

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/257612053>

The preparation of the ^{239}Np tracer from ^{243}Am and the purification of the stock solution

ARTICLE in JOURNAL OF RADIOANALYTICAL AND NUCLEAR CHEMISTRY · NOVEMBER 2013

Impact Factor: 1.03 · DOI: 10.1007/s10967-013-2521-z

CITATIONS

2

READS

55

3 AUTHORS:



Jana Strišovská

Comenius University in Bratislava, Faculty...

11 PUBLICATIONS 16 CITATIONS

SEE PROFILE



Veronika Drábová

Comenius University in Bratislava

8 PUBLICATIONS 9 CITATIONS

SEE PROFILE



Jozef Kuruc

Comenius University in Bratislava

33 PUBLICATIONS 104 CITATIONS

SEE PROFILE

The preparation of the ^{239}Np tracer from ^{243}Am and the purification of the stock solution

Jana Strišovská · Veronika Drábová ·
Jozef Kuruc

Received: 1 February 2013 / Published online: 5 May 2013
© Akadémiai Kiadó, Budapest, Hungary 2013

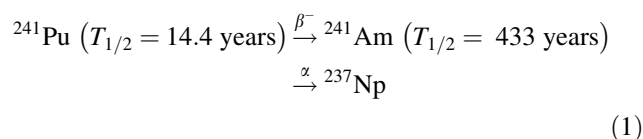
Abstract The present work describes preparation of ^{239}Np tracer from ^{243}Am stock solution and the purification of this solution from ferric cation. The method of the preparation of tracer involves stabilization of Np(IV) by ascorbic acid and ferric nitrate, separation of ^{239}Np from ^{243}Am by extraction chromatography and determination of recoveries of ^{239}Np by means of gamma spectroscopy. We used the commercially available sorbents TEVA[®] Resin for the ^{239}Np preparation and DGA Resin for ^{243}Am purification. All sorbents were purchased from Eichrom Industries, Inc. The first eluate from the column can be stored for a future preparation of the tracer and fraction with ^{239}Np will be used to monitor radiochemical yield of ^{237}Np .

Keywords Alpha decay · Americium 243 · Chemical preparation · Neptunium 239 · Solvent extraction · Tracer techniques

Introduction

The removing of long-lived actinides from high-level radioactive wastes is a subject for discussion and review with the aim of reducing of long-term risk of radioactive waste repository [1]. The research programs were established as a response to this fact that they are funded by national and international organizations. Neptunium is a particularly special problem in term of costs for the radiochemical determination.

The two isotopes of neptunium as ^{237}Np and ^{239}Np have the biggest impact on the environment, but their influence on the surroundings is different. ^{239}Np is a part of the radioactive fallout and also gets into the environment from nuclear facilities. ^{239}Np has short half decay $T_{1/2}$ (2.356 days) [2, 3] and therefore it has no long-term effects in the nature. The presence of ^{239}Np was identified in the soil of immediate areas of weapons testing sites and in water and sediments from nuclear facilities [4]. On the other hand ^{237}Np has long half-life $T_{1/2}$ (2.144×10^6 years) and constantly accumulates because it is formed by reaction:

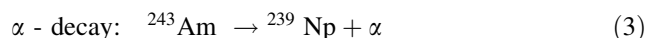
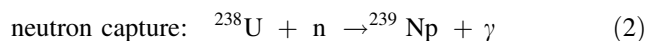


^{241}Pu is got to the environment especially during the nuclear testing of weapons in the atmosphere. ^{237}Np is the product of energy production in the nuclear power plants. In the future ^{237}Np will be the dominant radionuclide in long-lived radioactive wastes. Therefore it is necessary to pay attention to its determination in the environment.

In regard to the alpha-decay of ^{237}Np and its relatively low concentration in environmental samples, the chemical separation of neptunium from the interfering radionuclides must be completely finished before the measurement. The accurate determination of ^{237}Np requires the use of a tracer that is suitable to monitor the radiochemical yield. Ideally, the tracers should have the same chemical behaviour as analytes. But in the case of ^{237}Np ideal tracer does not exist. ^{235}Np ($T_{1/2} = 396.1$ days) is the potential tracer for the determination of ^{237}Np . It decays mainly by electron capture (99.9974 %) [5]. Moreover it is not possible accurate detection of ^{235}Np by ICP-MS due to the isobaric

