

Radiochemical separation advancements using extraction chromatography: A review of recent Eichrom Users' Group Workshop presentations with a focus on matrix interferences

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Radiochemistry laboratories are challenged to find efficient methods to handle a wide variety of sample types and sizes. To achieve accurate results, required decontamination factors and low detection limits, methods adequate for smaller, simpler matrices may need to be enhanced. This paper will review recent presentations made during Eichrom Users' Workshops. These include methods and data involving the analysis of actinides in large soil samples, ^{90}Sr in bone, uranium in air filters containing significant ^{210}Po and ^{99}Tc in samples high in ^{234}Th .

Introduction

Extraction chromatography (EXC) has developed into a leading technique for separation and preconcentration of radionuclides for analytical purposes. Originally developed as a preparative approach for specific metal separation, EXC involves the coating of an inert support with an organic extractant. This combination delivers the specificity of solvent extraction with the ease of use of resin based methods.¹

The need to establish rapid procedures for routine monitoring of radiation workers at Argonne National Laboratory provided the impetus to expand the role EXC into radioanalytical applications. TRU Resin (for actinides), UTEVA® Resin [Actinides (IV and VI)], TEVA® Resin [actinides (IV), Tc(VII) and Am/RE separation], Sr Resin (Sr, Pb), Ln Resin (lanthanides, ^{228}Ra) along with other EXC resins now are directly involved in hundreds of thousands of radiochemical analyses annually. Biological, environmental, geochemical, waste and nuclear process samples are routinely analyzed using EXC.

Eichrom Technologies provides a focal point to continue to expand and enhance the use of EXC. A key component of this effort involves hosting users' group workshops at various locations throughout the world. This paper provides some highlights of a number of users' group workshop presentations made during the last three years concentrating on research involving difficult sample matrices. Each of these presentations is available at www.eichrom.com² under the radiochemistry section, users' group workshops.

Actinides in soil

A one-column separation and analysis of isotopic Am and Pu in soil samples method was presented by

NIDAL JADALLA of Eberline Services during the workshop held in Knoxville, TN at the 2002 RRMC Conference.³ This separation involves the use of TRU Resin⁴ to hold back Am and Pu⁵ while other elements are rinsed through. Initially, the 1 g soil sample was heated to 500 °C and then taken to a microwave for further digestion. 1M HNO₃ was used in this digestion. Ammonium hydroxide was then added to form an iron hydroxide precipitate. The precipitate was then dissolved in a 3M HNO₃–1M Al(NO₃)₃ – ascorbic acid load solution for the TRU Resin. Actinides and lanthanides load on the TRU Resin under this condition. While Pu is loaded primarily as Pu(III), with the addition of ascorbic acid to reduce iron to (II), the Pu is oxidized to (IV) once on the column with the addition of 2M HNO₃–0.1M NaNO₂. Ferric iron, Fe(III), can lower the capacity of TRU Resin for other trivalent elements such as Am(III).⁴ Am can then be eluted with 4M HCl and then Pu is eluted with 4M HCl–0.833 ml 20% TiCl₃. The sample is then counted by alpha-spectrometry after source preparation by NdF₃ precipitation.

Two problems were identified through the results of a ten sample test plan. The Pu recovery was acceptable, averaging 76%, however, the alpha-spectra in the Pu range of energies indicated some Th interference. A separate test was carried out to determine the extent of the Th interference. Samples containing an average of 3.3 dpm/g ^{228}Th were run through the procedure. An average of 0.53 dpm/g was found in the Pu fraction, a decontamination factor of 6.2. To cut down on the amount of Th in the sample, a leaching procedure was substituted for digestion to cut down on the amount of Th loaded to the resin column. Also, 25 ml of 4M HCl–0.1M HF was added as a rinse step after the Am strip on TRU Resin.⁶ The average chemical recovery for Am was 34%. It is possible that iron from the sample, carried down with the hydroxide precipitate, loaded on the TRU Resin causing Am to breakthrough prematurely.

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A calcium oxalate precipitation was substituted for the iron hydroxide precipitate by adding oxalic acid and calcium carrier.

