

**Efficient Pre-concentration and Separation of Actinide Elements from Large
Soil and Sediment Samples**

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ABSTRACT

Large (~10 g) soil and sediment samples are often required for analysis of low-level man-made actinides for monitoring environmental radioactivity. However, use of large environmental samples often results in significant chemical losses during chemical separations due to matrix interferences. We present a technique based on the ion exchange resin "Diphonix" which selectively collects actinides and lanthanides into a common form which then behaves uniformly and predictably during subsequent separation schemes. Diphonix is attractive for this purpose because it has an extremely high affinity for actinides, a low affinity for most common ions, and is resistant to hydrofluoric acid. After being adsorbed onto Diphonix resin in a column mode at a pH ~1, actinides are completely eluted with 0.5M 1-hydroxyethylidenediphosphonic acid (HEDPA). After destruction of the HEDPA by ozonation or use of "Fenton's Reagent," Am, Pu, U, and Th are separated from each other and the remaining matrix by use of extraction chromatographic resins. We obtained high and consistent chemical recoveries (mean = 85%), as well as excellent chemical separations, for Am, Pu, U, and Th through the entire procedure for several 10-g soil and sediment samples.

INTRODUCTION

In general, when larger amounts of soil and sediment samples are used for actinide analysis, chemical recoveries are variable due to interferences from major ions, the so-called “matrix effects.” These effects are especially troublesome because there is a strong sample-dependency involving the composition and/or mineralogy of specific samples. Since one rarely has detailed information on the chemical composition of samples used for environmental monitoring, this can be a very serious issue. To tackle these problems, we have developed a technique which can effectively eliminate most major ions from soil and sediment samples before subsequent chemical separations.

The basis of this technique is use of Diphonix ion exchange resin (all resins used in this research were supplied by Eichrom Industries, Inc., 8205 S. Cass Ave., Suite 111, Darien, IL 60561, 1-800-422-6693). Diphonix is made of a polystyrene/divinylbenzene matrix in a spherical bead form, and contains geminally substituted diphosphonic and sulfonic acid groups bonded to a polymer matrix. The diphosphonic acid ligands contribute to the resin’s unique selective capability by preferentially removing multivalent cations of various metals from solution. In addition, because the resin effectively retains actinides in the presence of relatively high concentrations of HF, one can handle silica in soil samples much more effectively.^{1,2}

Chiarizia et al.² investigated two ways to recover actinides after sorption onto Diphonix resin: 1) actinides are eluted with HEDPA followed by destruction of the HEDPA molecule; or 2) the whole resin bed is destroyed without prior stripping of the actinides. Unfortunately, the oxidation steps they applied for either HEDPA or Diphonix resin destruction were tedious, time consuming, and inefficient (average recovery was approximately 50% for five grams of soil samples). Recently, there has been significant progress in a technique for resin destruction using a microwave digestion system.³ That approach has produced good results but requires about 4 hours and is only suited for a limited amount of resin (<2.5 g) because of microwave constraints. We sought to find an alternative way to recover actinides from Diphonix resin using wet

oxidation and ozonation techniques. We present these results here as well as a modified actinide separation protocol using an extraction chromatographic resin, TRU-Resin that tolerates the high phosphate released from the HEDPA.

EXPERIMENTAL SECTION

General Strategy. Our overall approach to matrix elimination and actinide separation is shown in Figure 1. Samples may be either totally dissolved using fusion or other techniques or leached in strong mineral acids to recover anthropogenically-derived radionuclides. We acknowledge that strong acid leaching may not mobilize some transuranic species such as highly-fired PuO_2 . Isotopic tracers are added early in the procedure to ensure isotopic equilibrium with the analyte nuclides. After converting to a load solution of dilute HCl - HF and reducing Fe^{3+} to Fe^{2+} with ascorbic acid, the sample is loaded onto a Diphonix resin column. This is where the major matrix reduction occurs as most common ions will pass through the column while retention of actinides (and lanthanides) is very high. Following elution with HEDPA, the extractant is oxidized and then normal separation procedures can be applied to samples which, from this point on, will have a common matrix.

