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Radionuclide Extraction by Ionic Liquids

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Marzieh Habibi

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Betreut von: Ao. Univ.-Prof. Mag. Dr. Gabriele Wallner

Zusammenfassung

Die Entfernung von radioaktivem Material aus Trinkwasser und Abwässern stellt ein großes Problem dar, da Radionuklide sehr gefährlich für die Umwelt und die Gesundheit der Menschen sein können. Neu entwickelte Substanzen, wie zum Beispiel Ionische Flüssigkeiten, können dazu verwendet werden, Metallionen und somit auch Radionuklide aus Abwässern zu extrahieren.

Ionische Flüssigkeiten bestehen aus einem organischen Kation und einem organischen oder anorganischen Anion, die die Eigenschaften der ionischen Flüssigkeit bestimmen. Ionische Flüssigkeiten sind bei Raumtemperatur flüssig. Sie können bis zu einer Temperatur von 300° C flüssig bleiben. Zudem können Experimente mit diesen Flüssigkeiten auf Grund ihres niedrigen Dampfdrucks auch bei höheren Temperaturen ohne Substanzverlust durchgeführt werden.

Im Rahmen dieser Masterarbeit werden vier Ionische Flüssigkeiten verwendet, die zwei verschiedene aromatische Anionen mit unterschiedlichen funktionalen Gruppen aufweisen, wie zum Beispiel Amine, Hydroxyl, und Nitro, und zwei verschiedene Kationen mit langer quaternärer Phosphonium- oder Ammonium-Kette. Die Fähigkeit dieser ionischen Flüssigkeiten zur Extraktion von UO_2^{2+} , Th^{4+} , Pb^{2+} und Po^{4+} aus wässrigen Lösungen in Abhängigkeit vom pH-Wert wird untersucht (Flüssig-Flüssig-Trennverfahren).

Eine Ionische Flüssigkeit mit hoher Uran-Extraktionsfähigkeit wurde auch auf Aktivkohle immobilisiert. Es konnte in Batch-Versuchen gezeigt werden, dass auch in dieser Form ihre gute Extraktionseigenschaft erhalten blieb.

Da die Ionischen Flüssigkeiten nach Möglichkeit wiederverwendet werden sollen, wurde versucht, die Radionuklide mit verdünnter HNO_3 -Lösung wieder aus den Ionischen Flüssigkeiten zurückzuextrahieren. Generell wurde bei guter Extrahierbarkeit eines Radionuklids zumindest mit HNO_3 -Lösung nur eine geringe Rückextrahierbarkeit beobachtet.

Abstract

The removal of radioactive materials from drinking water and wastewater is a huge problem, as these radionuclides are very dangerous for the environment and human health. There are new substances called Ionic Liquids, which are able to extract radionuclides from aqueous solutions and consist of two parts, namely an organic cation and an organic or inorganic anion. The properties of ionic liquids depend on the cation and anion composition.

Ionic liquids are liquid at room temperature. They have liquid ranges of over 300°C and experiments can be carried out with these solvents at high temperatures without any solvent degradation.

In this thesis four ILs, which have two different aromatic anions with various functional groups, for example Amine, Hydroxyl, Nitro and two different cations with long chain quaternary phosphonium or ammonium, were studied with regard to the extraction of UO_2^{2+} , Th^{4+} , Pb^{2+} and Po^{4+} from aqueous solutions with different pH-values (liquid-liquid extraction).

The Ionic Liquid with the best uranium extraction efficiency was immobilized on activated Carbon (AC). Batch-experiments have shown high extraction values also under these conditions.

As the Ionic Liquids should be reused in order to minimize costs of production and waste, back extraction of the radionuclides with HNO_3 -solutions was investigated. Generally back extraction with this medium was low when the radionuclides had been extracted with high efficiencies.

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I Introduction

There are different anthropogenic radionuclide sources, such as nuclear power generation, nuclear weapons production, nuclear medicine, mining, oil and gas production and scientific research (United Nations, 2013). These are radioactive isotopes from man-made sources, but there are also naturally occurring radioactive isotopes. Radionuclides naturally present in the environment, such as ^{238}U , ^{235}U and ^{232}Th are found in the lithosphere and constitute radioactive decay chains (AWWA Research Foundation, 2002). Additionally, natural uranium ($\text{U}_{\text{nat.}}$) comprises also ^{234}U , often in radioactive equilibrium with ^{238}U .

Natural radionuclides can also be found in groundwater due to leaching from the rock material, while surface water may contain radioactive substances due to man-made pollution additional to natural radionuclides deposited from the air (as e.g. ^{210}Pb and daughter products). (AWWA Research Foundation, 2002) During decay they release ionizing radiation in the form of alpha particles, beta particles, and gamma rays. Ionization can damage living tissue and damage in DNA can consequently cause genetic mutations, which could be passed on to future generations (Magill and Gally, 2005). Especially alpha particles with their high ionization density may cause damage if incorporated; external exposure doesn't risk one's health because of the low range of alphas (about 3 cm in air, about 0.04 mm in tissue). (Furr, 2000)

The incorporation of radionuclides into target organs can occur within a few hours after intake by inhalation or ingestion. (Powers and Daily, 2010) Considering Uranium, one of the elements investigated in this thesis, the intake through food is dominant. When water, which is an essential foodstuff, contains elevated levels of uranium, the majority of intake can be from ingestion of drinking water. "Absorption of uranium from the gastrointestinal tract is low and depends on solubility of the particular uranium compounds. Over 95 percent is eliminated in the feces and two-third of the adsorbed fraction is filtered by the kidney and excreted in the urine in 24 hours. Uranium within the body deposits at bone surfaces and is slowly cleared via blood and kidneys with a half-life of up to one year" (Blair, 2010).

So, for Uranium, the target organs are the kidneys, so usually kidney toxicity can be seen, however no radiological damage has been reported (WHO, 2003). This is due to extremely long half-life of uranium and corresponding very low specific activities (the specific activity is inversely proportional to the half-life). (Committee on Toxicology, 2008)

^{234}Th is a short lived daughter product of ^{238}U and it is formed from ^{238}U by alpha emission (Stoker, 2012). We investigated it in place of the much more abundant ^{232}Th . By breathing or swallowing a small amount of Thorium it can enter the bloodstream and be deposited in the bones where it may remain for 20-30 years (Dikshith, 2013). Therefore, bone cancer is also a potential concern for people exposed to Thorium. Breathing Thorium dust may cause an increased chance of developing lung disease and cancer of the lung or pancreas many years after being exposed (Agency for Toxic Substances and Disease Registry, 1990).

^{210}Pb , often also abundant in water, is a beta-emitter. When lead gets into the body it travels by bloodstream to the bones. (Agency for Toxic Substances and Disease Registry, 2007)

^{210}Po , a ^{210}Pb progeny, is a very radiotoxic alpha-emitter. If it is swallowed or inhaled in very small amounts, such as a microgram, it can cause death (Health Physics Society, n.y.). Once absorbed into the body, it can be many times more toxic than cyanide. The alpha radiation can rapidly destroy major organs, DNA and the immune system. (United States Nuclear Regulatory Commission, 2014)

So irrespective of treating radioactive waste materials from industry and commerce, an important topic of public concern is the removal of (natural) radionuclides from drinking water.

The application and variety of ionic liquids (IL) have increased during the last few years; e.g. they can remove metals from waste water streams. Also different radionuclides, for example Uranium, ^{210}Pb , ^{210}Po and ^{234}Th could be separated from the aqueous solution by ionic liquids (Srncik et al., 2009; Platzer et al., 2014).

The metal can be extracted from the aqueous phase to the organic phase (i.e. to the IL) at room temperature (Nash and Lumetta, 2011). As can be seen in Table 1, four different ionic liquids were used in this thesis for liquid-liquid separation to determine the respective ability to extract metal ions from the aqueous solution. The ionic liquids used in this study are supplied by colleges of the Institute of Inorganic Chemistry of Vienna University.

In a second step one of the investigated ILs was immobilized on activated carbon. We expected easier handling of the viscous ILs when immobilized on a solid.

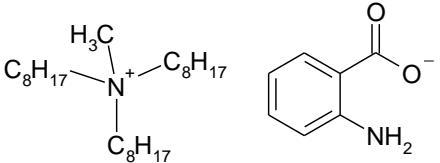
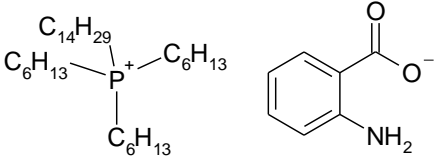
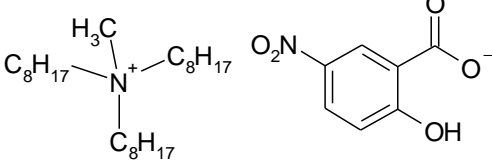
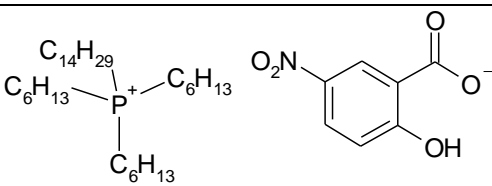
Lab-ID	Structure	Compound	MF	MW (g/mol)
Rale003		[A336][Ant] Trioctylmethylammonium anthranilate	C ₃₂ H ₆₀ N ₂ O ₂	504.84
Rale006		[PR4][Ant] Trihexyltetradecylphosphonium anthranilate	C ₃₉ H ₇₄ NPO ₂	619.99
Rale017		[A336][HNBA] Trioctylmethylammonium 2-hydroxy-5-nitrobenzoate	C ₃₂ H ₅₈ N ₂ O ₅	550.83
Rale018		[PR4][HNBA] Trihexyltetradecylphosphonium 2-hydroxy-5-nitrobenzoate	C ₃₉ H ₇₂ NPO ₅	665.98

Table 1: Ionic liquids used for the experiments. I received this formula from Ms. Raphlin Mirabeau Leyma

II Main Part

1. Ionic Liquids

Ionic liquids are a remarkable class of solvents. Most of them are liquid at room temperature. They have liquid ranges of over 300°C and experiments can be carried out with these solvents at high temperatures without any solvent degradation. The melting points of ionic liquids depend on the size of the anion or cation. If the size of the anion and cation is larger the melting point will decrease, so that small variations in the length of the alkyl chain in a cation can also lead to huge differences in the respective melting points (Freemantle, 2010).

