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## Evaluating bis(2-ethylhexyl) methanediphosphonic acid (H<sub>2</sub>DEH[MDP]) based polymer ligand film (PLF) for plutonium and uranium extraction

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## **Cover page**

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## **Title page**

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31 **Evaluating Bis(2-ethylhexyl) methanediphosphonic acid (H<sub>2</sub>DEH[MDP]) Based**  
32 **Polymer Ligand Film (PLF) for Plutonium and Uranium Extraction**

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40 **Abstract**

41 This paper describes a new analyte extraction medium called Polymer Ligand Film (PLF) that was  
42 developed to rapidly extract radionuclides. PLF is a polymer medium with ligands incorporated in its  
43 matrix that selectively and quickly extracts analytes. The main focus of the new technique is to shorten and  
44 simplify the procedure for chemically isolating radionuclides for determination through alpha spectroscopy.  
45 The PLF system was effective for plutonium and uranium extraction. The PLF was capable of co-extracting  
46 or selectively extracting plutonium over uranium depending on the PLF composition. The PLF and  
47 electrodeposited samples had similar alpha spectra resolutions.

48 **Keywords**

49 H<sub>2</sub>DEH[MDP], PLF, Plutonium, Uranium, Extraction, Actinide

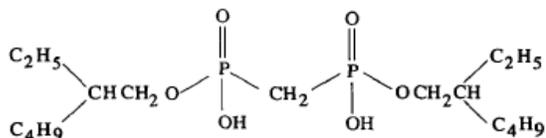
50 **Introduction**

51 A terrorist attack using nuclear device has been a great concern since the fall of the Soviet Union [1–5].  
52 There had been numerous incidents where large quantities of nuclear materials were trafficked by terrorist  
53 from the former Soviet Union countries [1, 6, 7]. These materials were most likely diverted with intended  
54 use as a weapon. In event of a terrorist nuclear attack, an accurate and fast determination of the activity of  
55 radionuclides in a sample is critical to implicate responsible parties and form a response in a timely  
56 manner. Also, it is critical to have a high sample throughput since there is a potential need to analyze an

57 enormous number of samples in a short time [1, 8]. Current radioanalytical techniques to analyze alpha  
58 emitting samples are quite mature and well established; however, they are slow and require highly trained  
59 personnel to perform extensive radiochemical separations and purification prior to analysis [8, 9]. These  
60 techniques are not well suited for rapid analysis or pre-screening of samples to determine which might be  
61 best suited for performing a more accurate but time-consuming set of analyses. Also, these classical  
62 methods require a fully functional chemistry laboratory to perform analyte separation to process the  
63 samples, which greatly limits the possibility of field analysis. These limitations of classical procedures  
64 greatly hinder the ability to accurately assess and respond to an incident in a prompt manner.

65 One of the possible solutions to improve the classical technique is to utilize ligands to combine separation  
66 and plating steps into a single step. The thin film extraction technique is similar to resin based extraction  
67 with the added benefit of an easier path forward for radiometric analysis for the alpha emitting elements.  
68 Selective extraction of analytes using a thin film substrate had been reported by several authors [10–19].  
69 Oldham and his group synthesized Klaui ligand and used it to produce thin films to extract plutonium [14].  
70 Plutonium recovery was high with Klaui ligand and alpha spectroscopy resolution was very good at  
71 ~33keV. Surbeck has used commercially available resin beads to prepare thin films for uranium extraction.  
72 The films were prepared from finely ground resin beads, and the fine powder was fixed onto a flat surface.  
73 Fifty percent of uranium was recovered within 4 hours, and 80% was extracted in about 20 hours [17]. The  
74 alpha spectroscopy peak resolution was not as good as the electrodeposited samples, probably due to the  
75 unevenness of the film surface. Wang et al. used a 54 mm<sup>2</sup> Aliquat-366/PVC liquid membrane system to  
76 extract Cd(II) from an HCl solution [19]. The membrane was prepared by dissolving commercially  
77 available Aliquat-366 and PVC in THF then poured into a mold.