Leaching of large samples. A significant fraction of natural U and Th in soils is not recoverable with a mineral acid leaching technique because much of the U and Th is contained in refractory silicate minerals. Recoveries of anthropogenically-derived transuranics by leaching with strong acids, however, range from essentially 100% for low-temperature deposition (such as fallout) to lower amounts when refractory oxides are present.⁴⁻⁶ We feel that as the acid leachable fraction must represent either the potentially available or total concentration, such measurements do provide valuable information. In this study, we have focused on analyses of actinides from the acid leachable fractions of 10-g soil and sediment samples in order to evaluate the efficiency of the proposed analytical scheme with real-world samples. Soil and sediment samples of approximately 10 g mass were leached with 70 mL 6M HCl and 70 mL 8M HNO_3 at

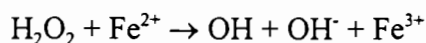
90°C for 4 hours with a coverglass in place and with appropriate radiotracers (^{243}Am , ^{242}Pu , ^{232}U , and ^{229}Th). The leachable fraction was separated from residual solids by centrifugation.

Preconcentration and matrix removal. The adsorption efficiency of ^{241}Am (and presumably other actinides) onto Diphonix increases with decreasing acidity in the presence of common salt ions. We found that Am recoveries increased from about 60% to nearly 100% when the HCl molarity was decreased from 2M to 0.01M in a load solution from a 10-g Fe-rich soil. Thus, to obtain minimum acidity of the sample solution before loading onto the column, we used two approaches after the leaching was complete: 1) actinides are first co-precipitated with $\text{Fe}(\text{OH})_3$ by adding ammonia solution, and the collected $\text{Fe}(\text{OH})_3$ precipitates are then dissolved in a minimum amount of 6M HCl to make up a final solution close to 0.1M HCl; or 2) ammonia solution is added to the acid leaching solution until a visible precipitation forms and then these precipitates are immediately re-dissolved with a minimum amount of 6M HCl. In both cases, to minimize adsorption of Al onto Diphonix resins, HF is added to maintain the load solution at 0.3M HF. One should use a caution in handling HF which is extremely hazardous (MSDS Number: H3994). In addition, ascorbic acid is added to completely reduce Fe^{3+} since divalent elements have much lower adsorption efficiency onto Diphonix resins.² Since the amount of ascorbic acid cannot be fixed due to variable natural Fe concentrations in soils, complete reduction to Fe^{2+} is confirmed by adding a few grains of ammonium thiocyanate directly into the sample solution (this will form a red color if any Fe^{3+} is present).

The samples are then loaded onto a Diphonix resin column (100-200 mesh; 1.2 cm i.d.; 10 mL wet vol.) after the resin has been preconditioned with 10 mL 0.5M HCl. The flow rate of the solutions is maintained at no more than $\sim 0.6 \text{ mL cm}^{-2} \text{ min}^{-1}$ for a 100-mL solution. We then rinse with 10 mL of a solution of 0.5M HCl - 0.5M HF with 300 mg ascorbic acid and 100 mg boric acid (ascorbic acid will reduce any Fe^{3+} , while boric acid will dissolve any fluoride precipitates which may be present). Then, 20 mL of 2M HCl - 0.5M HF are added to rinse the column, ensuring no significant retention of Ca^{2+} and Fe^{2+} . Actinides are then eluted from the column with 40 mL of 0.5M HEDPA.

The minimum volume of the required HEDPA solution was determined in a preliminary experiment by adding a high activity ^{241}Am spike to a load solution (with a soil matrix) followed by liquid scintillation counting of sequential 5-mL fractions (Figure 2). Since Am has the highest adsorption efficiency on Diphonix in 0.5M HEDPA,² elution of other actinides should also be complete. We also confirmed that only about 20 mL of 0.5M HEDPA is sufficient for Th elution based on a ^{234}Th tracer study.