The symmetry of the cation also influences the melting point. The melting point of the ionic liquids made from a small symmetric cation, such as 1,3-dimethylimidazolium cation with two methyl groups, is higher to those containing one methyl and an ethyl or larger alkyl group (Dunstan et al., 2004).

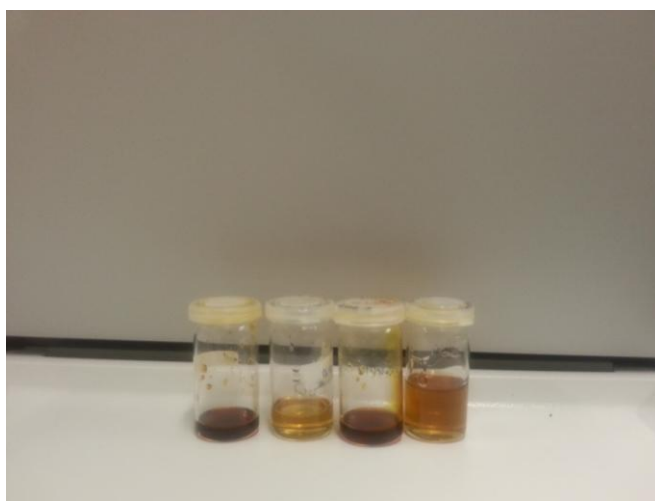


Figure 1: Ionic liquids investigated

Figure 1 shows the investigated ILs [A336][Ant], [PR4][Ant], [A336][HNBA] and [PR4][HNBA] (from left to right).

1.2 Radionuclides investigated

“Natural Uranium ($U_{\text{nat.}}$) consists of three isotopes, namely ^{234}U , ^{235}U and ^{238}U . All isotopes of uranium are radioactive. By far the most common is ^{238}U , making up about 99.276% of the mass of uranium found in the Earth's crust. ^{238}U also has longest half life, about $4,468 \times 10^9$ years.” (Chemistry Explained, 2015)

^{234}U has a half-life of 2.4×10^5 years and ^{235}U has a half-life of 7.1×10^9 years. ^{238}U (99.276%) and ^{235}U (0.7200%) are the parent nuclides of two independent decay series, while ^{234}U is a decay product of the ^{238}U series with 0.0055% mass abundance (Elderfield et al., 2006).

^{238}U decays by alpha emission to form the daughter nucleus ^{234}Th with a half-life of 24.1 days, which in turn transforms by beta-decay into ^{234}Pa with a half-life of 1.18 minutes that decays by beta emission to produce ^{234}U (Stoker, 2012). This means, that usually ^{234}U is in radioactive equilibrium with ^{238}U and showing the same activity, although its mass is much lower due to its much shorter half life. The nuclides under investigation in the “uranium solution” (or “uranyl solution”) are ^{238}U , ^{234}U and ^{234}Th . ^{235}U is not investigated because the mass percentage for ^{235}U is 0.72% compared to ^{238}U and this amount is negligible and not significant for the measurement. Investigation of ^{234}Pa is not possible because the half-life of ^{234}Pa is very short.

The second radionuclide solution investigated contains ^{210}Pb with a half-life of 22.3 a and its decay products. ^{210}Pb decays into ^{210}Bi (half-life: 5 d) by emitting a beta-particle, which in turn undergoes beta decay to ^{210}Po with half-life of 138.4 d. Then, ^{210}Po decays by alpha emission to form ^{206}Pb which is stable (Stoker, 2012).

Due to the short half-life of ^{210}Bi time correction of measurement results would be necessary; ^{210}Bi was not investigated in the frame of this thesis.

2. Experimental Part

2.1 Purification methods for (drinking) water

Besides the liquid-liquid extraction by ILs under investigation here, for water purification there are a lot of methods available, such as co-precipitation with iron hydroxide, adsorption or ion exchange. By the adsorption method the contaminants (water-soluble) are captured by sorption onto a solid phase (natural or synthetic) (Klasson and Taylor, 2009). "In adsorption processes, the contaminant is adsorbed on the surface of a solid particle or within the pores of the particles. In ion exchange, the radionuclides replaces [sic] another ion on the surface of a solid particle or within the pores of the particles." (Klasson and Taylor, 2009). In reverse osmosis, water is forced through a membrane with small pores by pressures ranging from 6 to 10 bar. Any molecules larger than the pore openings are excluded from the product stream along with a significant portion of the water (EPA (Environmental Protection Agency, 2015). Another method is stripping, which is only applicable for volatile contaminants, such as radon. Here the contaminated water is in contact with clean air degassing the volatiles (Klasson and Taylor, 2009).

2.1.1 Liquid-liquid extraction

To extract radionuclides from an aqueous solution, 10 mL of this solution containing uranyl UO_2^{2+} (or ^{210}Pb) together with their respective daughter products was mixed with an ionic liquid. After shaking and centrifugation, the phases were separated and the aqueous phase was analyzed with LSC.

The investigated ILs were Trioctylmethylammonium anthranilate [A336][Ant], Trihexyltetradecylphosphonium anthranilate [PR4][Ant], Tricaprylmethylammonium 2-hydroxy-5-nitrobenzoate [A336][HNBA], and Trihexyltetradecylphosphonium 2-hydroxy-5-nitrobenzoate [PR4][HNBA] Their structure is shown in Table 1.

2.1.2 Back Extraction Technique

The radionuclides taken up in the ionic liquid are back extracted into a 0.05 M nitric acid solution, which is again measured by LSC. Generally, the IL can be reused.

2.1.3 pH Setting

The samples containing different amounts of uranyl nitrate or ^{210}Pb in 10 ml distilled water were acidic (pH 3-4). For investigation of the pH dependency of the extraction step, the samples are brought to pH 2,4,6,7 and 8 with HNO_3 and NaOH , respectively.

2.2. Liquid Scintillation Counting (LSC)

For the measurement of the aqueous phase Liquid Scintillation Counting (LSC) is used. The aqueous sample is mixed with the LSC cocktail HiSafe III® (cf. Perkin Elmer). The aromatic solvent molecules will be excited through the energy released from a radioactive decay, the energy is next transferred to the scintillator (fluor). The energy absorbed through the scintillators produces excited states of the electrons, which decay to the ground state and produce a light pulse. The light is detected by the photomultiplier tube (PMT) of the liquid scintillation counter (Perkin Elmer).

Below is a schematic overview of the liquid scintillation counting process; we used a Quantulus 1220 LSC counter (Wallac Oy, Finland, now Perkin Elmer).

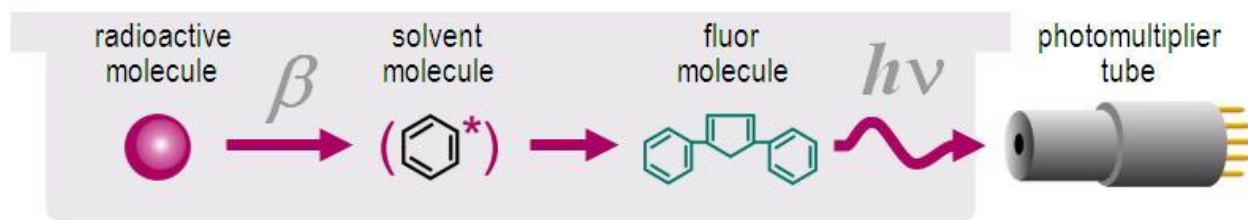


Figure 2: Schematic overview of LSC
(PerkinElmer, n.y.)

It is often required to measure mixtures of alpha and beta emitters. Beta radiation produces about ten times more light for the same amount of energy absorbed in a liquid scintillator than alpha radiation does. It results in a serious overlap of alpha and some energetic beta spectra. However, the pulse height spectra cannot separate alpha and energetic beta radiation (Dazhu et al., n.y.).

Nevertheless, the modern LSC counters optimize discrimination between alpha and beta radiations, due to different behavior of their pulse decay by using pulse shape

analysis (PSA) and measure them separately (PerkinElmer, n.y.). This can be done by a Time-Resolved Pulse Decay Analysis (TR-PDA).

“TR-PDA differentiates alpha from beta pulses according to their pulse decay characteristics. The pulse duration for alpha particles is typically longer than for betas. TR-PDA can run simultaneously with low level count modes, thereby achieving extremely low misclassification of beta and alpha particles, without compromising sensitivity.” (PerkinElmer, n.y.)

Figure 3 shows two spectra, one with a reasonably “sharp” peak generated by alphas and the other shows the typical broad peak from betas.

In each radionuclide solution investigated we had both alpha- and beta-emitters. In the “uranium solution” the alpha-emitters are ^{238}U , ^{234}U and ^{235}U (the amount of the latter is negligible and not significant for the measurement), and ^{234}Th is a Beta-emitter. ^{238}U , ^{234}U and ^{234}Th are in radioactive equilibrium, which means that each nuclide has the same activity. In the second solution ^{210}Po is an alpha-emitter and ^{210}Pb is a beta-emitter; again ^{210}Po is in radioactive equilibrium with ^{210}Pb .

Two factors influence radiation detection sensitivity: the geometry of the counting system and the energy of the radionuclide being measured. As the counting geometry is the same for all samples (20 mL vials), the kind and energy of the emitted radiation is the main factor in the LSC counting efficiency. Due to their high ionization density counting efficiency for alpha particles is always 100%, while betas are counted with lower efficiency. Natural alpha emitters have energies above 4 MeV and most beta emitters have maximum energies above 0.1 MeV (Krieger and Whittaker, 1980). Lower energy beta-emitters are detected with lower efficiencies than high energy beta-emitters. Because of this alpha and beta nuclides have different count rates in equilibrium of radioactivity. (Cooper et al., 2003)

Table 2 shows half-life, decay mode, decay energy (MeV) of the investigated radionuclides.

