

Alpha spectroscopy substrates based on thin polymer films

Joseph M. Mannion¹ · W. David Locklair² · Brain A. Powell² · Scott M. Husson¹

Received: 16 June 2015 / Published online: 12 November 2015
© Akadémiai Kiadó, Budapest, Hungary 2015

Abstract The objective of this work was to prepare a novel substrate for the simultaneous concentration of actinides and sample preparation for alpha spectroscopy. Substrate preparation involved forming ultrathin films (10–180 nm) of quaternary amine anion-exchange polymers on glass and silicon by dip-coating. Samples were loaded by submerging the polymer-coated substrates into acidified solutions of ²³⁸Pu or natural water with elevated uranium concentrations. High resolution (25–30 keV) alpha spectra were acquired from these substrates under certain loading conditions indicating that through further development they may be a useful, inexpensive, and potentially field deployable platform serving national security and environmental sampling applications.

Keywords Anion-exchange polymer · Environmental sensing · Isotopic analysis · Alpha spectrometry · Plutonium · Natural uranium

Introduction

The ability to rapidly and efficiently produce samples capable of quantifying actinide concentrations and isotope ratios by alpha spectroscopy has applications in water monitoring, emergency response, nuclear materials processing, nuclear forensics, and nuclear safeguards. For example, knowing the isotope ratio of U or Pu bearing samples can help to understand the source and/or intent of the material [1]. In many cases within both nuclear security and environmental applications, the ability to measure ultra-trace level (pg) quantities of actinide elements is necessary to nuclear security applications. Oftentimes, such sensitivity can only be achieved using mass spectrometric techniques. Alpha spectroscopy can be a simpler and cheaper alternative to mass spectrometry if samples can be prepared with sufficient resolution and capture efficiency. However, preparation of high quality alpha spectroscopy samples is a difficult task because the high linear energy transfer of alpha particles limits the distance an alpha particle can travel through virtually any medium. Thus, high quality alpha spectroscopy substrates must be (1) flat, (2) stable, and (3) have a means of chemically or physically sequestering the radionuclides on the surface.

There are several currently employed techniques to prepare alpha spectroscopy samples to avoid self-absorption of the alpha particles, which can have deleterious effects on the resolution of the alpha spectrum. Self-absorption occurs when alpha-emitting isotopes must pass through a portion of the solid source material, which causes energy loss of the particle and leads to a broadening of the spectrum. The result is low energy tailing in the spectrum that makes isotope discrimination more difficult if not impossible. This phenomenon rules out most porous materials, including many crystalline metal oxides, as

Electronic supplementary material The online version of this article (doi:10.1007/s10967-015-4498-2) contains supplementary material, which is available to authorized users.

✉ Scott M. Husson
shusson@clemson.edu

¹ Department of Chemical and Biomolecular Engineering, Clemson University, 127 Earle Hall, Clemson, SC 29634, USA

² Department of Environmental Engineering and Earth Sciences, Clemson University, 342 Computer Court, Anderson, SC 29625, USA

sorbents since they would produce spectra with excessive tailing. Rapid methods, such as lanthanum fluoride microprecipitation, can produce samples with high alpha energy resolution but require hazardous chemicals (i.e. hydrofluoric acid), which is not ideal for field application. Electrodeposition can produce good samples but requires specialized equipment and adds another time consuming step to sample preparation. Thus, a primary objective of this work was to develop a new method based on thin polymer films for the rapid, inexpensive, and efficient preparation of alpha spectroscopy samples that retains the high resolution of those prepared by electrodeposition or microprecipitation.

Organic films recently have been studied as a potential platform for the development of robust alpha spectroscopy substrates capable of rapid field deployment [2]. A variety of film formation techniques have been employed, including common techniques such as spin-coating and solvent casting, and less common methods such as fixing crushed anion-exchange resin beads to a surface [3]. A chemical strategy has been the use of polymer-ligand films [4] or polymer inclusion membranes [5] where a ligand is dispersed with a polymer in solution and co-deposited on the substrate surface. In concept and in preparation, polymer-ligand films are simple, but they present a number of engineering challenges for use as substrates for alpha spectroscopy. The ligands in these films are not bound covalently to the polymer matrix and, thus, are susceptible to leaching. To prevent excessive leaching of the ligand, the polymer matrix must have a low degree of swelling under aqueous loading conditions, which leads to slow uptake kinetics due to the high resistance for transport of aqueous ions into the polymer matrix. In these systems, a significant fraction of bound ions is likely to be deposited below the film-fluid interface, within the polymer matrix, contributing to energy tailing seen in spectra produced from thicker (2–3 μm) polymer-ligand films [6].