Oxidation of HEDPA. To oxidize the 40 mL HEDPA elution volume, the “Fenton’s Reagent” approach may be applied by addition of 1 mL conc. HNO_3 and 40 mL of 30% H_2O_2 , heating to 90°C , and addition of 0.17 g ferrous ammonium sulfate $[\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}]$.⁷ The catalyzed decomposition of H_2O_2 by iron (II) produces highly reactive intermediate OH radicals:



The generation of the hydroxyl radical creates a strong nonspecific oxidizing reagent which we found was very effective for the oxidation of HEDPA. The heating is continued at 90°C with a coverglass in place for 40 minutes (allowing slow evaporation). The heating is interrupted about every 10 minutes and 10 mL of 30% H_2O_2 are added. After 40 min, only about 5 mL of solution remains (if more remains, the coverglass is removed for more effective evaporation). A final 5 mL of 30% H_2O_2 is added to ensure complete oxidation of HEDPA (a spontaneous and thorough bubbling of the solution at this stage indicates that the oxidation is complete). We suggest using a tall form beaker (400-mL or larger) to prevent any sample loss during the oxidation.

Alternatively, HEDPA can be oxidized by ozonation which also generates hydroxyl radicals.⁸ The HEDPA solution is adjusted to pH ~9 (using 10M NaOH) and diluted to 150 mL with water in a 250-mL glass cylinder. We found that the ozonation is most effective by diluting 20 mL 0.5M HEDPA solution (we previously worked with this amount) to 75 mL before ozonation as shown in Table 1 (40 mL would be diluted to 150 mL). The dependence of oxidation efficiency on dilution may be due to the differences in physical effectiveness of ozone diffusion onto HEDPA molecules at a fixed ozone flow rate when the volume and/or

concentration of HEDPA is changed. Using a diffusion stone, ozone is bubbled through the sample at a rate of about 4.4 g ozone/hour using an ozone generator (Labozone Model L-50, Ozonology Inc., 1515 Paddock Drive, Northbrook, IL 60062, 1-847-998-8808). After about 5 minutes, 5 mL 30% H₂O₂ is added and a lid is placed on the cylinder. After an hour of ozonation, another 5 mL H₂O₂ is added. The oxidation is complete after about 2 hours of ozonation. The solution is then transferred to a 500-mL glass beaker. The glass cylinder is rinsed with 4M HNO₃ and the solution is added into the same beaker. About 50 mg Ca carrier is added to the solution and actinides are co-precipitated with CaH(PO₄) by adding ammonia solution to a pH of 8-9.

In the ozonation approach, we often encountered significant U loss after CaH(PO₄) precipitation, perhaps due to formation of soluble uranyl carbonate complexes which can form at high pH. This is one advantage of the Fenton's Reagent approach as it is performed in an acid medium. Although one could evaporate the ozonation solution to almost dryness, and convert to the load solution for loading onto the chromatographic resin, it should not be necessary in most cases since natural U from large samples would be easily detectable even with low chemical recoveries. However, use of Fenton's Reagent as described above does not produce any uranium loss since the entire solution is loaded onto the resin after the oxidation is complete. Furthermore, use of the simple Fenton's Reagent approach has several other advantages over ozonation or microwave techniques: 1) many samples can be treated in one batch; 2) there has been no observable loss of any of the actinides we have investigated (Am, Pu, U, and Th); 3) the required time for oxidation is shorter; and 4) the process is performed in glass beakers on a standard hotplate so the purchase of expensive equipment (e.g., ozone generators, microwave digestion systems) is not required.

Actinide separation via TRU-Resin. A flowchart of our chemical separation procedure is shown in Figure 3. After oxidation of HEDPA by use of Fenton's Reagent, the solution is taken to near dryness and 3 mL conc. HNO₃, 5 mL 2M Al(NO₃)₃, 2 mL 35% Fe(II) sulfamate,