J. Strišovská (✉) · V. Drábová · J. Kuruc
Department of Nuclear Chemistry, Faculty of Natural Sciences,
Comenius University, Mlynska dolina CH1,
842 15 Bratislava, Slovakia
e-mail: strisovskajana@gmail.com

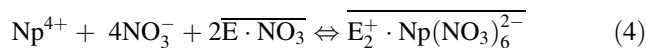
interferences. The presence of ^{237}Np as an impurity in the tracer of ^{235}Np and the necessity of the adding of the sufficient amounts of ^{235}Np set high demand to the analytical procedure in order to obtain a reliable signal in the low-energy spectrum derived from beta liquid scintillation spectrometer (LSC) [6]. For these reasons ^{235}Np is not suitable tracer for the determination of ^{237}Np . ^{236}Np ($T_{1/2} = 154 \times 10^3$ years) is another potential tracer. It decays by beta-emission (12.5 %), electron capture (87.3 %) and alpha-emission (0.16 %). ^{236}Np is not ideal isotope tracer for the determination of ^{237}Np by alpha spectrometry due to its long half-life, low specific activity and low probability of alpha-decay. Some studies [7, 8] point to the possibilities of this tracer for the determination of ^{237}Np from environmental samples by mass spectrometry. Radiochemical yield of ^{237}Np is monitored by the adding tracer of ^{239}Np . Its half-life is $T_{1/2} = 2.3565$ days [2]. ^{239}Np generates by neutron capture or α -decay [9]:



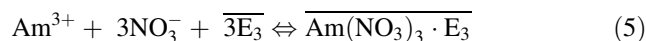
The short-lived radioisotopes, which are created by neutron capture, require the time that it is needed for their cooling [10]. Therefore preferable preparation of ^{239}Np tracer is from the ^{243}Am radionuclide. ^{243}Am is the long-lived α -emitter and its half-life is $T_{1/2} = 7,370$ years [2]. The radioactive equilibrium of this pair is reached after ten times of half-life of ^{239}Np (23.6 days). The separation of neptunium and americium is based on knowledge of their different chemical properties which confirms their easy separation. Wenzel et al. [11] prepared ^{239}Np from ^{243}Am feed solution in a nitric acid medium. The process includes the stabilization of Np^{4+} with ascorbic acid, isolation of Np^{4+} by using extraction with TOPO/dodecane and stripping of Np with $(\text{NH}_4)_2\text{CO}_3$. ^{243}Am remains in the feed solution and the milking process can be repeated after reequilibration which requires ~ 2 weeks due to the incomplete Np extraction.

The separation methods based on extraction chromatography have become popular in radiochemical analyzes because of their simplicity, speed and minimization of chemical agents, costs on waste disposal compared to a conventional separation methods [12–18]. The sorbent TEVA[®] Resin, which is one of the most versatile analytical products of the company Eichrom Industries, Inc., is often used to determine the tetravalent actinide. This sorbent can be used alone or can be easily combined with other sorbents for specific separation of complex analysis. An aliphatic quaternary amine, known as Aliquat[®]336 is the active component. As such it has properties similar to those of typical strong base anion exchange resins. However, because the functional groups are in a liquid form, rather than fixed to a polymer backbone, these groups have greater flexibility to

coordinate around target anions. This means that the uptake of these ions is generally higher and often at lower acid concentrations. [19]. The assuming equation for extraction of Np in the oxidation state IV is following:



where E is extractant. Neptunium can be in different oxidation states depending on the character and the molarity of the solvent. Horwitz et al. [20] has shown that Np(IV) is characterized by high values of retention capacity k' at the high molarity of nitric, hydrochloric acid and Np(V) does not show retention on the extraction-chromatographic sorbents. DGA Resin from Eichrom Industries, Inc. is extraction chromatographic materials in which the extractant system is either N,N,N',N' -tetra-*n*-octyldiglycolamide (DGA Resin, Normal) or N,N,N',N' -tetrakis-2-éthylhexyldiglycolamide (DGA Resin, Branched) [21]. The assuming equation for extraction Am^{3+} is following:



where E is extractant. Diglycolamides contain three oxygen atoms which have strong affinity to capture the metal ions, so they act as tridentate ligands [22].

The aim of the study is the preparation of ^{239}Np tracer from its parent nuclide of ^{243}Am by extraction chromatography, which will be suitable for the determination of ^{237}Np in the environmental samples. This paper also describes the purification the stock solution, which is permanently polluted by ferric cations.