In this work, we prepared and tested a novel substrate for the rapid concentration of actinides and simultaneous sample preparation for high-resolution alpha spectroscopy analysis. The substrate comprises an ultra-thin (10–180 nm), lightly cross-linked polymer film with *covalently* bound quaternary ammonium chloride pendant groups for actinide anion exchange. A thickness of 10–180 nm minimizes tailing due to energy deposition in the film while providing adequate mass of anion-exchange material to complex measurable quantities of actinides. The functionalized films are hydrophilic and readily swell in aqueous systems, eliminating the need for plasticizers to aid in ion transport within the film. Dip-coating was selected as the film formation method for these studies over solvent casting or spin coating. It offers a high degree of reproducibility and control over film thicknesses in the range of 10–1000 nm, produces highly uniform and smooth films

apart from edge effects, is more easily scalable than comparable methods, and can be applied to a variety of substrate geometries. The dip-coating film formation procedure can be applied to virtually any polymer systems and provides a simple, rapid, and inexpensive means for preparing large batches of ready-to-use substrates for alpha spectroscopy.

Quaternary amine resins and polymers have a long history of use in the production and purification of actinides. The characteristics of actinide-lanthanide binding with quaternary amine bearing resins has been well characterized and found to be non-selective, with complexation generally occurring at elevated acid concentrations. This is due to the formation of anionic complexes such as $\text{Pu}(\text{NO}_3)_6^{2-}$ or PuCl_6^{2-} at high acid concentrations that undergo anion-exchange with the resin. As such, to promote actinide uptake on quaternary amine bearing polymer films, actinide samples must be dissolved in concentrated acid solutions. The necessity of sample acidification combined with the non-selectivity of complexation limits the potential field deployability of quaternary amine based substrates. Loading on quaternary-amine based anion exchange polymer films from complex environmental samples likely would require purification procedures to prevent degradation of spectral quality from matrix interferences. A simpler loading scheme may be achieved through the use of more selective ligands; however, quaternary amine based films present a good model platform to explore the influences of various film parameters under ideal loading conditions. The effects of film properties such as thickness, cross-linking content, and active site distribution on alpha spectral quality are largely unexplored. Additionally, the non-selectivity of quaternary amine polymers provides a near universal substrate to explore mass loading effects from various actinide species. Elucidation of these characteristics will guide future efforts in the development of polymer thin-film alpha spectroscopy substrates possessing selective ligand chemistries that can operate under a wider range of loading conditions.

Experimental

Materials

The following materials were obtained from Sigma-Aldrich and used as-received: chloroform (Reagent Plus[®] $\geq 99.8\%$ with 0.5–1.0 % ethanol as stabilizer, CAS# 67-66-3); 1,4-diazabicyclo[2.2.2]octane (DABCO, Reagent Plus[®] $\geq 99\%$, CAS# 280-57-9); hydrogen peroxide solution containing inhibitor (30 wt% in water, CAS# 7722-84-1); poly(vinylbenzyl chloride) (PVBC), 60/40 mixture of 3- and 4- isomers (CAS# 121961-20-4); sulfuric acid (95–98 %, ACS reagent

grade, CAS# 7664-93-9). Triethylamine (TEA, 99 %, reagent grade, CAS# 121-44-8) was obtained from Fisher Scientific.

Silicon substrates were acquired from Nova Electronic Materials as 4" N/Ph <100> 1–10 Ω -CM 500–550 μ m SSP prime grade Si wafers diced to 1 cm \times 3 cm pieces.

Deionized (DI) water with a resistance of 18.2 M Ω was prepared in-house from distilled water that was passed through a Milli-Q water purification system (EMD-Millipore).