Nuclide	Half-Life	Decay Mode	Radiation energy (MeV)	
			Alpha (α)	Beta (β)
^{238}U	$4.5 \cdot 10^9$ a	α emission	4.2	
^{234}Th	24 d	β emission		0.2
^{210}Po	138.4 d	α emission	5.4	
^{210}Pb	22.2 a	β emission		0.06
^{234}U	$2.4 \cdot 10^5$ a	α emission	4.8	

Table 2: Nuclides investigated, their half-lives, decay modes, and energy of emitted particles

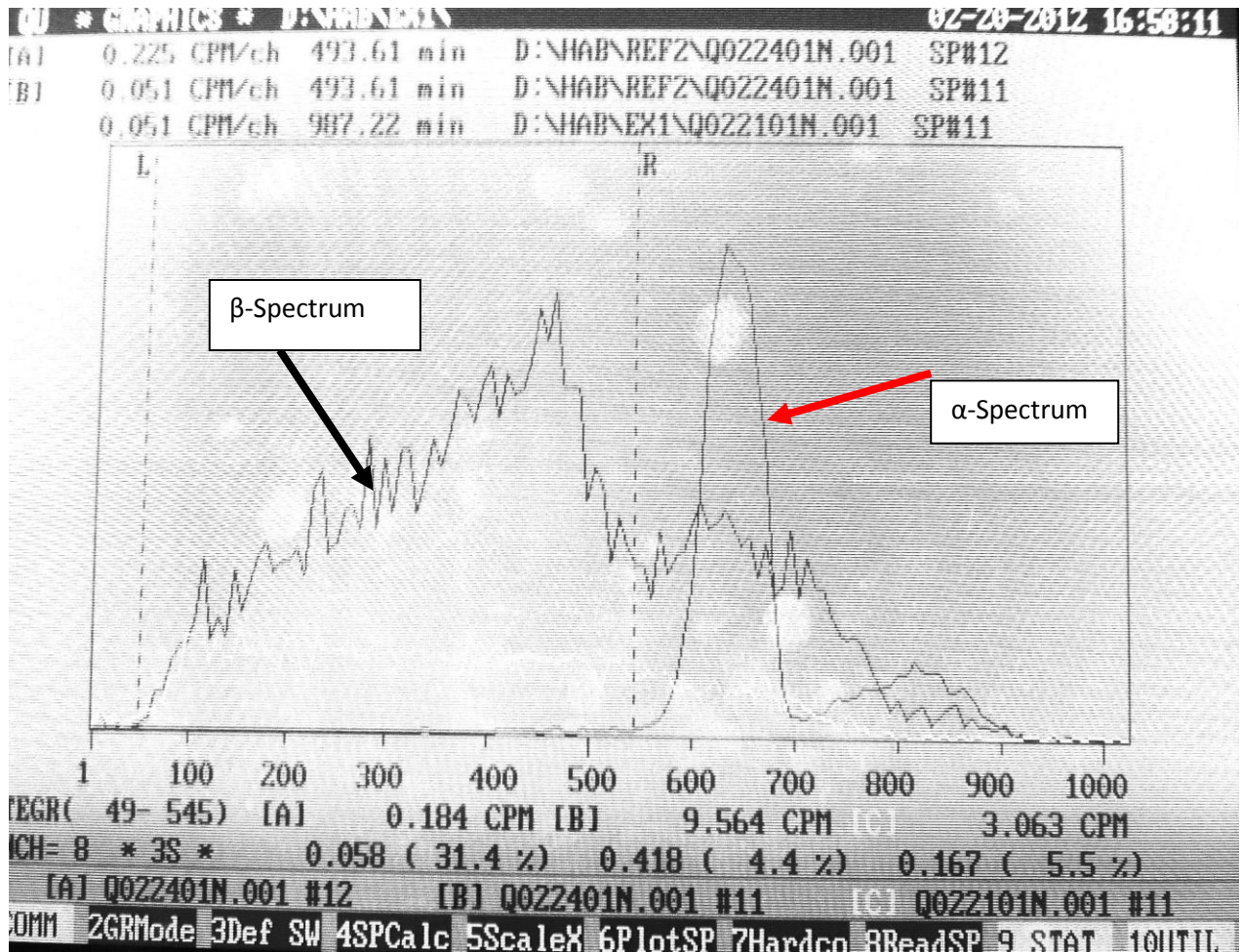


Figure 3: LSC spectra of ^{234}Th and $^{238,234}\text{U}$

2.3 Experiments

First of all, a blank sample was prepared: 3 ml distilled water was added to 17 ml cocktail and measured by LSC.

Then, the reference for uranium and ^{234}Th was prepared: 10 μl of uranium solution containing 0.344 Bq or 27.5 μg uranium was added to 3 ml distilled water and was then mixed with 17 ml Hisafe III cocktail and measured by LSC. The count rate of uranium (^{238}U and ^{234}U in radioactive equilibrium plus the negligible amount of ^{235}U) is 41 and of ^{234}Th it is 17 count per minute.

To prepare the reference for ^{210}Pb and ^{210}Po , 10 μL of ^{210}Pb solution containing 0.56 Bq ^{210}Pb and 0.56 Bq ^{210}Po was added to 10 ml distilled water. 3 ml of aqueous

solution was added to the 17 ml Hisafe III cocktail and measured by LSC. The count rate of ^{210}Pb is 26 and of ^{210}Po it is 33 counts per minute

The extraction experiments were done in the same way for all four investigated ILs. Five samples of uranyl solution and five samples of ^{210}Pb solution with the above given activities were prepared. These samples were brought to pH 2,4,6,7 and 8 with HNO_3 and NaOH and then 0.2 g of IL was added to the solution.

The aqueous solutions together with the ILs were shaken with 300 rpm overnight. Afterwards, they were centrifuged for one hour with 3000 rpm. When the layers were clearly separated, 3 ml of aqueous solution was mixed with 17 ml cocktail and the percentage of non-extracted uranium and ^{234}Th (or ^{210}Pb and ^{210}Po) was measured by LSC.

For the back extraction 20 ml 0.05 M nitric acid was added to the organic phase. After shaking the solution overnight and centrifuging it for about one hour, organic and aqueous phase were separated. Afterwards, 3 ml of the aqueous phase was mixed with 17 ml cocktail and the amount of back extracted uranium etc. was measured by LSC.

Each experiment was carried out at least twice. Then the average of the results was calculated and shown in the tables and the diagrams.

2.4 Experimental results: Extraction efficiency in dependence of pH

2.4.1 Experimental results for [A336][HNBA]

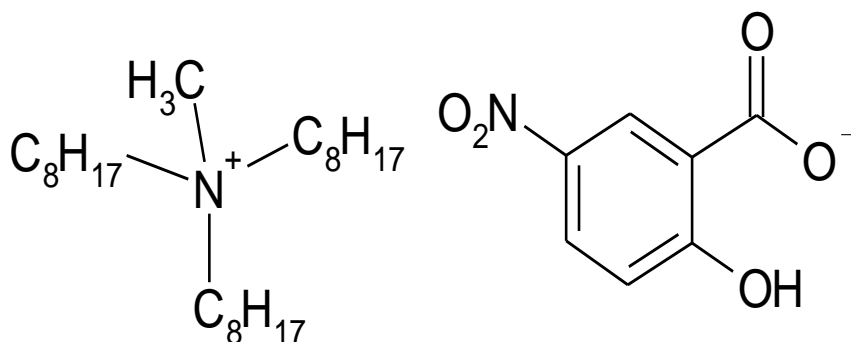


Figure 4: [A336][HNBA]

% Extraction					
[A336][HNBA]	pH	U	Th	Po	Pb
	2	100 ± 12%	12± 2%	98± 11%	23± 1%
	4	100 ± 11%	26± 2%	98± 14%	30± 1%
	6	100 ± 20%	21± 2%	99± 15%	30± 1%
	7	100 ± 15%	36± 3%	99± 16%	25± 1%
	8	100 ± 12%	25± 3%	97± 12%	25± 1%

Table 3: Extraction with [A336][HNBA]

As can be seen in Table 3 and Figure 5, [A336][HNBA] achieves complete extraction for Uranium and Polonium independent of pH values (average value of $100 \pm 14\%$ for U and $98 \pm 14\%$ for Po). The selectivity for Lead and Th for this agent is clearly lower between 20 % and 30 % (mean value $24 \pm 2\%$ for Th, and $27 \pm 1\%$ for Pb). The pH dependence of the extraction is rather low.