and H₂O are added to make up a load solution of 15 mL with a composition of approximately 3M HNO₃-0.7M Al(NO₃)₃. We add about 1 g ascorbic acid to reduce the Fe³⁺ which results from the oxidation process. The solution is loaded onto a TRU-Resin column (0.6 cm i.d.; 5 mL wet vol.) pre-conditioned with 5 mL 2.5M HNO₃. The column is rinsed with 20 mL of 2.5M HNO₃, followed by 10 mL of 2.5M HNO₃-0.1M NaNO₂ to oxidize Pu(III) to Pu(IV) which is required for Pu/Am separation. Then, 10 mL of 2.5M HNO₃ is added to rinse out the NaNO₂. The Am is eluted with 25 mL of 4M HCl following a rinse with 5 mL 9M HCl to convert the resin to the chloride form (both HCl fractions are collected). The Am in this fraction is separated from natural lanthanides by using thiocyanate as a complexing agent and performing the separation on TEVA-Resin (details explained in the next section). Then, Pu is eluted with 25 mL 4M HCl-0.05M TiCl₃. This fraction is radiochemically pure and is ready for source preparation. After the Pu is eluted, Ti is washed out by adding 5 mL 4M HCl followed by 10 mL of 2.5M HNO₃. Then, 10 mL of 2.5M HNO₃-0.1M NaNO₂ is pipetted directly into the column to oxidize any uranium which may have been reduced to U(IV) by the TiCl₃. After the NaNO₂ is washed out with 10 mL 2.5M HNO₃, 5 mL 9M HCl is added to convert the column to chloride form (this fraction is discarded). The Th is then eluted with 25 mL of 1M HCl and is pure enough for source preparation. If ²³⁷Np is present, it would be in this fraction and may easily be separated from Th using a TEVA-Resin column by oxidation state control. Finally, the U is eluted with 20 mL 0.1M ammonium bioxalate. Further purification is necessary for the U fraction to remove any residual Th and Pa which may still be present.

Further purification of Am and U. The Am fraction eluted from the TRU-Resin is evaporated, and any residue from the resin is thoroughly oxidized using treatment with small amounts of HNO₃-H₂O₂. If a perchloric-acid fume hood is available, a drop of perchloric acid helps to maintain things in solution during oxidation. Since perchloric acid is corrosive and its contact with readily oxidizable material may cause fire or explosion (MSDS Number: P1564), one should take special care. The residue from this treatment is dissolved in a minimal amount

(~0.05 mL) conc. formic acid and this is carefully evaporated until just the smallest drop remains. Another very small addition of formic acid is added and again evaporated to a small drop. Then, 10 mL 4M ammonium thiocyanate is added to the Am-formic acid solution. This is loaded onto a TEVA-Resin column preconditioned with 5 mL 4M NH_4SCN -0.1M formic acid. The column is then rinsed with 10 mL 1.5M NH_4SCN -0.1M formic acid which washes out the natural Ln elements. Then, Am is eluted with 20 mL 2M HCl and this solution is used for source preparation.

The U solution from the TRU-Resin is adjusted to about 4.5M HNO_3 by addition of 8 mL conc. HNO_3 and then loaded directly onto an UTEVA-Resin column previously preconditioned with 2.5M HNO_3 . The column is rinsed with 10 mL 2.5M HNO_3 , followed by 20 mL 5M HCl-0.05M oxalic acid to rinse out any residual Th. Uranium is then eluted with 20 mL 0.01M HCl and this solution is used for source preparation.

Source preparation and alpha counting. Alpha counting sources are prepared by CeF_3 co-precipitation and filtration.⁹ We add 100 μg of cerium carrier to each of the final fractions for U, Am, Th and Pu. In general, we use only a 20% aliquot of the Th fraction to avoid producing thick source because of the high ^{232}Th mass expected for 10-g soil samples. Since ^{238}U has a half-life about 3 times shorter than ^{232}Th , and as the abundance of Th is typically higher than U in soils, this has not been necessary for the U sources. It should be remembered that the large sample size is intended for achieving low detection limits for anthropogenically-derived actinides such as Am and Pu — U and Th can easily be determined in natural soils and sediments with sample masses of 1.0 g or less.

After U and Pu are reduced to U(IV) and Pu(III) respectively using 0.5 mL of 20% TiCl_3 , all actinide fractions are precipitated with CeF_3 by adding approximately 1 mL concentrated HF. The source is prepared by filtering onto a 0.1 μm , 25-mm diameter polycarbonate (Gelman Metricel) filter. These filters are dried briefly in a low-temperature (~60°C) oven and then attached to a stainless steel disc using glue stick or double-stick tape. The sources are counted

using low-background ion-implanted silicon detectors, whose backgrounds and detector efficiencies are monitored on a regular basis.

RESULTS AND DISCUSSION

Measurements have been made for five standard intercomparison soil and sediment samples and two Fe-enriched soil samples. We used the two Fe-rich samples to check our technique's applicability to samples which have challenging matrices. The chemical recoveries for Am and Pu for 10-g HNO₃-HCl leached aliquots of these samples were consistently lower than ~30% using a standard ion exchange technique (R. Kinney, pers. comm.).