Substrate preparation for coating

Silicon substrates were removed from their adhesive backing and etched with sample numbers. Glass substrates were prepared by cutting standard borosilicate glass slides into approximately 2.5 cm \times 2.5 cm squares. Piranha wash solution was prepared by slowly adding 1 part 30 wt% hydrogen peroxide to 3 parts concentrated sulfuric acid. (Caution: To prepare this solution, hydrogen peroxide was poured slowly into the concentrated sulfuric acid under a hood. Piranha solution is a very strong oxidant that may react violently if it comes in contact with organics.) Substrates were cleaned first by sonication (Aquasonic 75HT, VWR Scientific) with DI water for 15 min. Next, each substrate was placed in a test-tube with 10 mL of piranha solution and was heated in a water bath to 85 $^{\circ}$ C for 1 h. The used piranha solution was collected for safe disposal, and each test tube with substrate was washed with DI water 3 times before 15 min of sonication in DI water. The substrates were washed a final time with DI water and dried with compressed air.

Dip-coating

After cleaning, substrates were dip-coated from solutions of PVBC in chloroform. To produce a film with a thickness of approximately 10 nm, the substrate was withdrawn from a 0.5 wt% PVBC solution at a withdrawal rate of 100 mm/min using a Qualtecs Product Industry QPI-128 dip coater. Film thickness increases with increasing polymer concentration and withdrawal rate [7]; film thicknesses up to approximately 180 nm were produced by increasing polymer concentration to 2 wt% PVBC and withdrawal rate of 340 mm/min. Film thicknesses were determined with multi-angle ellipsometry (described in supplementary information). Immediately before dip-coating, DABCO was spiked into the solution to serve as a cross-linker. The molar amount of DABCO added was limited by stoichiometry based on a 1:2 reaction of DABCO to chloride sites along the PVBC chains, as depicted in Fig. 1. It was determined that to prevent dissolution of the polymer film in chloroform during the subsequent functionalization step,

a minimum of 5 % cross-linking was needed. A ratio of 18.4 mg DABCO:1 g PVBC was used to prepare films with 5 % cross-linking. Films with 50 % cross-linking also were prepared. After casting, films were heated in an oven at 80 $^{\circ}$ C for at least 24 h to complete cross-linking.

Functionalization of polymer thin-films

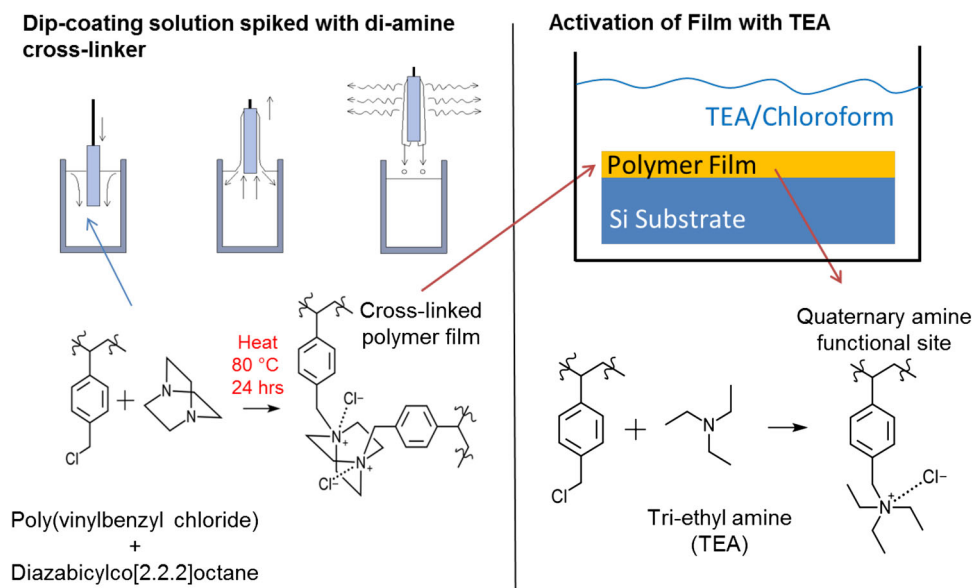
Substrates coated by the cross-linked polymer films were submerged in a 5 wt% solution of TEA in chloroform for 24 h at room temperature. After functionalization, the substrates were removed from solution and dried with compressed air.