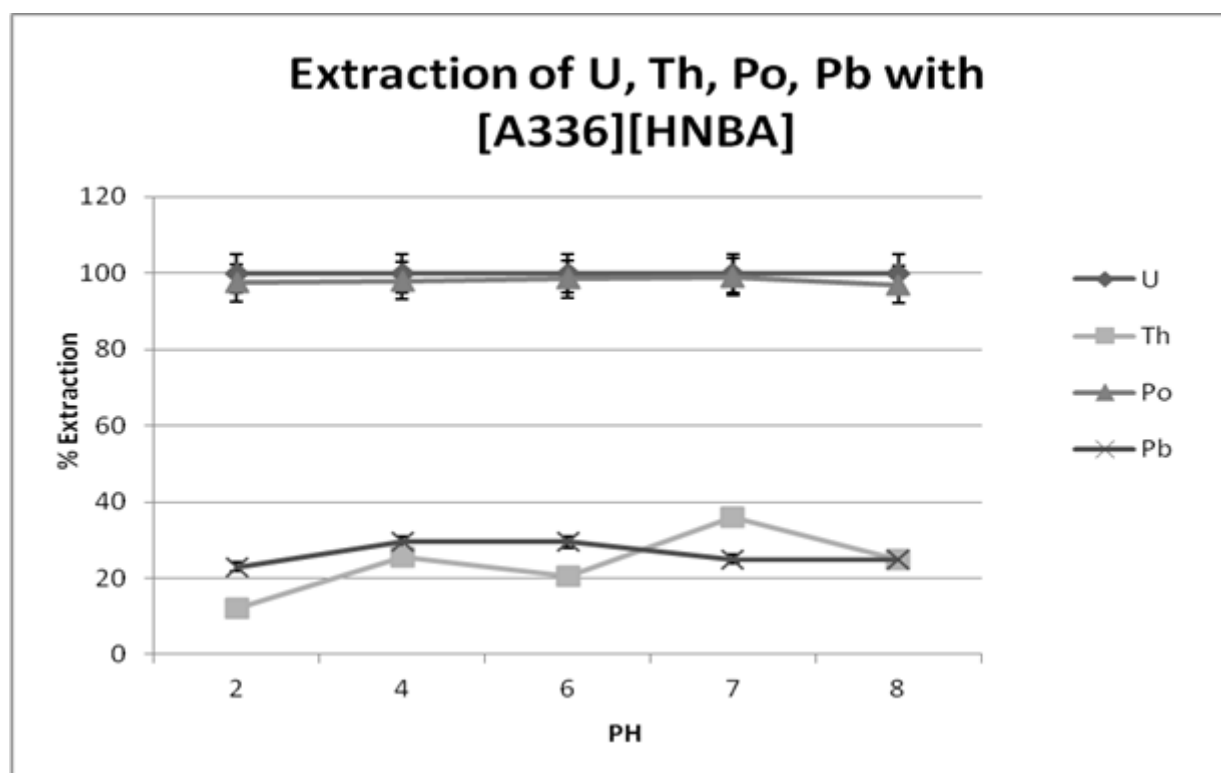


Figure 5: Extraction of U(VI), Th(IV), Po(IV), and Pb(II) extraction with [A336][HNBA]

% Back extraction					
[A336][HNBA]	pH	U	Th	Po	Pb
	2	16±3%	0	0	0
	4	13±3%	0	0	28±2%
	6	14±4%	0	0	61±9%
	7	17±4%	0	0	79±10%
	8	19±3%	0	0	87±9%

Table 4: Back extraction with [A336][HNBA]. The given pH value is the pH of the original solution, from where the radionuclides were extracted.

Po and Th could not be back extracted. The back extraction of U is very low with about 20%, while ^{210}Pb can be back extracted better than other radionuclides. The back extraction of lead is between 28 and 87%.

Table 4 and Figure 6 show the pH value of the radionuclide solution before extraction. This is done so that the back extraction results can be assigned to the extraction results. We do not know why the back extraction efficiency for ^{210}Pb depends on the pH of the original solution.

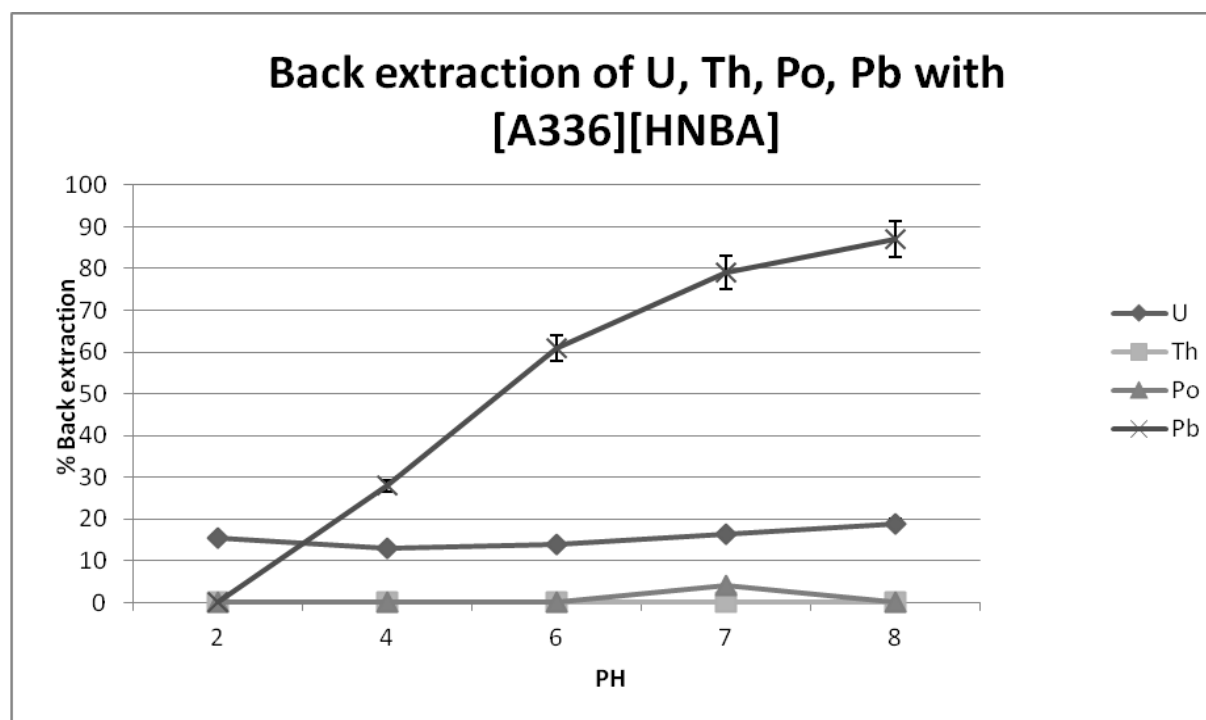


Figure 6: Back extraction of U(VI), Th(IV), Po(IV), and Pb(II) extraction with [A336][HNBA]

2.4.2 Experimental results for [A336][Ant]

Table 5 and Figure 8 show that the extraction of U gives a mean value of $96\% \pm 4\%$ (with the exception of $74 \pm 5\%$ value in pH of 2), while the extraction of Po gives a mean value of $93\% \pm 12\%$. The extraction of Th shows a mean value of $82\% \pm 4\%$, and of Lead a mean value of $39\% \pm 2\%$.

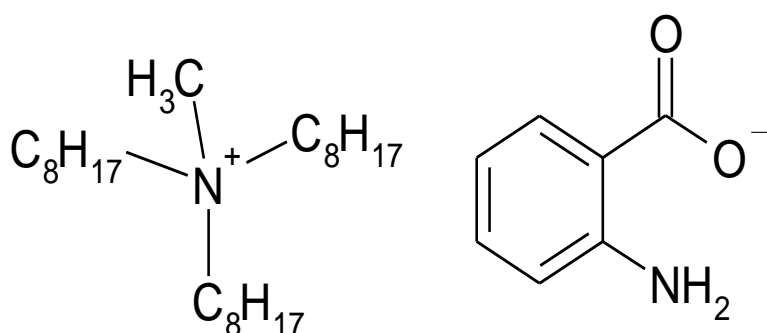


Figure 7: [A336][Ant]

% Extraction					
[A336][Ant]	pH	U	Th	Po	Pb
	2	$74 \pm 5\%$	$87 \pm 4\%$	$90 \pm 9\%$	$10 \pm 1\%$
	4	$94 \pm 7\%$	$82 \pm 5\%$	$96 \pm 14\%$	$76 \pm 2\%$
	6	$95 \pm 8\%$	$72 \pm 5\%$	$97 \pm 16\%$	$46 \pm 1\%$
	7	$96 \pm 8\%$	$86 \pm 5\%$	$91 \pm 10\%$	$31 \pm 2\%$
	8	$100 \pm 9\%$	$83 \pm 3\%$	$92 \pm 13\%$	$32 \pm 2\%$

Table 5: Extraction with [A336][Ant]

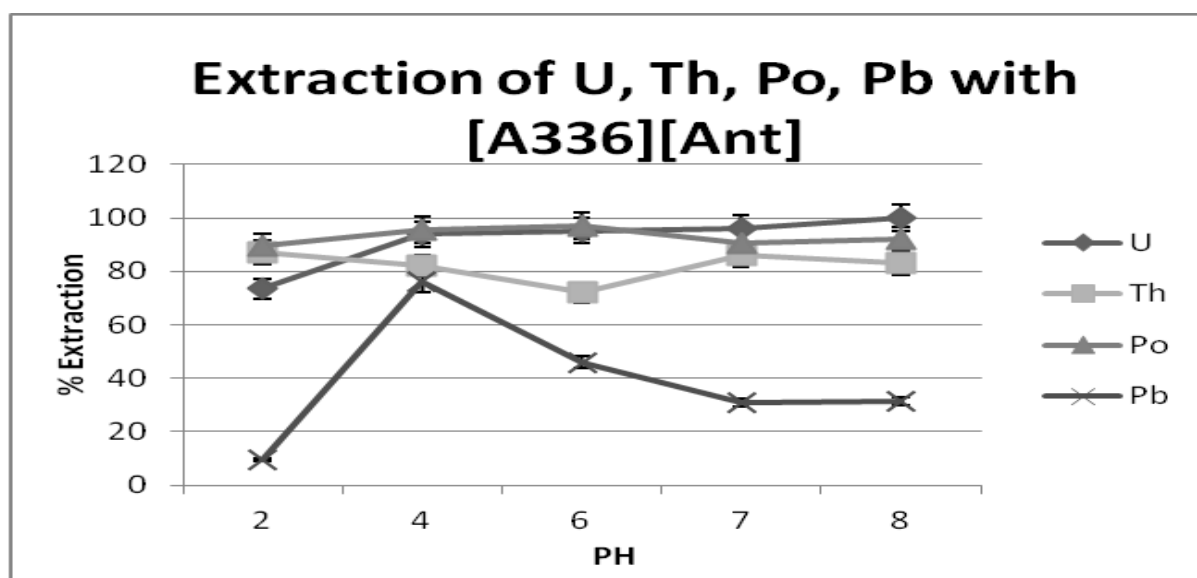


Figure 8: Extraction of U(VI), Th(IV), Po(IV), and Pb(II) extraction with [A336][Ant]

Summarizing, the extraction of U, Th and Po can be seen as satisfying, while the extraction of lead is only good with 76% at pH 4.

