

STUDY OF THE ALTERNATIVE ELUTION AGENT FOR THE DIPHONIX RESIN

by

Lukas KANKA¹ and Jiri JANDA^{1*}

¹NBC Defence Institute, University of Defence, Vita Nejedleho, Vyskov, Czech Republic

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The work was focused on the experimental determination of the separation-extraction properties of solid extractant DIPHONIX (Eichrom Industries, USA) depending on the used eluent. Extraction properties were tested for plutonium, americium, curium, and uranium. The used mobile phases were hydrochloric acid and nitric acid at various concentrations. The aim was to find the most appropriate combination of mobile phase and eluent, which would lead to the highest possible yield. The most commonly used eluent published in literature is 1-hydroxyethane 1, 1-diphosphonic acid (HEDP, Etidronic Acid). Based on the research the specific compounds were selected which are generally known for their complexing properties, such as the salts of oxalic acid and citric acid at different concentrations. Activities of the samples obtained by elution were measured by liquid scintillation spectrometry.

Key words: diphonix, elution, synergic effect, etidronic acid

INTRODUCTION

The radiochemical separation has gone through a great development and improvement in last 20 years. The ion exchange and solvent extraction were the ultimate techniques used in past. In these days these slightly modified techniques are used in radiochemical separation method known as extraction chromatography. Although this technique has been known for many years [1-3], the real expansion has begun after these extractants were discovered by Argonne National Laboratory and were introduced by Eichrom Industry Inc. to the market. The obvious advantage over the other techniques makes them the method of choice for almost all laboratories all over the world for extraction and separation of different ions. The production portfolio covers primarily actinides, lanthanides, alkaline earth metals and other radioactive elements. Provision of other accessories such as pre-filters, funnels, pre-packed cartridges, columns, vacuum box, inner liner and other accessories has made them even more popular. Furthermore, in these days there is an enormous pressure to make as little waste as possible. This is the one of the main reasons why classical solvent extraction is being abandoned. Nevertheless, it still has its own irreplaceable role, for example in re-processing of spent fuels and other large amount in separation techniques. But for laboratory, environmental and emergency samples it is not as convenient as the extrac-

tion chromatography via Eichrom products. This method is faster, safer, produces smaller amount of waste and is far more flexible than classical solvent extraction and is also more specific than what can be achieved by ion exchange.

In last twenty years a lot of papers were published on the field of extraction chromatography via Eichrom's extraction chromatographic resin [4-8].

All publications rely on original papers published by E. P. Horwitz, *et al.* Those papers describe the extraction characteristics of selected alpha radionuclides (Am, Pu, U, and Cm) by means of extraction chromatography (EXC) of different resins, *e. g.* TRU, TEVA, UTEVA, DN and also DIPHONIX resins (all Eichrom Industries, USA).

The solid ion exchange resin Diphonix was investigated as a potential universal extractant due to its affinity for the majority of transuranium elements and preconcentration and separation of radionuclides or heavy metals from sample for further analysis [9, 10-16].

The selected group of radionuclides was chosen with respect to military significant, radiotoxicity, and possibility of potential misuse. The other aspect is, that all these nuclides are part of the fuel cycle, thus they can be released during some unexpected events. The last example was given in Fukushima, where all listed radionuclides can be found. ²⁴¹Am, ²³⁸Pu, ²³²U, and ²⁴⁴Cm were selected as model radionuclides. The main reason for (pre)concentration is low occurrence in envi-

* Corresponding author; e-mail: jiri.janda@unob.cz

ronmental samples, which is normally in the order of millicuries. Besides mass spectrometry techniques, there are currently no techniques, which allow determining this concentration without the radiochemistry treatment. Even this technique needs some degree of sample preparation depending on the sample matrix. The usual technique used for determination of actinoids is solid-state alpha spectrometry. This technique needs very thin layer, ideally monoatomic layer, of the sample. Furthermore, due to some other effect like self absorption in the sample, air attenuation, absorption in dead layer of detector, *etc.* the energetic resolution (FWHM) of PIPS detector is normally about 20-80 keV mainly depending on the sample quality resulting in the needs of separation energetically closed radionuclides, *e. g.* plutonium and americium.