In addition, we ran two 10-g samples of NIST Rocky Flats II soil after leaching with HNO₃/HCl and adding high activities of a ²⁴¹Am spike to one sample and a ²³⁴Th spike to the other. This allowed us to check the recoveries from a small aliquot at each step through the entire procedure using liquid scintillation counting (Figure 4a). This experiment showed that there is no perceptible loss of Am and Th throughout any of the pre-concentration steps (HEDPA was oxidized by ozonation for both of these samples). The samples also showed high overall recoveries for Am and Th (~90%) by the end of the procedure.

The chemical yields for Am, Pu, Th, and U from the five natural matrix standards and the two Fe-rich samples (n=28) were all higher than 70% with an average of about 85% (Figure 4b). The Fenton's Reagent approach was used to destroy HEDPA in all these cases. These yields are a significant improvement in the chemical recovery of actinides from large soil samples relative to previous techniques. For example, in a recent approach using Eichrom's Actinide Resin, an extraction chromatographic version of Diphonix, Burnett et al. (1996) suffered from a major loss of Th (average yield ~20%) which apparently resulted from a combination of non-elution from the column and interference of oxidized phosphates on the subsequent UTEVA-Resin column used in that investigation. We have found that the adsorption of actinides in the presence of high phosphate onto TRU-Resin is much more effective than other chromatographic resins. This

suggests that TRU-Resin may also have useful applications for phosphate-enriched biological and geochemical samples. This allows one to avoid the tedious approach of using $\text{Fe}(\text{OH})_3$ co-precipitation at a controlled pH of 3.15-3.4 recommended by Toribara and Koval¹⁰ to remove excess phosphate before separations using standard anion exchange columns. The Fe-precipitation approach was used, for example, for U/Th analyses of phosphate nodules from the sea floor.¹¹ Although TRU-Resin has been used successfully in the past for analyses of actinides from other environmental samples such as aqueous¹² or bone-ash matrices¹³, the elution protocols were different than those reported here.

The fact that we achieved high chemical recoveries for all actinides investigated from a variety of terrestrial and marine samples including two samples which failed by standard ion exchange techniques indicates that the Diphonix approach works very well. Furthermore, good separations of actinides using extraction chromatographic resins were confirmed by close examination of the alpha spectra for each source. Thus the pre-concentration of actinides and matrix elimination from large soil and sediment samples using these resins ensures consistent chemical recoveries and good chemical separations.

Although the results for U and Th measurements by acid leaching are not expected to be comparable to the recommended standard values based on total dissolution, we analyzed U and Th as well as Am and Pu in these samples to evaluate the recoveries and assess the fraction of the actinides which are acid leachable from these samples (Table 2). In fact, virtually all the Am and Pu in the standard EML soil and IAEA sediment samples were leachable with 6M HCl and 8M HNO_3 , suggesting negligible refractory artificial actinides in these samples. In contrast, a very constant fraction of around 50% of the U was leachable from the EML soils. The constant leaching of U seems to be reasonable since all 3 EML soils were based on mixtures of the same uncontaminated soil with small amounts of contaminated material (A. Berne, pers. comm.). The fact that only about one half of the uranium is leachable is not surprising considering that natural U often occurs in very insoluble silicate minerals, usually resistant to treatment by even vigorous dissolution techniques.⁵ In the case of the marine sediment samples, the leachable U is

significantly higher — perhaps due to contribution from relatively labile authigenic and biogenic uranium derived from seawater. Unfortunately, reference values are not available for Th in the EML standards. We suspect that the fraction released by acid leaching is also significantly below the total concentration for these soil samples. The two IAEA sediments, which do have reference values, showed release of 48 and 72% of the thorium into the acid leaching solutions. For environmental monitoring of artificial actinides from low-temperature deposition, the much faster leaching technique seems realistic and has been shown to produce excellent results for anthropogenic actinides reported in Table 2.