% Back extraction					
[A336][Ant]	pH	U	Th	Po	Pb
	2	92±11%	82±10%	2±1%	27±2%
	4	75±9%	92±8%	3±1%	83±10%
	6	68±9%	100±11%	2±1%	80±9%
	7	84±10%	91±8%	0±0%	50±3%
	8	91±12%	100±11%	2±1%	62±9%

Table 6: Back extraction with [A336][Ant]

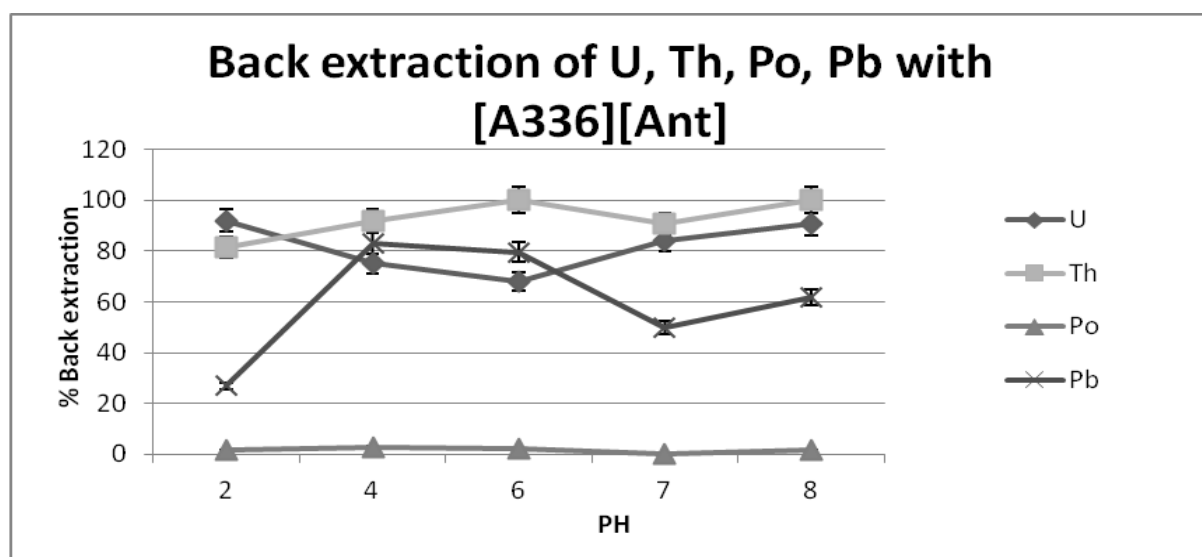


Figure 9: Back extraction of U(VI), Th(IV), Po(IV), and Pb(II) extraction with [A336][Ant]

Experimental data from Table 6 and Figure 9 shows that the back extraction of Uranium is between 68 and 92% and back extraction of Thorium is between 82 and 100%, but Polonium cannot be back extracted from this ionic liquid. Additionally, the back extraction of Lead is between 27 and 83%. Here again we do not know why the back extraction efficiency for ^{210}Pb depends on the pH of the original solution.

2.4.3 Experimental results for [PR4][HNBA]

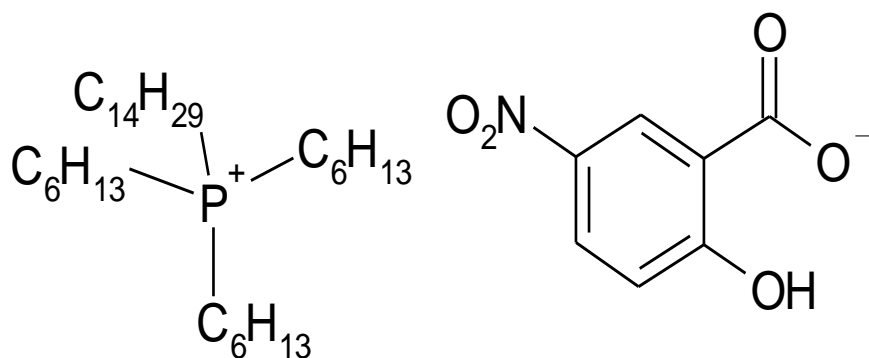


Figure 10: [PR4][HNBA]

% Extraction					
[PR4][HNBA]	pH	U	Th	Po	Pb
	2	100 ± 13%	95± 4%	99± 11%	26± 10%
	4	100 ± 14%	100± 4%	97± 11%	6± 10%
	6	100 ± 9%	84± 4%	97± 12%	14± 10%
	7	100 ± 15%	83± 5%	97± 11%	10± 10%
	8	100 ± 14%	69± 3%	98± 12%	0

Table 7: Extraction with [PR4][HNBA]

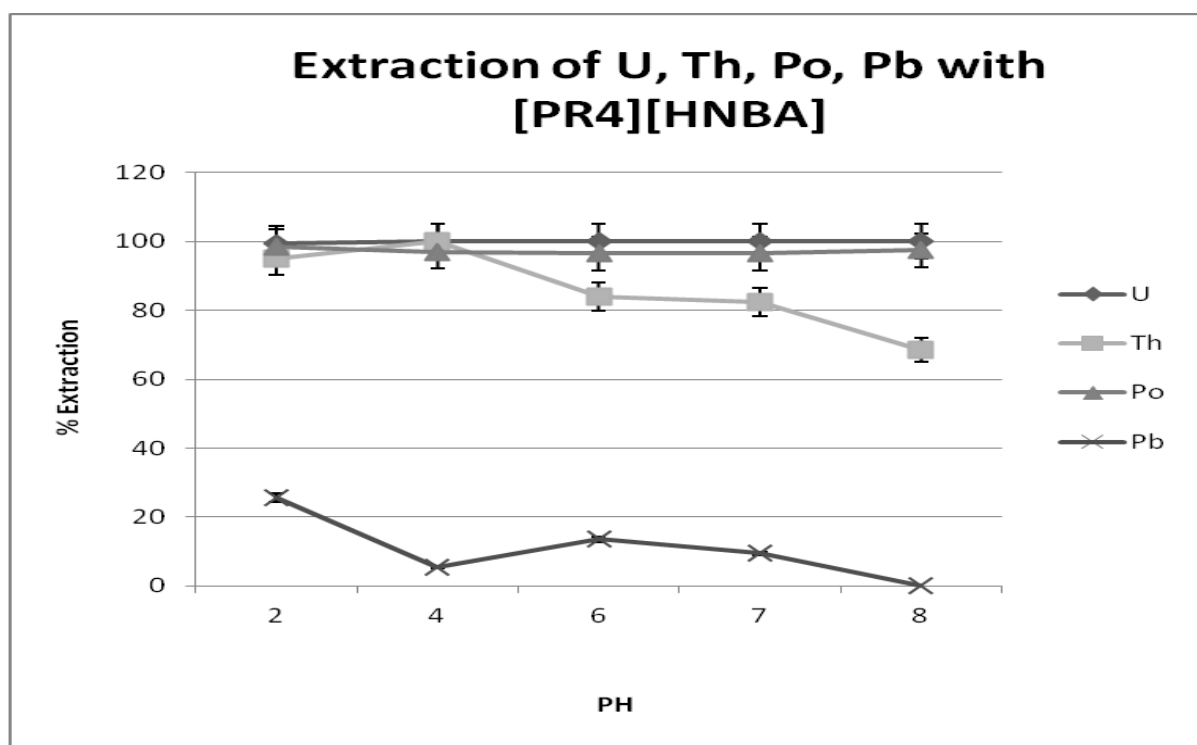


Figure 11: Extraction of U(VI), Th(IV), Po(IV), and Pb(II) extraction with [PR4][HNBA]

As can be seen in Table 7 and Figure 11, the organophosphorous compound [PR4][HNBA] is very efficient for the extraction of Uranium, Thorium and Polonium (average value of $87 \pm 4\%$ for Th and $98 \pm 11\%$ for Po). However, it doesn't act as a good agent for Lead (average value of $11 \pm 8\%$). Extraction behavior of Th is decreasing with increasing pH value.

% Back extraction					
[PR4][HNBA]	pH	U	Th	Po	Pb
	2	$2 \pm 1\%$	$0 \pm 0\%$	$0 \pm 0\%$	$0 \pm 0\%$
	4	$5 \pm 1\%$	$0 \pm 0\%$	$0 \pm 0\%$	$0 \pm 0\%$
	6	$5 \pm 2\%$	$0 \pm 0\%$	$0 \pm 0\%$	$0 \pm 0\%$
	7	$5 \pm 1\%$	$0 \pm 0\%$	$0 \pm 0\%$	$0 \pm 0\%$
	8	$5 \pm 2\%$	$0 \pm 0\%$	$0 \pm 0\%$	$0 \pm 0\%$

Table 8: Back extraction with [PR4][HNBA]

