Separation and Analysis of Actinides by Extraction Chromatography coupled with Alpha Liquid Scintillation Spectrometry

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Introduction

This work describes the development and testing of a new method for the separation and analysis of most actinides of interest in environmental samples. It combines simplified extraction chromatography using highly selective absorption resins to partition the individual actinides with the measurement of their alpha activities by liquid scintillation spectrometry. The liquid scintillation counting technique pioneered by McDowell has proven to be very useful in the determination of alpha emitting radionuclide in a wide variety of matrices [1]. Alpha emitters are chemically extracted into an organic phase which also contains the scintillation cocktail. Oxygen is purged from the solution to improve the energy resolution of the measurement and the counting sample is sealed in a small, glass tube for assay. The Photon-Electron Rejecting Alpha Liquid Scintillation (PERALS^{TM}) Spectrometer provides high counting efficiency, relatively low background, pulse shape discrimination for photon/electron/β particle rejection and moderate energy resolution in a compact package. Chemical extraction/liquid scintillation counting significantly reduces the extensive chemical purification and electroplating required for conventional alpha spectrometry with semiconductor detectors. PERALS^{TM} analyses have been used routinely for quickly surveying suspect samples and determining the source of unknown alpha activities.

However the limited chemical selectivity of a single extraction and the inherent problems such as phase separation and mechanical carryover in the liquid/liquid extraction proved insufficient for the analysis of actinides in complicated mixtures and/or difficult matrices such as certain soils. Particular problems were encountered with samples from the Savannah River Site (SRS) and other locations where a wide variety of actinide alpha activities are present along with small amounts of natural U, Th and their progeny. Current regulatory mandates frequently require setting limits on the minimum detectable amounts of man-made alpha activities from nuclear reprocessing in the presence of these natural activities. Sequential extractions using different extractants in the cocktail and adjusting the aqueous phase acidity could resolve problems such as separating ^{238}Pu and ^{241}Am but was unwieldy in practice and counteracted much of the ease of use inherent in the PERALS^{TM} method.

Conventional ion-exchange and ion chromatography have been used for initial separations in occasional cases but an effort was made to explore other, simplified separation techniques for use with the PERALS™. Initial studies with the extraction chromatography system developed by Horowitz and commercialized by EiChroM Industries, Inc. were very encouraging. The specialized chromatographic materials have very specific extractants for the actinides bound to inert polystyrene resins. The first tests used a single columns of TRU•Spec™ resin, specifically designed for the separation of the transuranic elements, which has CMPO/TBP (octyl-phenyl-N,N-diisobutyl-carbamoylmethyl phosphine oxide/tributyl phosphate) as the complexing agent.

Individual actinide fractions were eluted, collected and analyzed by PERALS™. The method was fast with excellent precision for separating U, Pu and Am in water and small (1-2 gram) soil samples which makeup the majority of requested analyses. Samples were typically run in duplicate along with a reagent blank of deionized water and a spiked sample to monitor chemical yields.

There were drawbacks however, in samples containing significant amounts of natural U and Th. Although the U/Pu separation was sufficient to analyze for small amounts of Pu in the presence of high levels of U, some Th activity consistently appeared in the Pu fraction, giving anomalously high values. For larger soil samples needed for higher sensitivity the removal of the actinides was still quantitative but loading of interfering elements resulted in poor resolution in the chromatography of the fractions. Following separation schemes developed by EIChroM a second column of U/TEVA•Spec™ resin with dipentyl pentyl phosphonate as the specific extractant for tetravalent actinides was used prior to the TRU•Spec™ column to improve the Th/Pu partitioning. A third column of TEVA•Spec™ resin which has Aliquat 336 (a mixture of trioctyl and tridecyl quaternary amine salts) as its' complexing agent can be used to separate Np and Th. Due to the infrequent requests for Np/Th values the third column is not routinely included in the separation procedure.

Procedure

Water samples of a liter or more are routinely acidified and evaporated to near dryness. The residue and any particulates are dissolved by heating with concentrated acids and/or hydrogen peroxide in Teflon beakers. Soil samples are acid leached [2] rather than totally dissolved to preferentially remove surface contamination and reduce the contribution of natural activities which are more tightly bound in the inorganic matrix. This increases the sensitivity for man-made activities from reprocessing operations which typically adhere to surface particles. The acid leachate is similarly evaporated to near dryness.

The residues are dissolved in about 10 ml of 3 N nitric acid with 0.5 N aluminum nitrate. 0.6 N ferrous sulfamate and 0.1 grams of ascorbic acid are added to reduce Pu to the +3 and Np (if present) to the +4 oxidation states. For leachates from large soil samples gram amounts of ascorbic acid are added to reduce the bulk amounts of salts in higher oxidation

states. The chromatography is performed in 1.5" long BioRad Poly Prep™ columns that are packed with ~2 ml of the EIChroM resins. The solution is loaded first on a U/TEVA•Spec™ column. Flow rates as high as 2-4 ml/min can be used without degrading the separations if reduced pressure is applied to the bottom of the column with a Speedmate™ vacuum system. The reduced pressure is particularly useful for soil leachates. For water samples the normal gravity feed flowrate is typically 1 ml per 4-5 minutes and no difficulties were encountered with allowing samples to load overnight unattended with the elutions completed the following day. Leaching large soil samples however produced highly concentrated salt solutions which required the reduced pressure during loading to attain reasonable flowrates.