78 Our research group has extensively studied the possibility of using commercially available ligands to  
79 rapidly extract radionuclides [10, 12, 13]. Only commercially obtainable ligands were investigated since  
80 these ligands simplified the PLF manufacturing process by eliminating ligand synthesis. Also, it was more  
81 cost effective and provided consistency in a large scale batch. These ligands were formed into a polymer  
82 thin film similar to the ones used by Wang [19]. Di(2-ethyl hexyl) phosphoric acid (HDEHP) and bis(2-  
83 ethylhexyl) methanediphosphonic acid (H<sub>2</sub>DEH[MDP]) ligands were both examined for radionuclide  
84 extraction in a PLF form. H<sub>2</sub>DEH[MDP], which contains the diphosphonic group, is known to effectively  
85 retain alkaline earth metals and actinides, particularly for tetra and hexavalent oxidation states [20, 21].  
86 Diphosphonic acids form strong complexes with metal ions through ionized phosphonic acid groups and  
87 P=O groups [22]. The chemical structure of Bis(2-ethylhexyl) methanediphosphonic acid (H<sub>2</sub>DEH[MDP])  
88 is shown in Figure 1. In previous H<sub>2</sub>DEH[MDP] studies, several extraction conditions were examined to  
89 find an optimal condition for plutonium and americium extraction. H<sub>2</sub>DEH[MDP] based PLF was effective  
90 in extracting plutonium and americium from the 0.1 M nitric acid solution [12].



91  
92 **Fig. 1** Chemical structure of H<sub>2</sub>DEH[MDP]

93 Several polymers were examined as a structure backing for ligands, and polystyrene has shown the best  
94 combination of analyte recovery and alpha spectra resolution [13]. The resolution of  
95 H<sub>2</sub>DEH[MDP]+polystyrene PLF was consistently better than PLFs based on nitrocellulose and  
96 poly(propylene) filter. Although many studies had been carried out on H<sub>2</sub>DEH[MDP] PLF, our group had  
97 not performed an in-depth extraction dependency study on solution acidity. H<sub>2</sub>DEH[MDP] ligand is  
98 extremely effective for actinide separation in a wide range of nitric acid concentration in resin bead form  
99 [23]. However, the extraction behavior may differ in PLF than in resin beads, and it is essential to find the  
100 best nitric acid concentration for analyte extraction.

101 Multiple PLFs were prepared on stainless steel substrates and used to test for plutonium and uranium  
102 extraction capability of the PLF system. The optimum analyte extraction conditions were found by  
103 changing the nitric acid concentration in tracer solution and the amount of extractants in PLF. Analyte  
104 extraction dependency on an equilibration time was also examined to optimize the exposure time. All the  
105 samples prepared in this experiment were examined using alpha spectroscopy, and high quality alpha  
106 spectra were obtained with minimal sample preparation steps.

## 107 **Experimental**

### 108 *Materials*

109 Bis(2-ethylhexyl) methanediphosphonic acid (H<sub>2</sub>DEH[MDP]) was obtained from Eichrom Technology  
110 Inc. No further purification was done to the ligands. Aqueous solutions were prepared using nitric acid  
111 from Fisher Scientific, and ultrapure deionized water was obtained from Barnstead Fi-Stream II Glass Still  
112 purification system. Tetrahydrofuran (THF) was obtained from Acros Organics. Polystyrene beads were  
113 obtained from Sigma-Aldrich. Polystyrene beads were not cross linked and density was 1.05 g/mL. <sup>239</sup>Pu  
114 tracer and natural uranium were obtained from Eckert & Ziegler Isotope Products Inc.