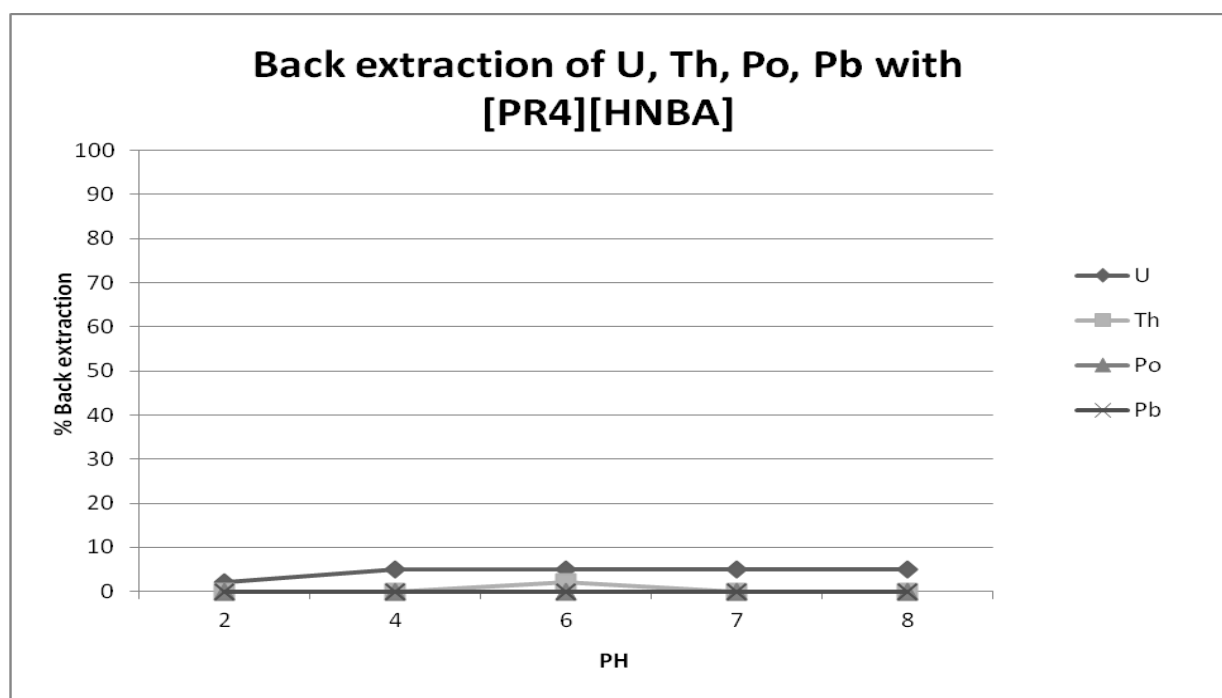


Figure 12: Back extraction of U (VI), Th(IV), Po(IV), and Pb(II) extraction with [PR4][HNBA]

Table 8 and Figure 12 show that all investigated radionuclides, namely $U_{nat.}$, ^{234}Th , ^{210}Po and ^{210}Pb practically cannot be back extracted from the IL.

2.4.4 Experimental results for [PR4][Ant]

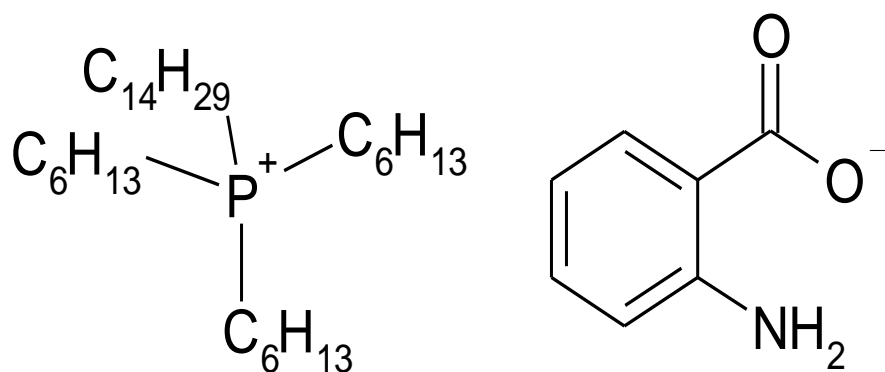


Figure 13: [PR4][Ant]

% Extraction					
[PR4][Ant]	pH	U	Th	Po	Pb
	2	98 ± 11%	36 ± 3%	91 ± 12%	14 ± 10%
	4	99 ± 9%	59 ± 3%	93 ± 9%	42 ± 10%
	6	100 ± 16%	47 ± 3%	86 ± 7%	36 ± 21%
	7	91 ± 7%	56 ± 3%	89 ± 8%	30 ± 10%
	8	92 ± 8%	59 ± 3%	89 ± 7%	36 ± 10%

Table 9: Extraction with [PR4][Ant]

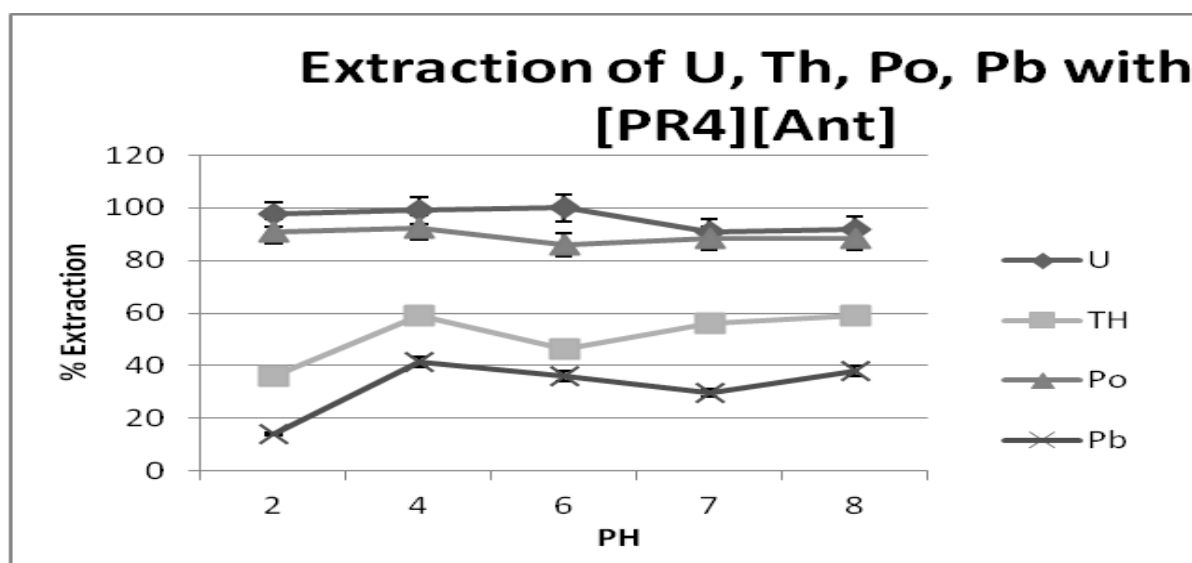


Figure 14: Extraction of U(VI), Th(IV), Po(IV), and Pb(II) with [PR4][Ant]

As can be seen in Table 9 and Figure 14, [PR4][Ant] achieves the highest selectivity for Uranium and Polonium independent from pH values (average value of $96 \pm 10\%$ for U and $90 \pm 9\%$ for Po). The extraction of Lead and Th by this agent is clearly lower (average value of $51 \pm 3\%$ for Th and $32 \pm 12\%$ for Pb).

% Back extraction					
[PR4][Ant]	pH	U	Th	Po	Pb
	2	49 \pm 9%	84 \pm 11%	3 \pm 1%	19 \pm 3%
	4	36 \pm 5%	33 \pm 9%	3 \pm 1%	98 \pm 10%
	6	40 \pm 6%	53 \pm 6%	1 \pm 1%	83 \pm 8%
	7	35 \pm 4%	44 \pm 8%	3 \pm 1%	100 \pm 11%
	8	35 \pm 4%	46 \pm 9%	5 \pm 1%	100 \pm 10%

Table 10: Back extraction with [PR4][Ant]

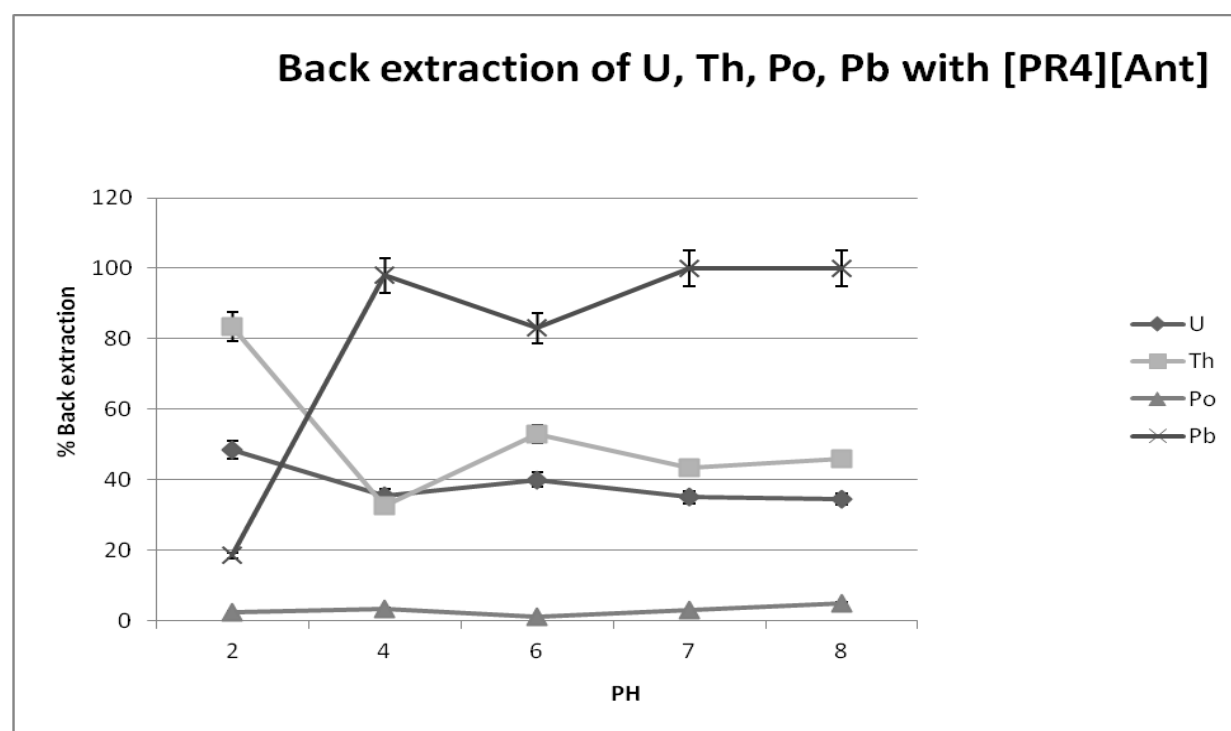


Figure 15: Back extraction of U (VI), Th(IV), Po(IV), and Pb(II) extraction with [PR4][Ant]

As shown in Table 10 and Figure 15, an increase in pH value of the original solution, from where ^{210}Pb had been extracted has a positive effect on the back extraction of Lead. Po cannot be back extracted from the IL and also the back extraction of U and Th is low.