Actinide loading and alpha spectroscopy

To demonstrate environmental applicability, uranium uptake studies used a groundwater sample collected from a well at Roundhouse point on Lake Jocassee in South Carolina on August 27, 2013. The water contains naturally occurring uranium at relatively high levels (166.5 ± 2.1 μ g/L (ppb) 238 U) as determined by direct analysis of the groundwater solution using ICP-MS after acidification to 2 wt% HNO₃. A NIST traceable uranium calibration solution was obtained from High Purity Standards (Charleston, SC) to determine the aqueous U concentration using ICP-MS. The uranium bearing groundwater samples were acidified to 3, 5, and 9 M HCl for uptake studies. Aliquots of each acid stock solution were placed in a petri dish to give the equivalent of 2.5 mL groundwater prior to dilution with the acid (i.e. to maintain a fixed uranium mass in each sample). A glass slide with a 5 % cross-linked, TEA functionalized film was submerged in each solution with no agitation. The solution was allowed to air dry completely and the bound uranium was quantified by alpha spectroscopy using an EG&G ORTEC Octète PC Alpha Spectrometer bank with phosphorous doped silicon detectors. A calibration standard for counting efficiency determination was prepared by spotting five 10 μ L drops of a 2966 dpm/mL 238 Pu solution across a 5 % cross-linked, TEA functionalized film that was carefully “smeared” using a pipette tip to cover the area of the film. Films from batch uptake studies were allowed to air dry prior to analysis. Each detector was energy calibrated using a NIST traceable 238 Pu, 241 Am, 235 U, and 238 U bearing source electroplated on a 25 mm diameter steel planchet. Due to the different geometry, this source could not be used as an efficiency standard.

Plutonium uptakes onto the 10 nm functionalized films were measured in the same manner as the uranium uptake experiments. However, to utilize a Pu source with higher specific activity, a 10 μ Ci/mL 238 Pu stock solution was obtained from Eckert and Zeigler Isotope Products (Valencia, CA). Two 238 Pu(IV) working solutions were prepared at \sim 1000 dpm/mL (1.1×10^{-10} mol/L 238 Pu) and

Fig. 1 Synthetic methods developed to produce chemically stable hydrophilic films with quaternary amine functionality



~100 dpm/mL (1.1×10^{-11} mol/L ^{238}Pu) in 9 M HCl using the same method described above for the uranium bearing samples. Separate films were submerged in 5 mL of each solution and allowed to air dry completely, and then the amount of ^{238}Pu on the film was quantified using alpha spectroscopy. Methods for plutonium loading onto 180 nm films are described in Supplementary Information.

Preparation of electrodeposited substrates

Preparation of electrodeposition solutions: For each sample, 1 mL of 1000 dpm/mL Pu^{238} in 9 M HCl solution containing sodium nitrate was diluted with 9 mL of DI water. Methyl yellow (2–3 drops) was added to solution and mixed by shaking. Sodium hydroxide solution (2 M) was added dropwise while shaking until a peach color was achieved indicating a pH of 3.2–3.8, which was confirmed with litmus paper.

Electrodeposition of Pu^{238} : Four stainless steel planchets were prepared by first removing the protective coatings. The planchets were loaded into four separate fluoropolymer electrodeposition cells that were then mounted to a fluoropolymer bracket. Electrodeposition solution was added to each cell (10 mL per cell), and a platinum anode was submerged below the surface of the solution and mounted in place. Care was taken to ensure the platinum anode was not in contact with the stainless steel planchets. The cathode was attached to the planchet and the power supply was tuned to 2 A (0.5 A/cell). Covers were placed over the cells to reduce evaporation of the electrodeposition solution while under current load. Current was applied for 2 h to complete the electrodeposition. Prior to turning off the power supply, approximately 1 mL of 2 M NaOH

was added to the cell to prevent re-dissolution of deposited Pu once the current was removed. The cells were removed from their mounts and the deposition solution was poured out of each cell. The planchets were dried in air before placing within the alpha spectrometer.

Results and discussion

PVBC films produced through dip-coating and activated with TEA were smooth apart from edge effects at all thicknesses upon inspection with atomic force microscopy (see Supplementary Information). Excess cross-linker was found to induce porosity within the film; however, films with 0–95 % cross-linking with DABCO remain smooth and non-porous.

TEA activated films with 5 % cross-linking were found to be stable in 9 M HCl. Stability was determined by measuring film thickness before and after acid exposure. Film thicknesses measured by multi-angle ellipsometry for stability testing are provided in Supplementary Information. Thicker films (~180 nm) were used for these studies so that small changes in thickness would be more evident. Film thicknesses remained the same within measurement uncertainties after soaking in 9 M HCl for 3 days. Delamination of the films was found to occur after multiple weeks of acid exposure; however, it was determined that contact times longer than 3 days were far longer than the time that is required to reach equilibrium in batch uptake studies (unpublished results).