Methods and experiments

Reagents and materials

All used reagents were commonly available analytical grade acids and chemicals. Nitric acid, hydrochloric acid were supplied by Slavus, Slovakia, ascorbic acid by Mikrochem, Slovakia, ferric nitrate nonahydrate by Lach-Ner, USA, hydroxylamine hydrochloride by Lachema, n.p., Brno, oxalic acid was supplied by Mikrochem, Slovakia and radionuclide tracers of ^{243}Am by Lacomed SK, Ltd., Slovakia.

Two different extraction chromatography resins were used for the radionuclide separation. TEVA[®] Resin (100–150 μm) and DGA Resin were supplied by Eichrom Industries, Inc.

TEVA[®] Resin separation procedure

The ^{243}Am tracer with the activity of 60 Bq was added to 4 cm^3 of 2.5 M HNO_3 . A valence adjustment was

performed by adding 1.2 mg of Fe^{3+} ions as $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 150 mg of ascorbic acid to the sample. Then we left sample to stand for 15 min because of reduction of neptunium to oxidation state IV. The separation is shown in Fig. 1. TEVA[®] Resin column was stacked on the vacuum box. TEVA[®] Resin column was conditioned with 10 cm³ of 2.5 M HNO_3 . After the valence adjustment, the sample solution was loaded onto stacked column at ~ 1 drop per second. First fraction which contained ^{243}Am was collected. A $3 \times 5 \text{ cm}^3$ of 2.5 M HNO_3 was added to TEVA[®] Resin to elute any residual americium before stripping the neptunium from the column. The ^{243}Am fraction was captured and stored. Neptunium was stripped from TEVA[®] Resin with 40 cm³ of 0.5 M HCl . The eluted Np fraction was collected into a vial.

The purification of the ^{243}Am tracer from Fe^{3+} cations

The ^{243}Am tracer solution was evaporated almost to dryness and the residue was dissolved in 6 M HCl and diluted to 3.5 M HCl in 30 cm³. For the reduction of Fe^{3+} to Fe^{2+} hydroxylamine hydrochloride was used. The solution was heated for 15 min to achieve complete reduction of Fe^{3+} . DGA Resin was used for the purifying of the tracer from ferric cations. The column was conditioned with 3.5 M HCl and the solution was loaded onto the column. Americium was eluted with 40 cm³ of 0.25 M HCl —0.03 M oxalic acid. The fraction was collected into a vial.

Measurements

The tracer of ^{243}Am and final ^{239}Np fractions were measured by the HPGe Gamma-Spectrometer Ortec 672. In particular, the gamma-activity of ^{239}Np was measured as soon as possible after separation from the stock solution due to its short half life (2.3565 days). Two gamma-energies of 228 and 277 keV were selected for the measurement of ^{239}Np . The samples were counted 10,000 s.

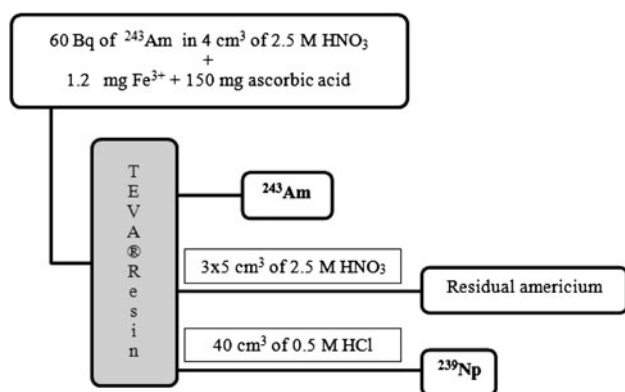


Fig. 1 Separation scheme of neptunium from americium

Results and discussion

Before the preparation of the tracer of ^{239}Np , a gamma-spectrometric measurement of the ^{243}Am stock solution was made. The standard solution of ^{243}Am contains an equal amount of ^{239}Np after the achievement of an equilibrium state. The peaks corresponding to parent's ^{243}Am and daughter's ^{239}Np nuclide are in a spectrum at different energies: ^{243}Am —75 keV (66 %), ^{239}Np —99.5 keV (15 %), 103.7 keV (24 %), 106.1 keV (22.70 %), 117.7 keV (8.4 %), 120.7 keV (3.2 %), 209.7 keV (15 %), 228.2 keV (10.2 %), 277.6 keV (14.1 %), 315.9 keV (1.6 %) and 334.3 keV (2 %).