The new procedure resulted in a decontamination for ^{228}Th of over 900 and the americium chemical recoveries averaged 79%. The Pu chemical recoveries averaged 64%. The new procedure was run on MAPEP (Mixed Analyte Performance Evaluation Program) samples. As shown in Table 1, the ^{238}Pu , ^{239}Pu and ^{241}Am results were all within 4.5% of the reference values.

SHANE KNOCKEMUS of US EPA/NAREL also presented during the Knoxville workshop. His talk, 'Pyrosulfate fusion vs. TEVA/TRU: Forcing the Issue' dealt with samples requiring total dissolution and the analysis of thorium, uranium, plutonium and americium. The idea of forcing the issue stems from the desirability to use an established TEVA/TRU⁷ Resin sequential method for Th, U, Pu and Am on a sample which contains significant matrix, a sample that has the added challenge of sulfate from the pyrosulfate fusion. Samples of 0.5 to 1 g of soil were fused with potassium fluoride and then 3 ml 18M H_2SO_4 and 2 g Na_2SO_4 . The fused samples were then taken through a TEVA column where Th was selected and a TRU column where Am, U and Pu were selected and then sequentially stripped. This was accomplished by reducing Pu to (III) so that it would not hold on TEVA Resin out of the nitric acid-aluminum nitrate load solution. Americium and uranium also do not load on TEVA out of nitric acid. Thorium is stripped from TEVA with 9M and 6M HCl. Any Np(IV) in the sample would remain on the TEVA column at this point, although this work did not specifically look at Np. On TRU Resin, after Pu is oxidized to (IV) with nitrite, Am is stripped with 9M and 4M HCl. Pu is then stripped with 0.1M HCl-0.1M oxalic acid and finally U is stripped with 0.1M $(\text{NH}_4)_2\text{C}_2\text{O}_4$. A series of six sets of experiments were performed to optimize the recovery of all four analytes. In the first experiment the fused samples were simply dissolved in the nitric acid-aluminum nitrate load solution. While Am and U tracer yields were good at 80%, there was poor separation of Pu from Th. Experiments two through five involved attempts to correct this. In experiment two, an attempt to cook the cake down in concentrated nitric resulted in a gooey sulfate blob with poor Th in the Pu spectra, 40% Am yields, very low Th yields (4%), 50% Pu but still 80% U. Reference 7 indicates that sulfate will reduce the uptake of tetravalent actinides on TEVA and

experiments three through five focused on this. First a calcium phosphate precipitation of HCl dissolved fused cake was performed. This improved the Am back to 80% but only raised the Th yield to about 15% and Th was still in the Pu spectra. SHANE picked up some ideas from DAVE SILL at the RESL Laboratory in Idaho USA involving a barium sulfate precipitation out of an HCl dissolved cake, followed by K+EDTA and titanous hydroxide precipitation. This finally produced a clean Pu spectra with 50% yields, 80% Th yields but only 5% Am. Experiment five added a reduction of uranium to (IV) so that it would precipitate with BaSO_4 . U and Th yields were 80% along with 75% Pu. Am was only 15%.

A final experiment, six, was performed with Diphonix® Resin which has been shown to be an excellent concentrator of actinides, even in the presence of hydrofluoric acid.⁸ The fused cake was dissolved in 30 ml 1M HCl-0.5 M HF and added to 0.3 g of Diphonix Resin, 100-200 mesh. While it is possible to strip the Diphonix resin with 1-hydroxyethane-1,1-diphosphonic acid (HEDPA, 0.5M),⁹ it was decided to destroy the resin by charring with sulfuric and nitric acids and then oxidation of organics with perchloric acid. The results were a clean Pu spectra free of Th, 75% Am, 85% U, 80% Pu and 50% Th. Additional work will be done to look at either increasing the concentration of the HF load solution to the Diphonix Resin or increasing the aluminum nitrate concentration in the load solution to the TEVA/TRU Resin to improve the Th yields. MAPEP reference soil samples were evaluated using the fusion, Diphonix Resin, TEVA/TRU Resin procedure. Table 2 shows agreement within 5% of the known values for ^{241}Am , ^{239}Pu , ^{234}U and ^{238}U . MAPEP did not certified values for Th nuclides.