The percent uptake of $^{238}\text{Pu}(\text{IV})$ onto the films with 50 % cross-linking by DABCO was much lower than on 5 % cross-linked films at the same acid concentration (see

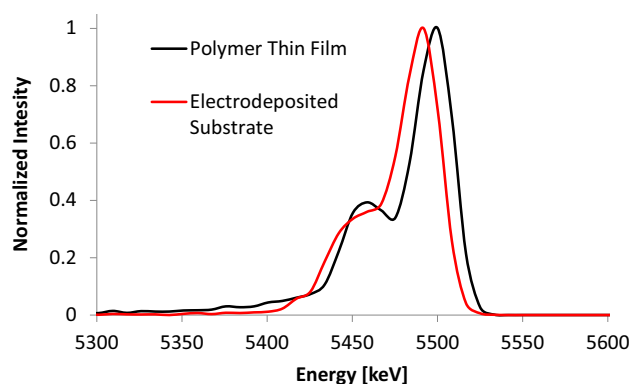


Fig. 2 Uptake of Pu(IV) out of 9 M HCl onto a 180 nm 5 % cross-linked, TEA activated PVBC substrate coated on silicon substrates; data determined by alpha spectroscopy (450 mm² detector) after: 22 h (thin film substrate) and 24 h (electrodeposited substrate)

Supplementary Information). This result likely is due to the lower actinide affinity provided by quaternary amines resulting from reaction with DABCO versus triethylamine. A maximal uptake of approximately 12 % was measured when loading from 1000 to 100 dpm/mL solutions of ²³⁸Pu(IV) and was achieved within 30 min of contact. These samples were loaded by simply submerging the substrate in actinide bearing acid solution for a given allotment of time. Despite low percentage uptake on 5 % cross-linked films, the resulting alpha spectra have a resolution of 25–30 keV, which is comparable to electrodeposition (Fig. 2). The high resolution provided by these substrates resolved the shoulder of the ²³⁸Pu alpha peak, which represents different alpha energies from the alpha decay: 5.499 MeV (70.91 %) and 5.457 MeV (28.98 %).

Figure 3 demonstrates that the HCl concentration strongly affects the uranium uptake onto the film. This result was expected as anion exchange within the polymer film occurs with the PuCl₆²⁻ or UO₂Cl₄²⁻ anionic species, which

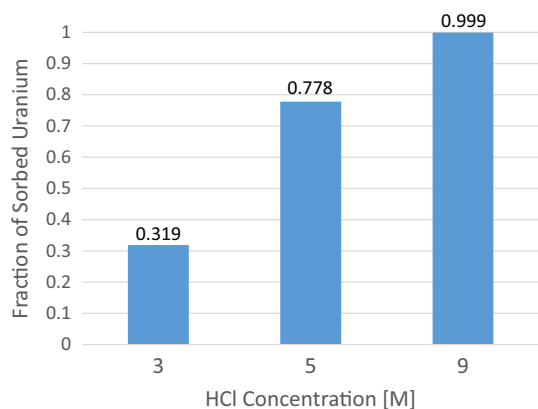


Fig. 3 Fraction of sorbed uranium on 10 nm 5 % cross-linked, TEA activated PVBC film after total evaporation of uranium solution; data determined from alpha spectroscopy after: 240 h (9 M), 300 h (5 M), and 435 h (3 M) of count time

becomes the dominant aqueous species for plutonium and uranium at high acid concentrations. The chloride:actinide ratio increases with increasing HCl concentration owing to formation of AnCl_x^{4-x} and AnO₂Cl_x^{2-x} complexes [8]. Due to the low specific activity of natural uranium, efforts were made to maximize the amount of uranium loaded onto these films. This objective was achieved by allowing the loading solutions to fully dry while in contact with the substrates.