The diphonix resin was established as a powerful tool for extraction, subsequent elution and separation of radionuclides proved to be problematic. Commonly used elution agent 1-hydroxyethylidene diphosphonic Acid (HEDPA, Etidronic acid) [9, 10] does not provide neither elution of 100 % of the retained radionuclides nor their separation. The absolute elution is crucial when one is dealing with a trace amount of element(s) with respect to the further losses in subsequent analysis. The other reason is the possibility of reuse of the sorbent for further extraction leading to minimalization of radioactive waste as well as analysis cost reduction. Moreover, HEDPA being an organic compound containing phosphonic groups is the cause of problems during subsequent analysis by means of liquid scintillation, during which its organic structure interferes with the scintillation process. Therefore, an effort is being made to find a more suitable elution agent that would not have the aforementioned disadvantages. The objective of this work is to find suitable elution agents for Diphonix resin and to determine their extraction ratios under conditions of varying concentrations of the mobile phase and of nitric and hydrochloric acids used to condition the columns. As can be seen in various sources the most frequently used complexing agents are organic compounds containing nitrous or phosphorous functional groups, *e. g.* tri-*n*-butylphosphate (TBP), tri-*n*-octyl-phosphine-oxide (TOPO), ethylenediamine-tetraacetic acid (EDTA), diglycolamides, and N, N, N', N'-tetraoctyl diglycolamide (TODGA) [17 - 20], Francis [21], Horwitz [22], and Perrier [23] describe the use of oxalates and citrates of various concentrations. Sanchez-Gonzalez [24] mentions carbonates for the extraction of uranium.

MATERIALS AND METHODS

The resin employed in this work was DIPHONIX resin® with grain size 50-100 μm and obtained from TRISKEM International SAS (Eichrom distributor for Europe). The resin was prepared in the same way as pre-packed cartridges distributed by Eichrom.

Nitric, hydrochloric, ammonium oxalate (all Penta, Inc., CZ), sodium citrate dihydrate (Merck,

Inc., CZ) and etidronic acid (Sigma-Aldrich) were prepared from reagent-grade chemicals. All water was obtained from a DEMIWA 5 rosa™ (Watek) water purification system. All other materials were ACS reagent grade and were used as received.

Radiochemical isotope tracers ^{232}U , ^{238}Pu , ^{241}Am , and ^{244}Cm were obtained from AEA Technology, UK, QSA Amersham International and CMI (the Czech Metrological Institute). ^{232}U tracer was prepared to be self-cleaning, removing its ^{228}Th daughter using ion exchange resin BIORAD AG 1-X8 (400-800 mesh).

The measurements were performed on Automatic LSC Triathler (Hidex, Finland) with 20 mL plastic vials. The data from the analyser were displayed by the program ComFiler. AquaLight (produced by Hidex) was used as a scintillation cocktail. The calibration standards of ^{90}Sr -ER2 etalon type with activity of 116.2 kBq (30/12/2005), manufactured by CMI-IIZ Prague, and ^{239}Pu -ER2 etalon type in solution with activity of 45.83 kBq (30.12.2005) were used for calibration. The etalon of ^{239}Pu contained impurities of ^{240}Pu and ^{241}Pu (it is the beta emitter with $E_{\text{max}} = 20.81$ keV and half-life = 13.2 years decaying to ^{241}Am , thus the activity of ^{241}Am rises with time). The level of impurities in the etalon at the time of measurement was 4.98 % ^{241}Pu and 0.56 % ^{241}Am . The measuring solution contained 0.1 mol/dm³ HNO₃.

PROCEDURES

Column preparation

DIPHONIX resin columns were prepared from a standard 2 ml cartridges filled with 1 g of Diphonix resin. Small particle size (50-100 micron) resin was employed, along with a vacuum extraction system (Eichrom Technologies, Inc.). Flow rates of approximately 1 drop per second were typically used. The resin cartridges were stacked on the lid of vacuum box. Fifty milliliter centrifuge tubes were used to collect the rinse or the fractions.

Extraction procedure of selected actinides

- 10 mL of the examined mobile phase (0.1-10 mol/dm³ HCl/ 0.1-10 mol/dm³ HNO₃) was loaded on the column. Subsequently the vacuum was created and maintained at value which guaranteed the flow rate of approx. 1 drop/second.
- 2 mL of solution consisting of selected mobile phase and examined radionuclide of activity of 100 Bq was loaded onto column (100 μL of ^{232}U , 50 μL of ^{241}Am , 20 μL of ^{238}Pu , and 50 μL of ^{244}Cm).
- The column was rinsed by 10 mL of the same mobile phase as used before.