According to the separation scheme, americium was separated from neptunium on TEVA[®] Resin column by the method of extraction chromatography. The time of separation was ~ 1 h. The used sorbent shows high affinity for actinides in oxidation state IV. On the basic we successfully separated ^{239}Np from ^{243}Am . After loading of the sample, only neptunium in the fourth oxidation state was retained on the column and americium passed through. It is very efficiently retained as an $\text{Np}(\text{NO}_3)_6^{2-}$ anions in a TEVA column in 2.5 M HNO_3 . We used ascorbic acid and Fe^{3+} for reduction of neptunium to fourth oxidation state. Ferric ions were reduced by ascorbic acid to ferrous cations, which effectively reduce neptunium to $\text{Np}(\text{IV})$. We used 0.5 M HCl as elution solution for Np because we supposed the best results in previous experiments with this concentration. After separation, activity of ^{239}Np was measured using HPGe detector. All the measurements were performed in the same geometry and time in order to keep to the same conditions during measurement. This measurement confirmed separation of neptunium from americium, because ^{243}Am was not found in the spectrum as we expected.

^{239}Np was examined at 228 and 277 keV energy lines. The relative method of calculation of recovery for ^{239}Np was used. Recovery Y of a tracer is typically used in radiochemical analysis and is a measure of the effectiveness of separation methods for some radionuclides. It is expressed as the percent recovery. Recovery Y was calculated as follows:

$$Y = \frac{N_m}{N_{eq}} \times 100 [\%] \quad (\text{A})$$

where N_m is number of counts of ^{239}Np after the separation and N_{eq} is number of counts of ^{243}Am in equilibrium with ^{239}Np before the separation. N_{eq} . For the stock solution Am and Np which is in radioactive equilibrium we determined 805 counts at 277 keV lines and 698 counts at 227 keV lines. During our experimental radiochemical analysis we made several preparations of ^{239}Np tracer. The results for recoveries are presented in Table 1 and in Table 2. The

Table 1 Recoveries in % for ^{239}Np at energy of 277 keV

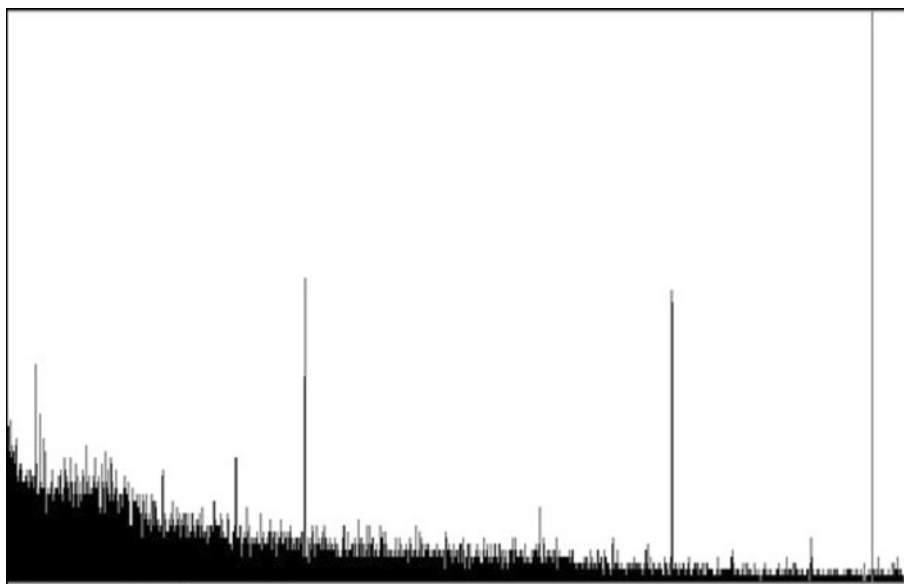
No. of sample	Counts (N_m)	Time t (s)	Recovery Y (%)
1.	515	10,000	63.98
2.	522	10,000	64.84
3.	548	10,000	68.07
4.	567	10,000	70.43
5.	572	10,000	71.06
6.	582	10,000	72.30
7.	599	10,000	74.41

Table 2 Recoveries in % for ^{239}Np at energy of 228 keV

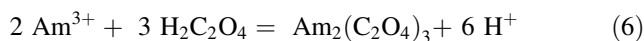
No. of sample	Counts (N_m)	Time t (s)	Recovery Y (%)
1.	430	10,000	61.60
2.	446	10,000	63.90
3.	450	10,000	64.47
4.	457	10,000	65.47
5.	471	10,000	67.48
6.	476	10,000	68.19
7.	487	10,000	69.77

recoveries for ^{239}Np at 277 keV lines were in the range from 64 to 74 % and at 228 keV lines from 61 to 70 %.

