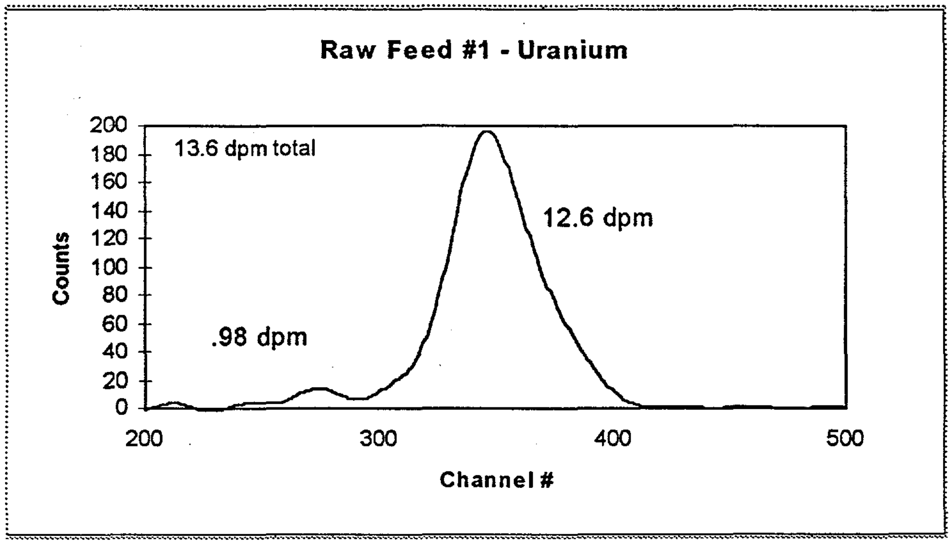


Table III Analysis of Raw Feed #1 Using Anion-Exchange Column Procedure

Total activity of 100 ml waste water aliquot: 11.8 pCi
Pu-242 spike: 9.94 pCi
Cm 244 spike: 9.51 pCi

Am/Cm Fraction
1st extraction: 6.76 pCi detected in Maestro
6.45 pCi detected in PeakFit
Difference attributed to the activity of Am: 0.31 pCi.

after 2nd extraction: 1.78 pCi detected in Maestro
1.73 pCi detected in PeakFit
Difference attributed to the activity of Am: 0.05 pCi.

Total Cm detected: 8.19 pCi (86.1% recovery)
Total Am estimated: 0.35 pCi, adjusted with recovery factor: 0.41 pCi

Th/Np Fraction
no activity detected

Pu Fraction
Pu-242 detected: 9.54 pCi (96% recovery)
Pu-239 detected: 2.46 pCi, adjusted with recovery factor - 2.57 pCi

U Fraction
Total U detected: 6.18 pCi

Results for waste aliquot: 11.8 pCi present
Detected Am: 0.41 pCi
Detected Pu: 2.57 pCi
Detected U: 6.18 pCi

Total alpha activity detected in sample - 9.16 pCi (77.6% recovery)

Presentations

"Separation and Analysis of Actinides in Water Samples and Waste Streams Using a PERALS® Spectrometer," D. W. Heeks and D. D. Ensor. Presented at the 215th National Meeting of the American Chemical Soc., Dallas, TX, March 29 - April 2, 1998.

"Analysis of Actinides in Water Samples and Waste Streams Using a PERALS® Spectrometer," D. D. Ensor, H. Wang, and D. W. Heeks. Presented at the 22nd Actinide Separations Conference, Chattanooga, TN, April 20 - 23, 1998.

Students Supported

David W. Heeks	Undergraduate Chemistry Major
Hao Wang	Graduate Student, M.S. Candidate