In some circumstances, detection limit requirements cause the need to increase the soil sample to 50 g or more. Research at Florida State University⁹ (FSU) as well as the Savannah River Site¹⁰ has demonstrated the performance of Diphonix Resin to eliminate sample matrix in these types of large soil samples and fecal samples too. Savannah River has demonstrated that Diphonix Resin can be destroyed using closed vessel microwave digestion. At the Knoxville Users' Group Meeting, SHERROD MAXWELL reported that the site has also begun to use HEDPA stripping coupled with hot plate destruction of the HEDPA using peroxide plus iron (Fenton's Reagent).¹¹ FSU has focused its recent research on the HEDPA stripping option.

Table 1. Comparison of average yield corrected ^{238}Pu , ^{239}Pu and ^{241}Am results with MAPEP (Mixed Analyte Performance Evaluation Program) known values

ID	^{239}Pu result	^{239}Pu reference value	Percent of reference	^{238}Pu result	^{238}Pu reference value	Percent of reference	^{241}Am result	^{241}Am reference value	Percent of reference
MAPEP-02-S9#59	72.3	72.9	99.2%	33.5	33.3	100.6%	43.3	43.5	99.5%
MAPEP-02-S9#59 Dup.	73.7	72.9	101%	34.8	33.3	104.5%	42.1	43.5	96.8%

All results reported in Bq/kg.

Table 2. Experiment 6, data compared to MAPEP Reference Standard

Nuclide	MAPEP value, mBq/g	Measured activity, mBq/g	Measured/known
²⁴¹ Am	61.1	58.1	0.95
²³⁹ Pu	74.4	72.6	0.98
²³⁴ U	90.4	85.6	0.95
²³⁸ U	93.0	96.7	1.04

Note: MEPEP did not have certified values for Th nuclides.

²¹⁰Po interference in ²³²U

ANIL THAKKAR of Eichrom Technologies presented research on ²¹⁰Po interference in the ²³²U alpha-spectra associated with a UTEVA Resin method for uranium at the Eichrom North American Users' Group Workshop held in May 2002 in Westminster, Colorado. The problem was investigated by spiking water samples with approximately 1100 pCi of ²¹⁰Pb/²¹⁰Po. The old Eichrom procedure started with the sample being made 3M nitric acid/1M aluminum nitrate/0.6M ferrous sulfamate/200 mg ascorbic acid. A 5 ml 3M nitric acid beaker rinse and 5 ml column rinse were followed by 5 ml of 9M HCl and 20 ml of 5M HCl-0.05M oxalic acid. These rinses remove any tetravalent actinides from the column. The uranium is stripped from the column with 15 ml of 0.01M HCl.

With no uranium added, this procedure resulted in 230 dpm of activity being measured in the ²³²U region by alpha-spectrometry. Interestingly, when no ferrous was added, only 3.5 dpm was measured in the ²³²U region. Ferrous is not actually required in a uranium method, but is sometimes added to reduce Pu to (III) so that it can pass through the UTEVA Resin and be collected by a subsequent TRU Resin column. In either case, however, it is important to eliminate the ²¹⁰Po which will cause a high bias in the ²³²U tracer chemical recovery and bias low the corrected uranium isotope results when measured by alpha-spectrometry.

Two approaches were investigated. One was to try to rinse the ²¹⁰Po off the UTEVA column with additional 3M nitric acid rinses. Up to 30 ml of addition rinses were tried. This helped but 28 dpm activity remained (ferrous added to load solution). Dr. BOND and Dr. HORWITZ suggested¹² that we try to leave the Po on the UTEVA Resin while stripping the uranium. Tests were performed by increasing the strip solution concentration from 0.01M HCl to 1M HCl. It is believed that the polonium is forming a PoCl_6^{-2} complex which is extracted by the phosphonate chemistry of UTEVA Resin. By only modifying the above procedure by increasing the strip concentration to 1M HCl, the activity in the ²³²U region decreased from 230 dpm to 1.84. By combining the 1M HCl strip with an additional 30 ml of 3M nitric acid rinse earlier in the procedure, the activity is reduced to background. An alternative

approach to the above is to separate U on TRU Resin⁴ by first rinsing with 6-7M nitric acid to remove Po while retaining U. This is especially useful in tandem separations where TEVA is used upfront to separate Th, Np and Pu and potentially when samples have even higher ²¹⁰Po activity.