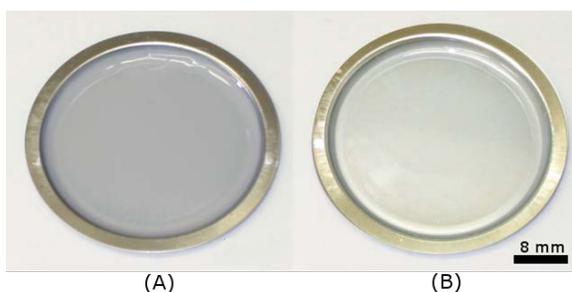
### 115 *Alpha Spectroscopy*

116 An Octet Plus system from Ortec, equipped with 900 mm<sup>2</sup> ion implanted silicon detectors, was used in the  
117 entire experiment performed in this study. The manufacturer's rated resolution for the detectors was 27 keV  
118 FWHM for <sup>241</sup>Am at 5.486 MeV energy. Each detector was for calibrated energy and efficiency using a  
119 secondary NIST traceable source. Samples were counted on the top shelf, 4 mm away from the detector

120 surface, for a minimum of 1440 minutes each to measure plutonium activity. Alpha spectroscopy data was  
121 analyzed using Bortels' single tail alpha peak fitting algorithm [24].

### 122 *PLF Preparation and Experimental Conditions*

123 Polymer ligand films were prepared by incorporating H<sub>2</sub>DEH[MDP] in the polystyrene structure. The  
124 stock solution was prepared by dissolving the ligands and the polystyrene beads in Tetrahydrofuran (THF).  
125 Once the stock solution was prepared, it was directly deposited onto a 40 mm diameter stainless steel  
126 substrate. The deposited solution was air dried at room temperature overnight to evaporate THF and form a  
127 solid film. PLFs prepared with solvent casting deposited about 220 mg of film after evaporation of THF.  
128 The physical appearance of the PLFs changed depending on the amount of ligand in the film. The  
129 polystyrene used is clear in its natural form and the ligand is the only component causing the color change.  
130 Typically the films become more opaque with increasing ligand mass. An image of the PLFs is shown in  
131 Figure 2, where (A) has larger amount of ligand used compared to (B). More detailed PLF preparation  
132 method was discussed in detail previously<sup>10–12</sup>. Five PLF compositions were tested to find the optimum  
133 PLF for plutonium extraction. The PLF composition is described as the ratio between ligand and the entire  
134 solid mass. For example, PLF with one part ligand and one part polystyrene was assigned 1:2 (w/w) ratio.  
135 The ratios tested in this experiment were 1:5, 1:10, 1:15, 1:20 and 1:25 (wt/wt). 1:2 PLF was also prepared  
136 for the study, but it did not form a solid film and was excluded from any testing. The amount of polystyrene  
137 was kept constant in all four ratios but the mass of ligand in the solution was adjusted.



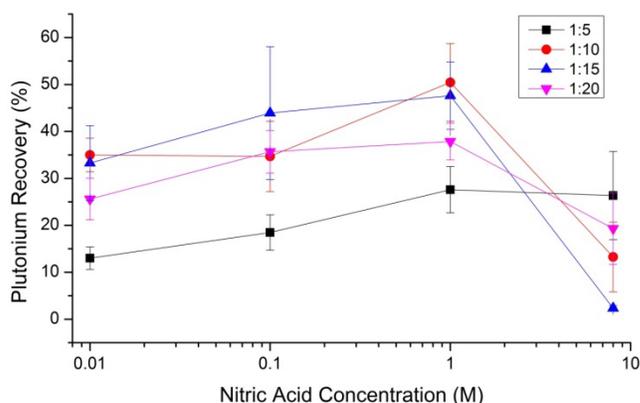
138 (A) (B)  
139 **Fig. 2** (A) 1:5 H<sub>2</sub>DEH[MDP] PLF and (B) 1:25 H<sub>2</sub>DEH[MDP] PLF