- The elution was performed by 20 mL of Etidronic acid (0.4 mol/dm³), ammonium oxalate (saturated; 10 times diluted) or sodium citrate (1 mol/dm³, 0.01 mol/dm³, 1 10⁻⁴ mol/dm³). This phase was retained to determine the extraction ratio. The concentration of Etidronic acid was selected as optimal based on [9, 10]. The concentrations of the oxalate and citrate were determined according to [21-23] to cover their whole probable range.
- 4 mL of sample were transferred into 20 mL scintillation vial filled with 10 mL of scintillation cocktail AquaLight.
- Well shaken cocktail with sample was placed to LSA Triathler and after 15 minutes measured for 120 s.

RESULTS AND DISCUSSION

The possibility of misusing heavy unstable elements, especially transuranic elements, for military or terrorist purposes, their involvement in nuclear accidents or in fuel cycle makes them elements of interest. Among the most important elements belong uranium, plutonium, americium and curium. These radionuclides are both military significant [25] and also important for nuclear safety. Horwitz *et al.* published papers [26, 27] about extraction and stripping these elements on various resins among them TRU, TEVA, UTEVA, and DN. Our main effort was to revise the existing data concerning DIPHONIX resin, determine the dynamic properties and behavior of the resin in previously untested conditions and more importantly transfer values of the number of free column volumes k' to percentage of extraction, which is more convenient for faster orientation and better understanding.

DIPHONIX resin is a high performance, gel-type cation resin for the selective separation of metals, especially for actinides [28-30]. The main disadvantage of this resin is that because of its very high affinity to the ions generally, it is extremely difficult to find the appropriate elution agent. Many papers suggested Etidronic acid [30-33]. As far as we know, the elution results using Etidronic acid are not clearly published elsewhere. The first step was to investigate the extraction-elution properties of diphonix resin in connection with Etidronic acid as the elution agent.

As can be seen in fig. 1, the diphonix resin conditioned by hydrochloric acid of various concentrations is capable of recovery of 55-75 % of the tested radionuclides, when using Etidronic acid as an elution agent. The highest yields of 65 %, 70 %, and 75 % for Pu, Cm, and Am, respectively, from HCl concentrations from 0.1 to 2 mol/dm³ for Am and Cm and from 0.1 to 0.5 mol/dm³ for Pu. Relatively stable plateaus of Am and Cm could be used for their individual extractions. However, close extraction ratios of all radionuclides including Pu do not support any possible separation.

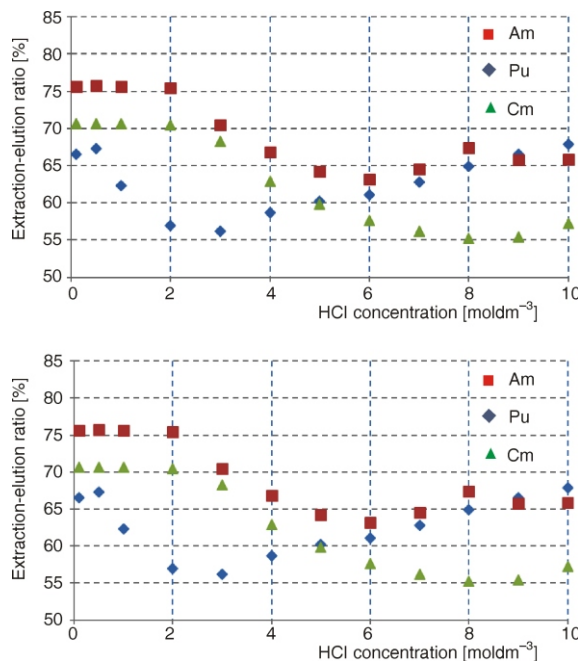


Figure 1. Extraction-elution behavior of Diphonix resin using Etidronic acid

The results from the conditions of nitric acid show that the recovery of Pu reaches almost 95 % for the concentrations of 3 mol/dm³ and higher, whereas the extraction of Am and Cm peaks at 67 % with decrease at concentrations 3-5 mol/dm³, the decrease of extraction of Am being more prominent. As in the case of conditioning with HCl, this method could be used for recovery of individual radionuclides, however extraction-elution ratios of Am and Cm are still high enough to prevent a successful separation.

The usage of Etidronic acid as an eluent introduces the need of its removal from the eluate. This could be done by classical open digestion or by closed vessel microwave digestion. Thus the further efforts of our work were devoted to find the solution, which would eliminate the removal step of etidronic acid from the eluate.