For the purification of the tracer of ^{243}Am from ferric cations we used extraction-chromatographic material—DGA Resin. DGA Resin only retains americium in the third oxidation state. The spectrum of the fraction after passing through the DGA column is shown in Fig. 2.

Fig. 2 Gamma-spectrum of fraction after passing through the DGA column

Americium was stripped from DGA Resin with solution of hydrochloric acid with oxalic acid additive. The cation of Am^{3+} makes complex with oxalic acid:

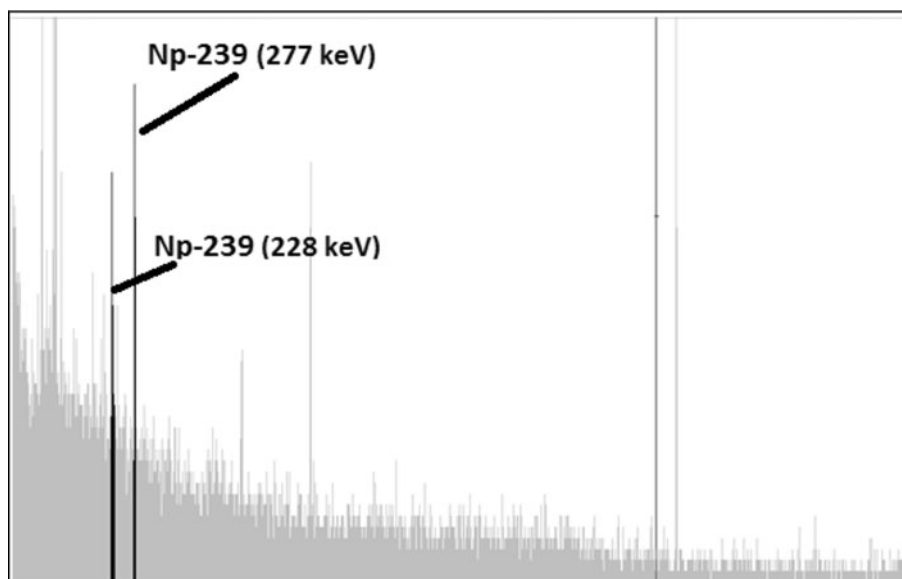


Oxalate complexes form very strong binding with cations of actinides, concretely in our case with Am^{3+} . Americium was eluted from DGA column as oxalate complex $\text{Am}_2(\text{C}_2\text{O}_4)_3$. The breakdown of bind between americium and extractant system comes up and americium is released from DGA resin in the complex form. In Fig. 3 in gamma-spectrum ^{239}Np was identified at energies of 228 and 277 keV.

Conclusion

The aim of this study was to prepare a tracer ^{239}Np from ^{243}Am by extraction chromatography. ^{239}Np was measured by HPGe detector in a well-defined geometry and it was measured immediately after the separation due to the short half decay $T_{1/2}$. The obtained eluate of ^{239}Np will be used as a tracer to determination of radiochemical yield of ^{237}Np . The aim of this work was to determine the effectiveness of the modify separation process so we used the method of relative determination of recovery in %. Time of 2 h from the disruption of equilibrium of the Np and Am to gamma-measurements in comparison with the half decay $T_{1/2}$ of ^{239}Np was not take for important for the recovery determination. The recoveries for ^{239}Np at 277 keV lines were in the range from 64 to 74 % and at 228 keV lines from 61 to 70 %. On the basis of study [23] we can conclude that ^{243}Am stock solution is possible to re-use for ^{239}Np tracer preparation after 5 days of ingrowth. The

Fig. 3 Gamma-spectrum of fraction after elution from the column



re-using of ^{243}Am solution, which passed through TEVA Resin column immediately after loading of the sample, is the advantage. The presented results point to the successful removal of ferric cations from the stock solution by extraction chromatography.