140 H<sub>2</sub>DEH[MDP] PLFs were tested over 0.01 to 8M nitric acid solutions to generate a plutonium extraction  
141 performance. <sup>239</sup>Pu solutions used in this study were prepared with 0.01, 0.1, 1, or 8M nitric acid solution.  
142 Plutonium tracer solution was first dried on a hot plate then re-dissolved in a concentration adjusted nitric  
143 acid solution. Plutonium activity per volume was approximately 3 dpm/ml. For the PLF testing, 2.5 to 3mL  
144 <sup>239</sup>Pu tracer was directly stippled on the PLF surface, allowing the analyte to equilibrate for 3 hours before  
145 removing the solution. The solution volume was selected to cover the entire PLF surface. Some of the  
146 tracer solution evaporated during the equilibration time and 1 to 2 ml of solution was remaining on the PLF  
147 substrate after 3 hours. After removing the tracer solution, PLFs were thoroughly rinsed with deionized  
148 water to remove any nitric acid remaining on the surface and to remove any tracer that was not bound to the  
149 surface. PLFs were then allowed to air dry to remove any water that may have been left on the polymer

150 medium. The plutonium activity of each sample was measured by direct alpha counting to quantify the  
151 plutonium recovery by H<sub>2</sub>DEH[MDP] PLF.

## 152 Results and Discussion

153 The plutonium recovery by H<sub>2</sub>DEH[MDP] PLF showed a dependency both on the nitric acid concentration  
154 and the composition of the polymer film. H<sub>2</sub>DEH[MDP] PLF was able to extract plutonium in all nitric  
155 acid concentrations tested as shown in Figure 3. 1:10, 1:15, and 1:20 PLFs were all effective in plutonium  
156 extraction from 0.01 to 1M nitric acids. The highest recovery for these PLFs all occurred at 1M tracer  
157 solution. The percent recoveries were 50.44±8.27 and 47.61±7.17 for 1:10 and 1:20 PLF, respectively.



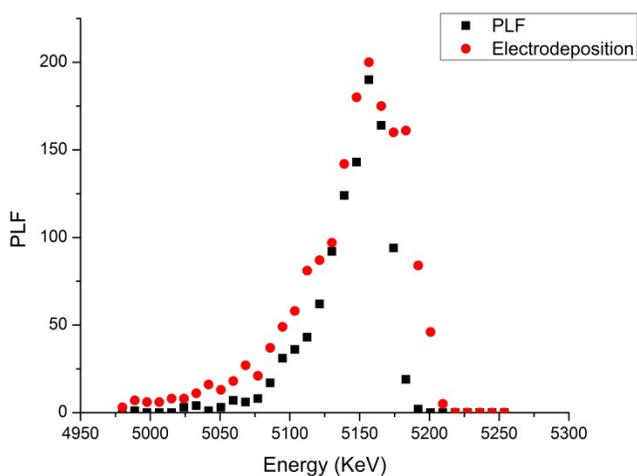
158  
159 **Fig. 3** The baseline performance of H<sub>2</sub>DEH[MDP] PLF in plutonium extraction as a function of nitric acid  
160 concentration

161 The plutonium recovery for 1:5 PLF was noticeably lower than the other PLFs from 0.01 to 1M. However,  
162 the recovery was higher at 8M than other PLF types tested. 1:25 PLFs were also tested but those were  
163 unstable and showed a tendency to develop bubbles while in the vacuum chamber of the alpha  
164 spectroscopy system. About 90% of the 1:25 PLFs developed bubbles, and in some cases the polymer film  
165 shattered into pieces. The bubbles were believed to have been caused by gas trapped in the polymer  
166 structure, most likely THF. Larger ligand content in the PLF is believed to provide more porous surface for  
167 gas to escape from the polymer structure. In the 1:25 PLF, which contained the lowest amount of ligand,  
168 large amount of gas was being trapped during the PLF synthesis due to inadequate venting. Once vacuum  
169 was applied, the trapped gas in the PLF expanded and caused a ballooning effect on the surface as it  
170 escaped from the polymer structure. Due to the stability issue, 1:25 data was not included in Figure 3.