2.5 pH measurement before and after extraction and back extraction

As Table 11 shows for [A336][Ant], the pH value of solution increases during the extraction process (with the exception of pH=6). On the other hand, pH decrease is more pronounced when using [A336][HNBA] (with the exception of pH=2). The reason can be that [A336][Ant] is a weaker base than [A336][HNBA]. Therefore, the proton donation of [A336][HNBA] is stronger than [A336][Ant].

pH	Extractant: [A336][Ant]		Extractant: [A336][HNBA]	
Before extr.	After U-extr.	After Pb-extr.	After U-extr.	After Pb-extr.
2	3.5	3.3	2.1	2.2
4	5.2	4.8	3.6	3.6
6	6.2	4.9	3.9	3.8
7	8.7	8.1	4.1	3.9
8	8.7	8.3	4.1	4.2

Table 11: pH measurement before and after extraction with [A336][Ant] and [A336][HNBA]

With back extraction the pH has not changed (only the second number after comma has changed).

2.6 Extraction with immobilized ionic liquids

One of the treatments of wastewater is the extraction method with immobilized ionic liquids, which can be an effective operation to remove a metal ion from waste water. As the image below shows, the surface and pores of activated carbon will partly be covered by ionic liquid. Ionic liquid supported by activated carbon can remove the metal ion, for example Uranyl, from water.

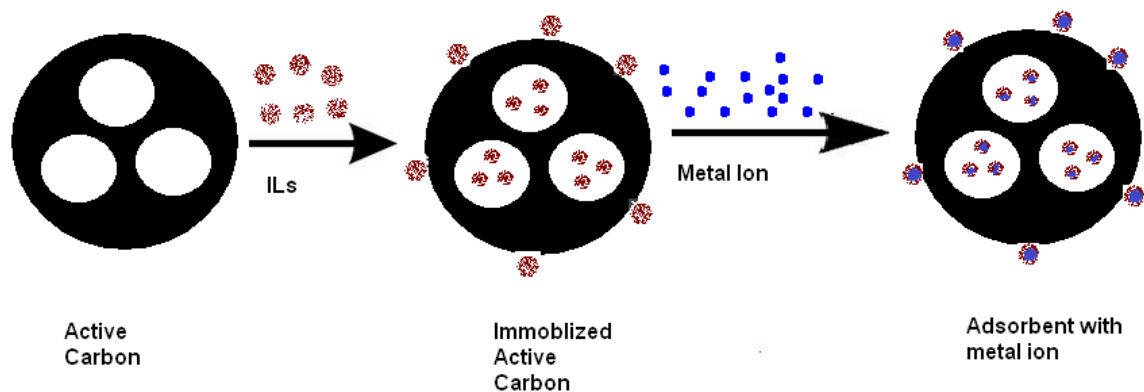


Figure 16: Extraction with immobilized ionic liquids

Commercial AC (Hydraffin 30 N) is supplied by Donau carbon and

Specifications are classified below:

Granulation (mesh) 8 x 30
(0.6 - 2.36 mm)

Apparent density (kg/m³) 470 ± 30

Moisture content (wt. %) < 5
(as packed)

Iodine adsorption (mg/g) 1000 ± 50

Typical characteristics:

Apparent density after approx. 430

Backwash and drainage (kg/m³)

Total surface area (m²/g) approx. 950
(BET-method)

Hardness (wt. %)	90
Ash content (wt. %)	< 15

The aim of this work was to investigate if ILs can be immobilized on AC, and if the immobilized IL is unchanged by this procedure and therefore will also extract Uranium from the aqueous solution. Additionally the extraction (or more exactly: the adsorption) of U by the activated carbon directly was measured.

2.6.1 Experimental details

2.6.1.1 Treatment of AC

The AC (Hydraffin 30) is supplied by Donau Carbon. In order to modify the surface chemical composition of AC, HCl treatment is used. Activated carbons and coal chars are frequently treated with HCl. "Acid treatment was generally used to oxidize the porous carbon surface; it enhanced the acidic property, removed the mineral elements and improved the hydrophilic group of surface" (Shen et al., 2008: 28) by reflux of 1 g AC in 200 ml of 1 M HCl in a hood at 50°C for about two hours. After filtering, the AC is washed with distilled water until neutral and dried overnight at 70°C.

2.6.1.2 Immobilization of IL on AC

[A336][Ant] was chosen for this investigation, because this agent shows a mean value of 96%±4% for uranium extraction for pH≥4, and also uranium back extraction is higher than 70%.

Immobilization of IL [A336][Ant] on AC is carried out by magnetically stirring 1 g of IL in 20 ml methanol with 5 g AC in a closed flask for about one hour. Then it is dried by evaporation in a rotating flask. Generally 0.2 g of IL immobilized on 1g AC is used for extraction experiments.

2.6.2 Adsorption / extraction experiments

The equilibrium adsorption tests are carried out as batch experiments in 50 ml bottles placed in a shaker at 300 rpm equivalent stirring rate and 25°C overnight. Duplicates of five aqueous sample solutions with a volume of 10 mL are prepared with concentrations C_0 from 1.37 to 6.8 µg/mL Uranium (the pH was set to 8 with NaOH).

In the first experiment 1 g of AC alone is mixed with the first sample set. In the second experiment 0.2 g of IL immobilized on 1g AC is used for extraction. The equilibrium time is 12 hours. Afterwards, the mixture is centrifuged for one hour with 3000 rpm and then the solid is filtered off. 3 ml of aqueous solution is mixed with 17 ml cocktail and then measured by LSC.

We found complete U uptake by AC alone as well as by IL immobilized on AC. As the relatively low amount of IL used does not completely cover the surface of the AC, uranyl ions may either be adsorbed on the AC or be extracted into the immobilized IL.

2.6.3 Desorption / back extraction experiments

Desorption / back extraction experiments are carried out with 20 ml 0.05 M nitric acid. After shaking with 300 rpm overnight and centrifuging for one hour with 3000 rpm, 3 ml of the aqueous phase is mixed with 17 ml cocktail and analyzed by LSC counting.

Desorption/back extraction of U with 1 g AC and 1 g AC+0.2 g IL		
C_0 [mg/L]	% Desorption AC	% Desorption / back extraction AC+ IL
1.37	23± 2%	62± 2%
2.75	28± 2%	59± 4%
4.12	33± 3%	60± 5%
5.48	35± 3%	66± 5%
6.87	36± 6%	66± 4%

Table 12: Desorption / back extraction of U with 1 g AC and 1 g AC+ 0.2 g IL.

Table 12 and Figure 17 show that desorption from AC is only between 23 % and 36 %, while desorption / back extraction from AC and IL is clearly higher (59 % - 66 %). This is the proof that at least part of the U is extracted into the immobilized IL, from where it can be retrieved with higher yield than from the AC.

Enhancing the amount of IL immobilized on AC until total coverage could minimize the problem of uranium adsorption on the AC, but on the other hand this would lead to leaching of the IL into the aqueous phase. In future we plan to use calcium ions to occupy the reactive centers of the AC.

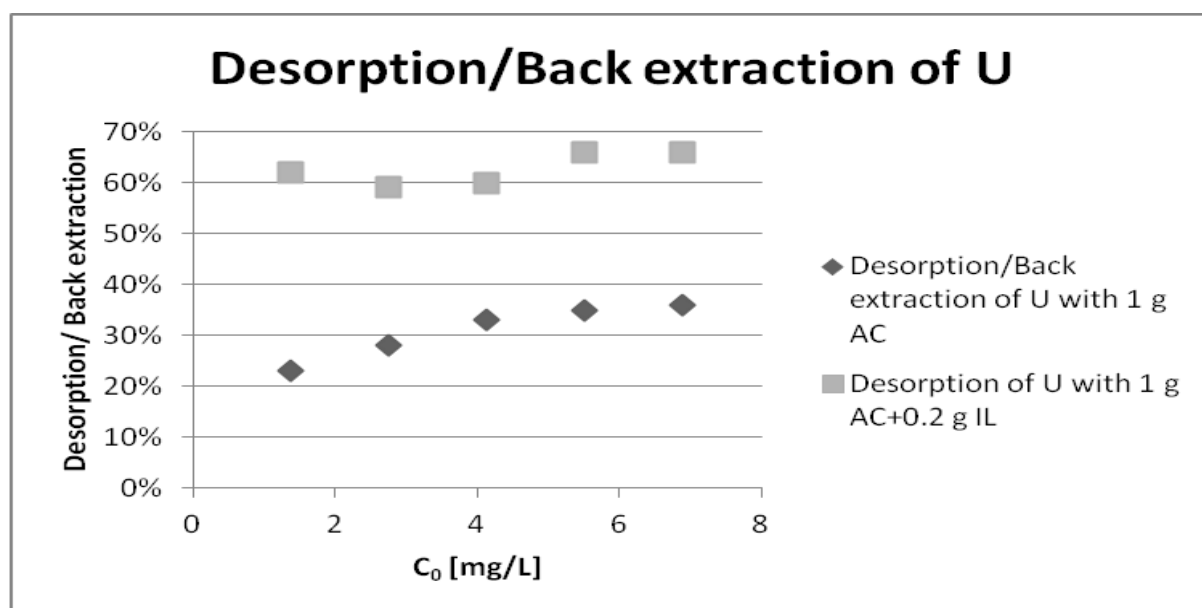


Figure 17: Desorption / Back extraction of U with AC and AC + IL

2.6.4 Adsorption/extraction of U with lower amount of IL and AC

In the above described experiment we found complete extraction of U by 1 g AC alone as well as by 0.2 g IL immobilized on 1g AC. In this experiment the concentrations of the investigated uranium solutions were the same as in the first experiment, but we used a lower amount of IL (0.02 g) and AC (0.1 g) in order to determine the maximum amount of uranium extracted into the ionic liquid.