References

- Dulanská S, Meloun M, Mátl L (2010) Scaling model for prediction of radionuclide activity in cooling water using a regression triplet technique. *J Radioanal Nucl Chem* 285(3):547–553
- Table of Nuclides (2000) Nuclear Data Center, Korea Atomic Energy Research Institute. <http://atom.kaeri.re.kr/index.html>. Accessed 13 September 2011
- Tuli JK (2005) Nuclear wallet cards. Brookhaven National Laboratory, New York, p 115
- Coughtrey PJ, Thorne MC, Jackson D (1983) Radionuclide distribution and transport in terrestrial and aquatic ecosystems. Taylor & Francis, Inc., USA, p 372
- Harvey BR, Sutton GA (1987) The properties of ^{235}Np as a tracer and yield monitor in studies of the environmental behaviour of neptunium. *Nucl Instrum Methods Phys Res A* 254:172–181
- Salminen S et al (2009) ^{237}Np in peat and lichen in Finland. *J Radioanal Nucl Chem* 281:405–413
- Kelley JM, Bond LA, Beasley TM (1999) Global distribution of Pu isotopes and ^{237}Np . *Sci Total Environ* 237–238:483–500
- Kenna TC (2002) Determination of plutonium isotopes and neptunium-237 in environmental samples by inductively coupled plasma mass spectrometry with total sample dissolution. *J Anal At Spectrom* 17(11):1471–1479
- Loveland W, Morrissey W, Seaborg G (2006) Modern nuclear chemistry. Wiley, New Jersey
- OECD (1999) Actinide and fission product partitioning and transmutation status and assessment report. <http://www.oecd-nea.org/trw/docs/neastatus99/>. Accessed 14 Dec 2012
- Wenzel U, Bisplinghoff B (2002) Milking process for the preparation of ^{239}Np . *J Radioanal Nucl Chem* 254(3):527–532
- Galanda D, Mátl L, Dulanská S (2011) Monitorovanie obsahu uránu vo vzorkách životného prostredia z oblastí potencovaných ložísk uránovej rudy. *Chemické Listy* 105(12):948–954
- Galanda D, Mátl L, Dulanská S (2010) Aplikácia metód extrakčnej chromatografie pri stanovení alfa-rádionuklidov v rádioaktívnych odpadoch. *Bezpečnosť jaderné energie* 18(1/2):45–47
- Mátl L, Rosskopfová O, Rajec P, Galanda D, Švec V (2002) Distribution of radionuclides in soils in surroundings of Bratislava, capital of the Slovak Republic: II Man made radionuclides. Eichrom Users Group Meeting, Vienna
- Galanda D, Ferencová M, Matel L (2007) Separácia alfa rádionuklidov extrakčnou chromatografiou pomocou vákuum box systém. 29. dny radiační ochrany 2007, Zborník rozšírených abstraktov, České vysoké učení technické, Praha
- Dulanská S, Remenec B, Galanda D, Němec M, Dvorská L (2012) Statistical suitability testing of 3 M EmporeTM Sr disc and AnaLig[®] Sr-01 use for ^{90}Sr determination. *J Radioanal Nucl Chem* 293:965–971
- Dulanská S, Remenec B, Durkot E, Galanda D, Matel L (2012) Determination of $^{239,240}\text{Pu}$, ^{238}Pu isotopes in soil samples using molecular recognition technology product AnaLig[®] Pu-02 gel. *J Radioanal Nucl Chem* 293:847–850
- Dulanská S, Remenec B, Mátl L, Galanda D (2011) The selective separation of Pu isotopes using molecular recognition technology product AnaLig[®] Pu02 gel and extraction chromatography TRU[®] resin. *J Radioanal Nucl Chem* 287(3):841–845
- Eichrom Technologies, Inc. TEVA[®] Resin. http://www.eichrom.com/products/info/teva_resin.cfm. Accessed 07 Oct 2012
- Horwitz EP et al (2005) Novel extraction of chromatographic resins based on tetraalkyldiglycolamides: characterization and potential applications. *Solvent Extr Ion Exch* 23:319–344
- Eichrom Technologies, Inc. DGA Resin. http://www.eichrom.com/eichrom/products/info/dga_resin.aspx. Accessed 21 March 2013
- Van Hecke K, Modolo G (2004) Separation of actinides from low level liquid wastes (LLW) by extraction chromatography using novel DMDOHEMA and TODGA impregnated resins. *J Radioanal Nucl Chem* 261(2):269–275
- Reich M, Rajec P (2005) Extraction chromatography for separation of ^{239}Np from ^{243}Am . *J Radioanal Nucl Chem* 266(1): 71–74