U, Th and Np remain on the first column. Pu and Am/Cm pass through in the effluent which is fed directly to a TRU•Spec™ column where they are retained. Np/Th are eluted from the U/TEVA•Spec™ column with 5 N HCl / 0.5 N oxalic acid after which the U is removed with 0.01 N HCl. From the TRU•Spec™ column Am/Cm is eluted first with 4 N HCl; the Pu elutes second with 0.1 N ammonium bioxalate. Fractions are typically 10-20 ml in volume and are heated with nitric acid/hydrogen peroxide and evaporated to near dryness repeatedly to oxidize them and destroy oxalate salts and any organic material contributed from the columns.

The residues from the various fractions are dissolved in dilute nitric acid solutions at the appropriate acidities for PERALS™ extraction with bis-(2-diethylhexyl) phosphoric acid (HDEHP) as the complexing agent. U, Th, Np and Pu are extracted from 0.8 N nitric acid, while Am/Cm are extracted from a formate buffer solution at pH 2.5-3.0. After equilibration the organic phases are separated, sparged with argon to remove the oxygen in solution and sealed for counting. For most of our analyses and the data presented here, samples were counted overnight (approximately 1000 min.). Backgrounds on reagent blanks processed through the column separations and PERALS™ extractions were typically measured from 2 to 10 days. Chemical processing of three samples in duplicate along with two blanks and two spikes requires 1-2 days for pretreatment (evaporation & leaching) and 1 day for column separations and PERALS™ extraction.

Results and Discussion

In many samples analyses for U, Pu & Am in water are requested and there is little or no natural background radioactivity in solution. Previous work demonstrated that we could consistently get ± 5% precision using a single column separation prior to PERALS™ extraction and counting.[3] In soil samples with very diverse compositions there were often measurable amounts of natural U and Th activity which interfered with the Pu measurement. In particular small, variable amounts of Th activity were found in the Pu chemical fraction. This interference was quite apparent when soil sample size was increased above 10-20 grams.

Checks on the accuracy of the EIChroM/PERALS™ and other methods for actinide analyses are routinely monitored by processing "blind" quality assurance samples from the US Department of Energy's Environmental Monitoring Laboratory (EML) Quality Assurance Program (QAP). Table 1 shows the results from a single TRU•Spec™ column separation of actinides from a 27 grams soil sample of EML QAP XXXVIII. The actinides were loaded on a standard size column from ~100 ml of acid leachate with a high salt content. In spite of these conditions the actinide removal from solution was quantitative.

Alpha activities from ^{228}Th, ^{232}Th and their progeny caused difficulties in determining the net activity in the 5.2 meV peak of ^{239}Pu. Several different methods to quantify the contribution to the alpha activity in the 5.2 meV region from Th isotopes and their descendants were tried. This included: 1) estimating the Th activity based upon the U content, 2) using the 4.2 meV peak of ^{232}Th and 3) using peaks in the 6.0 meV region due to ingrowth of daughter activities. These methods all gave similar but imprecise estimates of the contribution to the 5.2 meV peak. As a result the ^{239}Pu content calculated from the residual activity in the region was off by about 20%. Unfortunately the energy gain available with the PERALS™, electronics package does not quite allow the analysis of the 8.78 meV peak from the ^{212}Po descendent of Th. The energy scale does not extend high enough. At equilibrium the background at that high alpha energy is negligible and would have provided a much more precise measurement of the Th contribution.

Table 1

Nuclide	EIChroM/PERALS™ (pCi/g)	EML Value (pCi/g)
^{234}U	1.03±0.05	1.02
^{238}U	0.92±0.02	1.02
^{239}Pu	0.38±0.06	0.31
^{241}Am	0.15±0.01	0.18
^{232}Th	0.62±0.02	-

The addition of a second column resulted in a minimal increase in processing time but provided better separations and chemically pure Pu fractions. Due to the effort entailed in the pretreatment of the water and soil samples, the second column is routinely included in the separations. The two column EIChroM/PERALS™ method has been used to provide reportable values for actinides in EML quality assurance samples. Duplicate 50 ml aliquots of EML water sample QAP XLII were processed simultaneously with two spiked deionized water samples and two reagent blanks. Actinide values from the analyses (column 2) are compared with listed EML values (column 3) in Table 2. Background count rates in the blanks were used to calculate minimum detectable activities (MDAs).

Table 2

Nuclide	EIChroM/PERALS™ (pCi/g)	EML Value (pCi/g)	MDA (pCi/g)
Total U ($^{234}U + ^{235}U + ^{238}U$)	0.0166 ± 0.0014	0.0154 ± 0.0008	0.00010
^{239}Pu	0.0154 ± 0.0011	0.0160 ± 0.0013	0.00007
^{241}Am	0.0387 ± 0.0024	0.0360 ± 0.0020	0.00006

The PERALS™ detection part of the method has also been directly compared with alpha spectrometry of electroplated samples and with the kinetic phosphorescence analysis (KPA) of elemental U (Table 3). Contaminated ground water samples were prepared identically and separated on EIChroM columns. The number of replicate values included in the averages shown are listed in parentheses. The ^{238}U activity for KPA was calculated from the total U concentration assuming the natural U isotopic distribution (99.3 % ^{238}U) based on the $^{234}U/^{238}U$ ratio in the PERALS™ spectrum. Am and Cm are not fractionated by the EIChroM columns although they can be chemically separated by other, higher efficiency techniques such as ion chromatography.[4]

Table 3

Detection Method	^{244}Cm (pCi/g)	^{238}U (pCi/g)
PERALS™	0.874 ± 0.027 (3)	0.221 ± 0.018 (3)
α Spectrometry	0.842 ± 0.036 (2)	
KPA		0.189 ± 0.018 (4)

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References

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