The elution of the transuranium elements by saturated solution of ammonium oxalate proved to be possible, but not viable as the extraction ratios do not reach the values provided by Etidronic acid. The extraction of americium from HCl plateaus at 50 % and from HNO₃ at 30 % for concentrations 4 mol/dm³ and higher. The extraction of curium from HCl has maximum of 60 % for concentrations 2-8 mol/dm³, from HNO₃ the maximum settles at 40 % for concentrations 4 mol/dm³ and higher. The extraction of plutonium does not follow the previous trend as from HCl it has maximum of 70 % at concentrations from 0.1 to 0.5 mol/dm³ and then falls to 60 %, whereas extraction from HNO₃ peaks at 80 % at concentrations from 6 mol/dm³ higher. The extraction of uranium has maximum of 40 % for HCl and of 30 % for HNO₃ at concentrations from 0.1-0.5 mol/dm³ and then both fall to

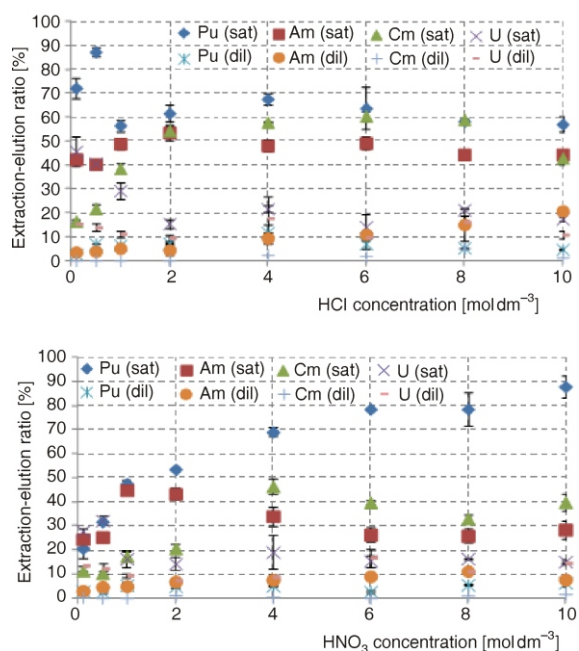


Figure 2. The elution of the transuranium elements by saturated and diluted solution of ammonium oxalate in hydrochloric and nitric acids

20 %. The extraction using diluted oxalate proved to be inconsequential for all radionuclides as the ratio does not exceed 20 % in any case. As can be seen in fig. 2, the extraction by the saturated solution of oxalate can be used to separate plutonium from the rest of the tested radionuclides from HNO₃ at concentrations 6 mol/dm³ and higher since the ratio for plutonium reaches 80 % and remains 30 % for the rest of the radionuclides.

The elution by solutions of citrate of various concentrations was tested for curium and plutonium. The method showed no reasonable results for either radionuclide at any concentration as the measured activities of all samples were within the activity range of the background.

CONCLUSIONS

The data confirm the ability of Etidronic acid to successfully elute the selected actinides from Diphonix resin with varying efficiency, which exceeds 90 % only in the case of extracted Pu from the resin conditioned by nitric acid and is in other cases around 60 %. Therefore, the difference between extraction ratios of individual radionuclides is too small for their separation by means of this method.

The results show that oxalate solutions are capable of limited elution of the actinides from Diphonix resin. However, even the highest extraction ratio for plutonium is lower than the ones achieved by Etidronic acid as Etidronic acid is capable of 95 % extraction of plutonium from HNO₃. The ratios for the

remaining radionuclides do not support utilization in extraction. Nevertheless, there is a potential for separation of plutonium from the rest of radionuclides from HNO₃, because the ratio for plutonium surpasses 80 % and ratios of the rest do not exceed 40 %.

A future study will be aimed at extraction properties of other complex forming agents, mainly carbonates. Agents displaying suitable qualities will be tested in with Etidronic acid to determine a possible enhancement of its extraction capabilities to achieve 100 % extraction ratio for all radionuclides of interest. The next step will be an addition of redox agents as reduction to oxidation state +1 or oxidation to state +7 should lead, based on the declared properties of Diphonix resin, to successful extraction. The possibility to improve the selectivity will be the primary focus at that stage.