Although the alpha peaks for uranium were clearly evident (Fig. 4), the spectra showed considerable peak broadening especially at low acid concentration. Energy resolutions for the ²³⁸U peaks at 4.2 MeV were 35 keV (9 M), 32 keV (5 M), and 54 keV (3 M). The relatively poor quality uranium spectra are attributed to several factors. While although the mass loading of uranium is high, the specific activity of its naturally occurring isotopes is low, and so several days of counting is necessary. The high mass loading also results in a large degree of self-attenuation of the alpha particles, causing tailing of the alpha peaks and subsequently decreased resolution. In addition, the uranium daughter products can be observed in the spectrum. These daughters can overlap with uranium peaks. For example, ²²⁶Ra has an alpha peak at 4.870 MeV that overlaps with the ²³⁴U peak at 4.859 MeV and hampers isotopic analysis without effectively purifying the solution prior to uptake.

To examine the influence of uranium mass loading on the sample, one film was initially loaded by submerging in a “clean” solution containing ²³⁸Pu(IV) and the alpha spectrum was collected. Then the same film was returned to a petri dish and loaded with natural uranium by allowing the natural uranium bearing solution to fully evaporate onto the substrate. Figure 4 shows the spectra for the films after each uptake period. The ²³⁸Pu prior to addition of uranium shows 25–30 keV resolution and relatively little tailing (though it is exaggerated on the logarithmic y-axis of Fig. 5). After loading the same substrate with natural uranium the plutonium peak shows a substantially reduced count rate (by about an order of magnitude) at the max peak energy, as well as extensive tailing. The tailing arises from attenuation of the plutonium alpha particles due to the large mass loading of precipitates covering the plutonium. Well water used in this study was not purified prior to loading and thus contained an abundance of natural salts that were deposited during drying. Due to the low specific activity of natural uranium isotopes, the uranium does not have sufficient activity to be observed above the substantial tailing of the ²³⁸Pu peak.

The relationship between film thickness and resulting alpha spectra resolution will be the subject of future investigation. Preliminary results can be seen in Supplementary Information.

Fig. 4 Alpha spectra of uranium from natural well water loaded onto 10 nm 5 % cross-linked, TEA activated PVBC substrate in 3 M HCl (**a**), 5 M HCl (**b**), and 9 M HCl (**c**); data determined from alpha spectroscopy after: 240 h (**a**), 300 h (**b**), and 435 h (**c**) of count time

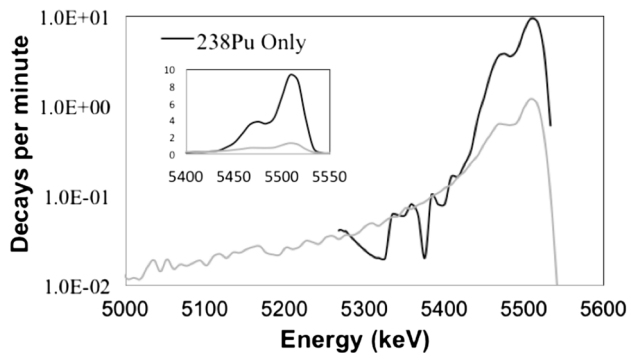
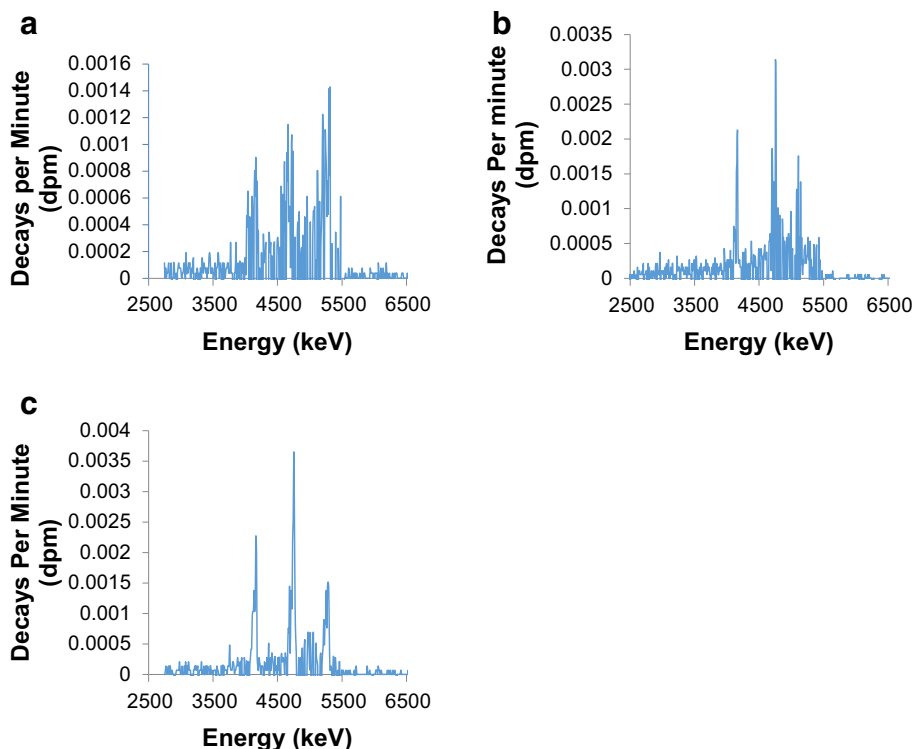