171 It was expected for 1:5 H<sub>2</sub>DEH[MDP] PLF to have the highest recovery due to having a higher number of  
172 ligands presented in the PLF compared to the other PLF compositions tested. The ligand is the only  
173 component within the PLF to have any significant affinity to plutonium, and the more ligands meant more  
174 binding sites for plutonium<sup>11</sup>. This result clearly showed that the plutonium extraction was not only  
175 dependent on the amount of ligand presented in the PLF but many other factors, such as ligand orientation,

176 ligand complexation, and plutonium oxidation state. Plutonium has five oxidation states, and up to four  
177 different oxidation states can co-exist in a solution [25]. It was impossible to measure the plutonium  
178 oxidation states in the solutions used in the experiment due to low plutonium quantity in each solution.  
179 However, it is suspected that both +3 and +4 oxidation states co-exist in the tracer solution [25]. The  
180  $H_2DEH[MDP]$  have shown effectiveness in both Pu(III) and Pu(IV). The  $H_2DEH[MDP]$  ligands are  
181 theorized to form various length complexes with each other as the PLF is synthesized and plutonium  
182 extraction behavior changes based on the length of the complex. This means that certain complexes are  
183 only effective for Pu(III) extraction, and the other complexes are only effective for Pu(IV). More ligands in  
184 the stock solution seems to cause  $H_2DEH[MDP]$  to form complexes that are mostly effective for Pu(IV)  
185 extraction. As the amount of ligand in the stock solution decreases, two distinctive ligand complexes form,  
186 one for Pu(III) and the other for Pu(IV). Another possible explanation for the plutonium extraction  
187 behavior observed is that nitric acid is changing the orientation of ligands to be more favorable for  
188 plutonium extraction at certain nitric acid concentrations. For example, ligands in 1:10, 1:15, and 1:20  
189 PLFs are oriented more favorably for plutonium extraction at 0.1 or 1M nitric acid.

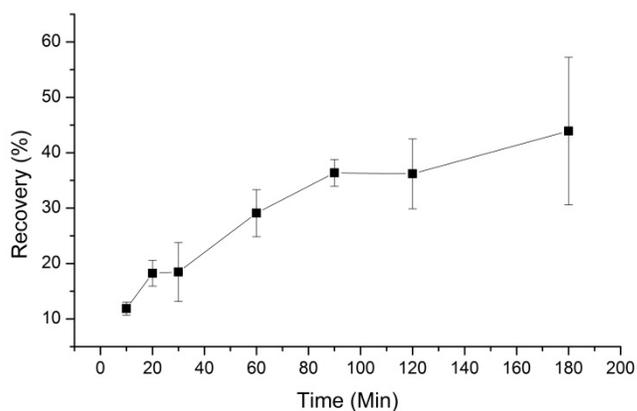
190 The quality of alpha spectra obtained from the PLF system was compared to one from electrodeposited  
191 sample. Figure 4 was plotted with normalized count data from PLF and electrodeposited samples. Both  
192 spectra had similar resolution and tailing characteristics. 1:10, 1:15, and 1:20 PLFs were all suitable for  
193 plutonium extraction. Out of three compositions, 1:20 used the least amount of  $H_2DEH[MDP]$  ligands to  
194 manufacture PLFs, which makes it more cost effective.



195  
196 **Fig. 4** PLF and electrodeposition sample alpha spectra comparison

197 The equilibration time of 3 hours was used to generate a baseline for plutonium extraction behavior for the  
198  $H_2DEH[MDP]$  PLF. The time was chosen to provide enough time for ligands to form complexes with the  
199 plutonium. However, the PLF method is being developed to rapidly process samples, and it is a key to have  
200 the shortest equilibration time possible. It is important to examine plutonium extraction dependency on  
201 equilibration time to decrease analysis time. In this experiment, 1:20  $H_2DEH[MDP]$  PLF was tested with