AUTHOR CONTRIBUTIONS

The idea for the study was put forward by J. Janda. The measurements and the theoretical calculations were carried out by L. Kanka. The data were evaluated and interpreted by J. Janda.

REFERENCES

- [1] Stary, J., *et al.*, Separation Methods in Radiochemistry, Academia, Praha, 1975
- [2] Marcus, Y., Kertes, A. S., Ion Exchange and Solvent Extraction of Metal Complexes, John Wiley and Sons, New York, USA, 1969
- [3] Dean, A. J., Chemical Separation Methods, Van Nostrand Reinhold Company, New York, USA, 1969
- [4] Maxwell, S. L., *et al.*, Rapid Determination of Actinides in Emergency Food Samples, *J. Radioanal Nucl. Chem.*, 292 (2012), 1, pp. 339-347
- [5] Maxwell, S. L., *et al.*, Rapid Fusion Method for Determination of Plutonium Isotopes in Large Rice Samples, *J. Radioanal Nucl. Chem.*, 298 (2013), 2, pp. 1367-1374
- [6] Maxwell, S. L., *et al.*, Rapid Method for Determination of Plutonium, Americium and Curium in Large Soil Samples, *Journal of Radioanalytical and Nuclear Chemistry*, 275 (2008), 2, pp. 395-402
- [7] Maxwell, S. L., Culligan, B. K., Rapid Column Extraction Method for Actinides in Soil, *Journal of Radioanalytical and Nuclear Chemistry*, 270 (2006), 3, pp. 699-704
- [8] Maxwell, S. L., Rapid Column Extraction Method for Actinides and Strontium in Fish and other Animal Tissue Samples, *Journal of Radioanalytical and Nuclear Chemistry*, 275 (2008), 3, pp. 605-612
- [9] Croudace, I. W., *et al.*, A Novel Approach for the Rapid Decomposition of Actinide™ Resin and Its Application to Measurement of Uranium and Plutonium in Natural Waters, *Analytica Chimica Acta*, 577 (2006), 1, pp. 111-118
- [10] Jassin, L. E., Radiochemical Separation Advancements Using Extraction Chromatography: A Review of Recent Eichrom Users Group Workshop Presentations with a Focus on Matrix Interferences, *Journal of*