²³⁴Th interference with ⁹⁹Tc

ANIL also presented in Colorado a matrix interference problem with ²³⁴Th tracking with ⁹⁹Tc in some very high activity samples. To study the problem, water samples were spiked with 2000 dpm ²³⁴U/²³⁸U and the old Eichrom ⁹⁹Tc in Water procedure was run. This procedure involved spiking 20 ml of 0.01M nitric acid and loading on to a 2 ml TEVA column. 25 ml of 0.1M nitric acid was used to rinse the column. The resin was then extruded into an LSC vial and 15 ml of cocktail was added. The sample was counted by LSC. Up to 72 cpm were measured in this sample.

To eliminate the thorium interference, an additional 25 ml rinse of either 0.5M HF/0.02M HNO₃ or 1M NaF/0.02M HNO₃ was used. This reduced the activity to within the error of the blank, 14.7±0.9 cpm. Rinses of 5 ml each of 0.1M nitric acid occur before and after the fluoride rinse. The fluoride complexes the Th but does not affect the ⁹⁹Tc retention on TEVA Resin.

Strontium in bone and muscle

ROBERT JUMP of Paragon Analytics presented data on the analysis of strontium in bone and muscle samples during the 2001 North American Users' Workshop in Alcoa Tennessee. Ashed samples were digested in 1000 ml of a nitric acid, hydrochloric acid and peroxide solution. 1 mg of stable strontium was added to each sample which was then processed by a standard Eichrom Sr in water method, SRW01. This method involves preconcentrating the sample on strong acid cation exchange resin and then loading the Sr Resin¹³ with 8M nitric acid. After rinsing with addition nitric acid, the resin is stripped with 0.05M nitric acid. An ICP spectrometer was used to monitor the concentration of Sr and other matrix elements before and after loading on the cation exchange resin and after the strontium resin.

Table 3. Mass constituents before and after cation resin and after Sr Resin

ID = 0012164-1 (muscle)	Sr	Ca	K	Fe	Mg	Na	Zn
Cation feed	0.985	11	730	9.5	55	149	11.5
Cation strip		10	450	6	49	46	10
Sr Resin strip	0.911	<1	<1	<0.1	1	1	<0.02
Recovery:	93%						
ID = 0012164-2 (bone)	Sr	Ca	K	Mg	Na	Zn	
Cation feed	1.604	998	3	15	28	0.24	
Cation strip		670	<1	4	2	0.09	
Sr Resin strip	1.380	<1	<1	<1	1	<0.02	
Recovery:	86%						

All units in mg.

Despite potassium concentrations 700 times that of Sr in the mussel sample and calcium concentrations greater than 600 times that of Sr in the bone sample, the final Sr fraction contained less than detectable amounts of each, respectively. The Sr chemical yield was 93% in the muscle sample and 86% in the bone sample. A thorough ICP analysis of the sample at each of the three stages of sample preparation is provided in Table 3. The ICP data was also helpful in identifying native strontium in the bone sample.

Conclusions

Matrix interferences, radiochemical, elemental and mass can be overcome efficiently by a combination of method techniques. This can include additional rinses to extraction chromatographic resins or by utilizing different precipitation techniques. HF was found effective for the removal of Th during the analysis of Tc while additional rinses helped remove Po during U analysis.

Also group actinides separation can be accomplished with Diphonix Resin. The actinides can then be more easily separated from one another by using a combination of TEVA, UTEVA or TRU Resins. In the case of different precipitation techniques and Diphonix Resin, the matrix is simplified before final separation is achieved on the extraction chromatographic resins. Other techniques can include varying the size of the resin column or using different combinations of resins in tandem. With this in mind, extraction chromatography can be used effectively in methods covering a wide range of sample matrices and sizes.

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