202 0.1M nitric acid. The extraction condition was kept consistent throughout the experiment except for the  
203 exposure time. The exposure times used in this experiment were from 10 to 180 minutes. The plutonium  
204 recovery linearly increased from 10 to 90 minute exposure time then started to level off after 90 minute  
205 exposure time as shown in Figure 5. The maximum plutonium recovery of 44% was achieved at 180  
206 minute equilibration time. However, the standard deviation at 180 minute exposure time was larger than  
207 other measurements. 90 and 120 minutes recoveries were within the standard deviation of the 180 minutes  
208 recovery. Student's t-test was performed to confirm and assess the statistic difference between plutonium  
209 recoveries between 90 to 180 minutes. The recoveries measured at 90 and 120 minutes exposure time was  
210 statistically indifferent from the 180 minutes measurement at 95% confidence level.

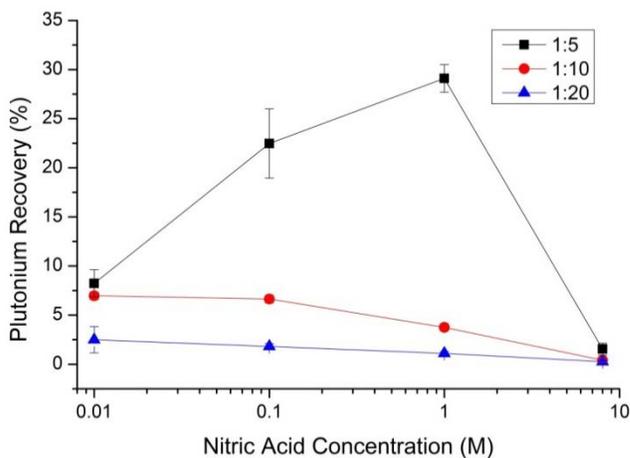


211  
212 **Fig. 5** H<sub>2</sub>DEH[MDP] PLF plutonium recovery at different exposure time

213 The most important aspect that can be gathered from the time study is that the PLF was able to extract  
214 plutonium even at 10 minute equilibration time. The recovery was only slightly higher than 10%; however,  
215 even 10% may provide sufficient activity to perform a radiometric analysis depending on the sample  
216 activity. In a post-detonation situation, sample activity near ground zero is expected to be high enough for  
217 even a very short equilibration time to extract enough plutonium for a radiometric analysis. In the case of  
218 environmental samples, which typically have low activity, 10% recovery would likely only allow  
219 qualitative analysis using radiometric techniques. However, if the PLF technique is only used as a  
220 screening method before performing a more precise analysis, such as mass spectroscopy, a qualitative  
221 analysis will provide adequate information to select critical samples and shorten the total analysis time.

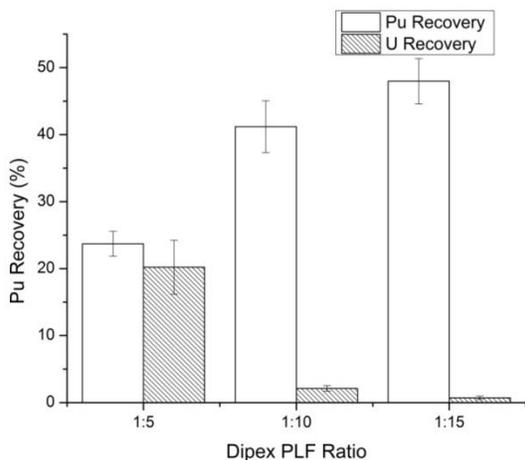
222 H<sub>2</sub>DEH[MDP] was designed for an actinide group separation and also showed high affinity for uranium.  
223 Since uranium alpha spectra peaks are well separated from plutonium peaks, it is possible to co-extract  
224 plutonium and uranium onto PLF then perform alpha spectroscopy to qualify. PLFs were examined for  
225 uranium extraction using a natural uranium tracer. The condition tested for uranium extraction was the  
226 same as the baseline plutonium experiment; 1:5, 1:10, and 1:20 H<sub>2</sub>DEH[MDP] PLFs were tested over 0.01  
227 to 8M nitric acid solutions. The uranium extraction behavior was entirely different than the plutonium  
228 extraction. Neither 1:10 nor 1:20 PLF was effective in uranium extraction over all nitric acid ranges tested.  
229 1:5 PLF showed the highest recovery of ~30% with 1M nitric acid as shown in Figure 6. Also, about 22.5%