- Radioanalytical and Nuclear Chemistry*, 263 (2005), 1, pp. 93-96
- [11] Vajda, N., Kim, Ch., Determination of ^{241}Am Isotope: a Review of Analytical Methodology, *Journal of Radioanalytical and Nuclear Chemistry*, 284 (2010), 2, pp. 341-366
- [12] Olsen, S. C., Determination of Actinides in a Variety of Matrices, *Czech J. Phys.*, 53 (2003), Suppl. 1, pp. A313-A324
- [13] Thakur, P., Mulholland, G. P., Determination of ^{237}Np in Environmental and Nuclear Samples: A Review of the Analytical Method, *Applied Radiation and Isotopes*, 70 (2012), pp. 1747-1778
- [14] Maxwell, S. L., III: Rapid Method for Determination of Plutonium, Americium and Curium in Large Soil Samples, *Journal of Radioanalytical and Nuclear Chemistry*, 275 (2008), 2, pp. 275-395
- [15] Kolodynska, D., Diphonix Resin® in Sorption of Heavy Metal Ions in the Presence of the Biodegradable Complexing Agents of a New Generation, *Chemical Engineering Journal*, 159 (2010), 1-3, pp. 27-36
- [16] Stricklin, D. L., et al., Application of low Energy Gamma-Spectrometry in Rapid Actinide Analysis for Emergency Preparedness, *Journal of Radioanalytical and Nuclear Chemistry*, 251 (2002), 1, pp. 69-74
- [17] O'Boyle, N. C., A Review of Plutonium (IV) Selective Ligands, *Applied Radiation and Isotopes*, 48 (1997), 2, pp. 183-200
- [18] Qiao, J., et al., Determination of Plutonium Isotopes in Waters and Environmental Solids: A Review. *Analytica Chimica Acta.*, 652 (2009), 1-2, pp. 66-84
- [19] Warwłk, P. E., et al., Review of Analytical Techniques for the Determination of Americium-241 in Soils and Sediments, *Applied Radiation and Isotopes*, 47 (1996), 7, pp. 627-642
- [20] Št'astna, K., et al., Separation of Curium from Americium Using Composite Sorbents and Complexing Agent Solutions, *Journal of Radioanalytical and Nuclear Chemistry*, 304 (2015), 1, pp. 349-355
- [21] Francis, A., Arab-Chapalete, B., Actinide Oxalates, Solid State Structures and Applications, *Coordination Chemistry Reviews*, 266-267 (2014), May, pp. 28-68
- [22] Horwitz, E. P., et al., Separation and Preconcentration of Actinides by Extraction Chromatography Using a Supported Liquid Anion Exchanger: Application to the Characterization of High-Level Nuclear Waste Solutions, *Analytica Chimica Acta.*, 310 (1995), 1, pp. 63-78
- [23] Perrier, T., et al., Am-241 Remobilization in a Calcareous Soil under Simplified Izospheric Conditions Studied by Column Experiments, *Journal of Environmental Radioactivity*, 79 (2005), 2, pp. 205-221
- [24] Sánchez-Gonzales, S., et al., Natural Gamma Radiation and Uranium Distribution in Soils and Waters in the Agueda River Basin (Spain-Portugal), *Procedia Earth and Planetary Science*, 8 (2014), pp. 93-97
- [25] ***, AEP-66, Nato Handbook for Sampling and Identification of Biological, Chemical, and Radiological Agents (Sibcra), 2009
- [26] Horwitz, E. P., et al., Separation and Preconcentration of Actinides from Acidic Media by Extraction Chromatography, *Anal. Chim. Acta.*, 281 (1993), 2, pp. 361-372
- [27] Hortwitz, E. P., et al., Extraction Chromatography of actinides and Selected Fission Products: Principles and Achievement of Selectivity Eichrom, International Workshop on the Application of Extraction Chromatography in Radionuclide Measurement, IRMM, GEEL 9-10, Belgium, 1998, <http://www.eichrom.com/docs/bib/pdf/HP199-Actinides%20and%20strontium%20in%20Mixed%20Samples.pdf>
- [28] Lee, S. H., et al., The Development of Sequential Separation Methods for the Analysis of Actinides in Sediments and Biological Materials Using Anion-Exchange Resins and Extraction Chromatography, *Journal of Radioanalytical and Nuclear Chemistry*, 263 (2005), 2, pp. 419-425
- [29] Kolodynska, D., Diphonix Resin in Sorption of Heavy Metal Ions in the Presence of the Biodegradable Complexing Agents of a New Generation, *Chemical Engineering Journal*, 159 (2010), pp. 27-36
- [30] Kim, G., et al., Efficient Preconcentration and Separation of Actinide Elements from Large Soil and Sediment Samples, *Analytical Chemistry*, 72 (2000), Oct., pp. 4882-4887
- [31] Dulaiova, H., Separation of Am and Pu from 50 g Soil and Sediment Samples (Diphonix-HEDPA-TRU-TEVA), 2001
- [32] Gula, M. J., et al., The Ion Exchange Control of Iron in Copper Electrolyte Streams Using Eichrom's Diphonix Resin, SME Annual Meeting, Phoenix, Arizona, SME Pre-print No. 96-39, 1996
- [33] Gula, M. J., et al., The Role of Hydrometallurgy in Treating Nuclear Waste, *The Journal of the Minerals, Metals & Materials Society*, 47 (1995), 9, pp. 54-57

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Лукас КАНКА, Јиржи ЈАНДА

**ИСПИТИВАЊЕ АЛТЕРНАТИВНИХ АГЕНАСА ЗА
ЕЛУАЦИЈУ СА ДИФОНИКС СМОЛОМ**

Рад је усмерен ка експерименталном одређивању сепарационо екстракционих својстава дифоникса (Eichrom Industries, САД) у чврстом стању у зависности од коришћеног елуента. Тестирана је ефикасност екстракције плутонијума, америцијума, киријума и уранијума. Као мобилне фазе коришћене су хлороводонична и азотна киселина различитих концентрација. Циљ је био налажење најприкладније комбинације мобилне фазе и елуента која би довела до највећег могућег приноса. Најкоришћенији елуент који се може пронаћи у литератури је 1-хидроксиетан 1,1-дифосфораста киселина (HEDP, етидронска киселина). На основу истраживања одабрана су специфична једињења која су позната по својим комплексирајућим својствима, као што су соли оксалне и лимунске киселине при различитим концентрацијама. Активности узорака добијених елуацијом измерене су течним сцинтилационим спектрометром.

Кључне речи: дифоникс, елуација, синергетски ефекти, етидронска киселина