CONCLUSIONS

Actinide elements in large soil and sediment samples can be analyzed with consistently high chemical yields by using Diphonix resin for eliminating the major portion of the matrix and concentrating the ions of interest. In addition, the separation scheme applied here provides excellent separations and is amenable to the high-phosphate matrix resulting from the HEDPA which is used to elute the actinides from the Diphonix resin. We plan further investigations to apply this new technique to still larger samples (i.e., ~50 g) from acid leaching and ~5 g samples by total dissolution. Presumably, the amount of Diphonix and HEDPA required would have to be adjusted accordingly. The subsequent separations, however, should be essentially identical to those outlined here as the Diphonix resin approach ensures a constant matrix.

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Figure Captions:

Figure 1. A schematic illustration of the entire actinide analysis procedure.

Figure 2. Incremental and cumulative recoveries of Am by 0.5M HEDPA solution from a 10 mL Diphonix column. About 99% of the Am is recovered after a 40-mL HEDPA elution.

Figure 3. Flowchart for the separation scheme for U, Th, Pu, and Am using a TRU·Resin column followed by a TEVA/SCN column for Am and a UTEVA column for U. The final solutions for Pu and Th sources are from the TRU column. Each rinse on elution step is numbered with corresponding explanations listed on both sides.

Figure 4. (A) Chemical recovery of Am and Th at each step from two NIST 10-g Rocky Flats II samples (the ^{241}Am and ^{234}Th tracer experiments were performed on two different aliquots of this sample). The final recoveries for Pu and U were approximately 80% for both samples based on alpha counting of natural level spikes at the conclusion of each experiment. (B) Chemical recoveries for Am, Pu, U, and Th for seven 10-g samples, two Fe-rich soils and five natural matrix standards. Fenton's Reagent was used to oxidize HEDPA for all these samples. Error bars represent the standard deviation of the chemical yields for these seven samples.

Table 1. Tests of factors controlling efficiency of Am recovery from ozonation of HEDPA

	Factors	Oxidation Efficiency (%)
Test A	Diluted volume	
	17	15
	30	18
	50	30
	75	58
	100	18
Test B	Time	
	60	10
	90	67
	105	87
	120	99
	135	100
	150	100

Test A: Variation of oxidation efficiency as a function of diluted volume from 17 mL of 0.5 HEDPA. The ozone bubbling rate was 4.4 g ozone/hour for 1.5 hours at pH~9 in all cases.

Test B: Variation of cumulative oxidation efficiency with ozonation time. A steady flow rate of ozone (4.4 g ozone/hour) was maintained through the 75 mL HEDPA solution diluted from 20 mL 0.5M HEDPA at pH~9.

Table 2. Measured activities of Am, Pu, U, and Th in acid leaching fractions from 10-g soil and sediment samples relative to the recommended standard values

Sample ID	Bq/kg (ratio to standard values, AR)*			
	²⁴¹ Am	²³⁹⁺²⁴⁰ Pu	²³⁸ U	²³⁰ Th
Description				
EML 9409	1.7±0.1 (0.98±0.06)	8.1±0.2 (1.04±0.05)	16.0±0.2 (0.48±0.04)	21.9±0.4
Soil				
EML 9509	1.7±0.1 (0.98±0.08)	5.3±0.1 (1.02±0.03)	14.9±0.2 (0.49±0.03)	20.6±0.4
Soil				
EML 9803	2.7±0.2 (1.00±0.11)	5.2±0.1 (0.98±0.04)	16.1±0.2 (0.50±0.04)	24.2±0.4
Soil				
IAEA300	1.3±0.1 (0.92±0.09)	3.4±0.1 (0.96±0.04)	51.5±0.7 (0.80±0.04)	66.0±4.3 (0.75±0.06)
Marine sediment from Baltic Sea				
IAEA135	304±16 (0.96±0.06)	207±7 (0.97±0.04)	11.1±0.1 (0.85±0.34)	48.2±0.9 (0.70±0.05)
Marine sediment from Irish Sea				
Average AR	(0.97±0.03)	(1.00±0.04)	(0.63±0.18)	(0.72±0.04)

* The reference activities for EML 9409, 9509, and 9803 inter-comparison samples were reported by the Environmental Measurements Laboratory, New York, and values for IAEA300 and IAEA135 were from the International Atomic Energy Agency, Vienna, Austria. The error propagation for the measured activities is based on 1σ counting statistics. In the case of U and Th, our results were expected to be lower than standard values because total dissolution is required for full recoveries of U and Th from most soils and sediments.