230 of uranium was extracted using 1:5 PLF at 0.1M nitric acid. Data shows that H<sub>2</sub>DEH[MDP] PLF can be  
 231 used to selectively extract plutonium over uranium or simultaneously extract uranium and plutonium by  
 232 changing the composition of the PLF. For example, with 1:5 PLF, uranium can be co-extracted along with  
 233 plutonium at 0.1 or 1M nitric acid. At the same nitric acid concentration, 1:20 PLF can be used to extract  
 234 plutonium over uranium.



235  
 236 **Fig. 6** Uranium recovery by H<sub>2</sub>DEH[MDP] PLF as function of nitric acid concentration

237 The analyte selectivity based on PLF composition was further verified in the co-extraction experiment by  
 238 using mixed uranium and plutonium tracer solution. The mixed tracer solution was prepared by drying  
 239 <sup>239</sup>Pu and natural uranium then re-dissolved in 1M nitric acid. The standard PLF testing procedure was used  
 240 with the mixed tracer solution. 4.95 dpm of plutonium and 5.24 dpm of uranium were used to prepare each  
 241 sample. The experiment confirmed that H<sub>2</sub>DEH[MDP] PLF is capable of co-extracting or selectively  
 242 extracting plutonium over uranium depending on the PLF composition. Plutonium and uranium percent  
 243 recovery by each PLF is shown in Figure 7. 1:5 H<sub>2</sub>DEH[MDP]PLF simultaneously extracted 23% of  
 244 plutonium and 20% uranium. However, neither 1:10 nor 1:20 PLFs showed any affinity to uranium and  
 245 selectively extracted plutonium over uranium.



246  
 247 **Fig. 7** H<sub>2</sub>DEH[MDP] PLF Pu and U extraction efficiency with 1M nitric acid

248           **Conclusions**

249       The PLF method is a great screening tool to deploy to decrease the number of samples required for more  
250       extensive analysis. The entire sample preparation to analysis was done within one to two days. Compared  
251       to the PLF method, the classical method for alpha samples takes two days to a week. The exact analysis  
252       time may vary as the counting time may have to be adjusted depending on the sample activity. The  
253       technique also requires minimal chemicals, and it is field deployable. The reduction in time and simplified  
254       procedure make this technique ideal for the post-detonation emergency response.

255       H2DEH[MDP] PLFs were effective in plutonium and uranium extraction. 1:10, 1:15, and 1:20 PLFs  
256       showed similar plutonium extraction behavior. Since 1:20 H2DEH[MDP] PLF was most cost effective,  
257       most experiments were performed with 1:20 PLFs. Close to 50% of plutonium was extracted by 1:20 PLF  
258       with 1M nitric acid. H2DEH[MDP] PLF showed consistency similar to the electrodeposited samples. The  
259       overall analyte recovery was lower than the electrodeposited samples. However, PLF is designed to be a  
260       rapid field deployable screening technique, and consistency is more important than the recovery.  
261       H2DEH[MDP] PLF was capable of co-extracting or selectively extracting plutonium over uranium  
262       depending on the PLF composition. With 1:5 PLF, about 23% of plutonium and 20% uranium were  
263       simultaneously extracted with 1M nitric acid. 1:10 and 1:20 PLFs preferably extracted plutonium over  
264       uranium with 1M nitric acid. The uranium alpha spectra peaks were well separated from the plutonium  
265       peaks, and it was possible to perform isotopic measurements.

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