Fig. 5 Alpha spectroscopy of ^{238}Pu on 10 nm 50 % cross-linked, TEA activated PVBC substrate loaded from 9 M HCl (*black line*) and spectrum after film was re-submerged in 5 mL of well water in 9 M HCl (*grey line*). The data for ^{238}Pu only below 5300 keV are equivalent to background so the data cannot be plotted on the log y-axis. Original plutonium alpha spectrum was collected over a 50 min acquisition time; after uranium exposure a 90 h acquisition time was used to collect the alpha spectrum

Conclusions

Thin-film polymer substrates yielded alpha spectra for Pu(IV) with high resolution that is comparable to electrodeposition under ideal loading conditions. High acid concentrations were needed to drive uptake of actinides into the films, requiring special considerations if these are

to be used in a field deployable method; however, this limitation primarily is due to the selected polymer chemistry. Substrates loaded with uranium sorbed from natural well waters performed poorly when compared to thin film substrates loaded from “clean” plutonium solutions. Removing or preventing deposition of precipitates on the surface of the films and purification of the uranium solution to remove daughter products is needed to improve analyses for samples loaded from natural waters. Complete drying of natural samples upon the substrates exacerbated problems associated with complex sample matrices and should be avoided as a loading method.

The influence of film thickness and active site distribution on substrate performance needs further elucidation and the degree of cross-linking needs careful consideration. Some cross-linking is needed to ensure film stability during functionalization; however, high levels of cross-linking within the film were found to reduce actinide uptake by up to one order of magnitude. Plasma cleaning of the substrates can be used as an alternative method to piranha washing to minimize hazards associated with the substrate fabrication method.

Acknowledgments We are grateful for the financial support of this work by the National Nuclear Security Administration NA-221 Office of Proliferation Detection under Award No. DE-NA0001735.

References

1. Moody K, Hutcheon I, Grant P (2005) Nuclear forensic analysis. CRC Press, Boca Raton
2. Hanson SK, Mueller AH, Oldham WJ (2014) Kläui ligand thin films for rapid plutonium analysis by alpha spectrometry. *Anal Chem* 86:1153–1159
3. González E, Peterson D (2009) Rapid radiochemical sample preparation for alpha spectrometry using polymer ligand films. *J Radioanal Nucl Chem* 282:543–547
4. Rim JH, Gonzales ER, Armenta CE, Ünlü K, Peterson DS (2013) Developing and evaluating di(2-ethylhexyl) orthophosphoric acid (HDEHP) based polymer ligand film (PLF) for plutonium extraction. *J Radioanal Nucl Chem* 296:1099–1103
5. Mahanty BN, Mohapatra PK, Raut DR, Das DK, Behere PG, Afzal M (2015) Polymer inclusion membranes containing N,N,N',N'-tetra(2-ethylhexyl) diglycolamide: uptake isotherm and actinide ion transport studies. *Ind Eng Chem Res* 54:3237–3246
6. Chavan V, Paul S, Pandey AK, Kalsi PC, Goswami A (2013) Thin extractive membrane for monitoring actinides in aqueous streams. *J Hazard Mater* 260:53–60
7. Zhou J, Jianyong J, Haldeman AT, Wagner EH, Husson SM (2013) Formation and characterization of perfluorocyclobutyl polymer thin films. *J Appl Polym Sci* 129:3226–3236
8. Environmental Protection Agency, Multi-Agency Radiological Laboratory Analytical Protocols Manual, 2004, NUREG-1576, EPA 402-B-04-001A