Four aqueous sample solutions with a volume of 10 mL are prepared with concentrations from 2.75 to 27.5 $\mu\text{g/mL}$ Uranium. The pH of the solution is adjusted to 8 with NaOH. (10 ml is the amount of aqueous solution after pH adjustment). In the

first experiment 0.1 g of AC alone is mixed with the samples. In the second experiment 0.02 g of IL immobilized on 0.1g AC is used for extraction. In order to achieve the equilibrium, the mixtures are shaken overnight and centrifuged for one hour and then aliquots of the aqueous phases are analyzed by LSC. The study is performed at room temperature.

Adsorption/Extraction of U with 0.1 g AC and 0.1 g AC+0.02 g IL				
C_0 [mg/L]	% Adsorption AC	Q_e [mg/g] AC	% Adsorption /Extraction AC+ IL	Q_e [mg/g] AC+IL
2.75	74± 3%	0.20	78± 3%	1.16
5.5	98± 2%	0.59	97± 4%	2.92
13.75	92± 3%	1.49	96± 3%	8.02
27.5	71± 4%	2.52	85± 4%	15.08

Table 13: Adsorption/Extraction of U with 0.1 g AC and 0.1 g AC+0.02 g IL

Again as can be seen in Table 13 the amount of extracted/adsorbed uranium to AC as well as to AC + IL is rather high and the same in both cases with the exception of the sample with the highest uranium concentration: here the uptake into AC + IL is higher.

The amount of radionuclide extracted (Q_e) is calculated according to the equation below.

$$Q_e = \frac{(C_0 - C_e)}{m} * \frac{V}{1000}$$

C_e [mg/L] stands for the equilibrium Uranium concentration in the liquid phase and Q_e [mg/g] for the equilibrium uranium concentration in the ionic liquid. C_0 [mg/L] is the initial concentration of uranium in the liquid phase and m [g] is the mass of the extractant: if AC is used alone, m is the mass of AC, if the IL supported by AC is used (AC + IL) m is the mass of the ionic liquid only. However, as the IL probably doesn't cover the whole surface of the AC, these results are preliminary.

2.7 Adsorption Isotherms

To avoid the problem of having two extracting substances in our experiment, again the liquid-liquid extraction technique is used for adsorption isotherm determination. In this experiment we measure the relationship between the mass of uranium extracted into a unit mass of IL and the uranium concentration of the aqueous solution at equilibrium conditions. A fixed amount of 0.02 g of IL [A336][Ant] is used, six sample solutions are prepared with Uranium amounts from 84.5 to 361.6 μg in 10 ml water. The pH of the solution is adjusted to 4 with NaOH. In order to achieve the equilibrium, the mixtures of the solution are shaken overnight and centrifuged for one hour and then aliquots of the aqueous phases are analyzed by LSC. The study is performed at room temperature.

Extraction of U into 0.02 g ionic liquid		
C_0 [mg/L]	C_e [mg/L]	Q_e [mg/g]
27.5	0.55	15.88
109.85	1.1	54.5
163.99	3.2	80.5
219.7	26.4	96.8
362	66.01	110.6
362	119.46	121.2

Table 14: Experiment with 0.02g IL and U

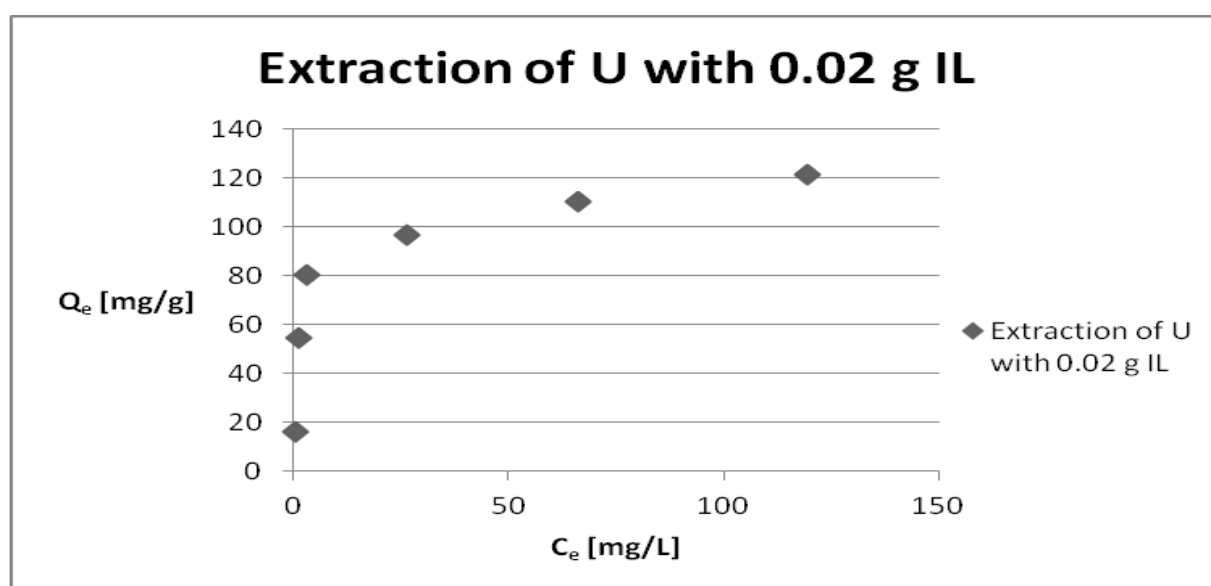


Figure 18: Equilibrium extraction isotherm U(VI) onto IL at 27°C

Table 14 and Figure 18 show the amount of uranium extracted into the ionic liquid versus the equilibrium concentration in the aqueous phase. We found a surprisingly high maximum uranium uptake of about 120 mg U per g of ionic liquid [A336][Ant] (5.04×10^{-4} mol ^{238}U per 0.002 mol of IL, or 0.25 mol uranium per mol of IL).

III Conclusion

We investigated four ILs, namely Trioctylmethylammonium anthranilate [A336][Ant], Trihexyltetradecylphosphonium anthranilate [PR4][Ant], Tricaprylmethylammonium 2-hydroxy-5-nitrobenzoate [A336][HNBA] and Trihexyltetradecylphosphonium 2-hydroxy-5-nitrobenzoate [PR4][HNBA] for the extraction of radionuclides by using the liquid-liquid extraction method. All four ILs achieved near to 100% selectivity for Uranium and Polonium independent of the pH value of the aqueous solution. The selectivity for Th with [A336][Ant] showed a mean value of $82\% \pm 4\%$, but the three others didn't show a good extraction of Th. Generally, the extraction of lead was very low. The only agent which showed a good extraction of lead with 76% at pH4 was [A336][Ant].

As the reusability of ionic liquids is important, we also carried out back extraction experiments with 0.05 M HNO_3 .

[A336][Ant] showed a good value of back extraction of Uranium between 68% and 92% and again a good value between 82% and 100% for Th. However, Polonium could not be back extracted from this ionic liquid. Additionally, the back extraction of Lead was between 27% and 83%.

[PR4][Ant] showed only a low back extraction of U and Th. Po could not be back extracted at all. Back extraction of Lead was higher in this case.

Po and Th could not be back extracted with [A336][HNBA] and also the back extraction of U was very low. The back extraction of lead was between 28% and 87%.

All investigated radionuclides could not be back extracted from [PR4][HNBA].

The ionic liquid [A336][Ant] was also successfully immobilized on AC. Our experiments verified that uranium was also taken up by the immobilized ionic liquid.

The liquid-liquid technique was used for adsorption isotherm determination for the ionic liquid [A336][Ant]. With this method we achieved a **maximum uranium uptake of about 120 mg U per g of ionic liquid [A336][Ant], corresponding to 25 mol%.**

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Appendix

Extraction		U			Th			Po			Pb		
[PR4][Ant]	PH	Serie A	Serie B	Average	Serie A	Serie B	Average	Serie A	Serie B	Average	Serie A	Serie B	Average
	2	96	99	98	41	31	36	84	98	91	28	0	14
	4	100	98	99	58	60	59	98	87	93	72	11	42
	6	100	100	100	54	39	47	96	76	86	39	33	36
	7	100	82	91	65	47	56	97	80	89	56	3	30
	8	100	84	92	76	42	59	99	78	89	65	11	38

Extraction		U			Th			Po			Pb		
[A336][Ant]	PH	Serie A	Serie B	Average	Serie A	Serie B	Average	Serie A	Serie B	Average	Serie A	Serie B	Average
	2	52	95	74	74	100	87	83	96	90	0	19	10
	4	97	91	94	64	100	82	91	100	96	87	65	76
	6	97	94	95	44	100	72	94	100	97	18	74	46
	7	100	92	96	72	100	86	87	94	91	0	62	31
	8	100	100	100	75	91	83	90	94	92	16	47	32

Extraction		U			Th			Po			Pb		
[A336][HNBA]	PH	Serie A	Serie B	Average	Serie A	Serie B	Average	Serie A	Serie B	Average	Serie A	Serie B	Average
	2	100	100	100	24	0	12	98	97	98	46	0	23
	4	100	100	100	39	12	26	99	97	98	46	13	30
	6	100	100	100	41	0	21	98	99	99	37	22	30
	7	100	100	100	34	38	36	100	98	99	33	17	25
	8	100	100	100	10	40	25	93	91	97	19	31	25

Extraction		U			Th			Po			Pb		
[PR4][HNBA]	PH	Serie A	Serie B	Average	Serie A	Serie B	Average	Serie A	Serie B	Average	Serie A	Serie B	Average
	2	100	99	100	100	90	95	97	100	99	37	14	26
	4	100	100	100	100	100	100	97	97	97	0	11	6
	6	100	100	100	68	100	84	97	96	97	0	27	14
	7	100	100	100	65	100	83	97	96	97	0	19	10
	8	100	100	100	37	100	69	95	100	98	0	0	0

Back extraction		U			Th			Po			Pb		
[A336][Ant]	PH	Serie A	Serie B	Average	Serie A	Serie B	Average	Serie A	Serie B	Average	Serie A	Serie B	Average
	2	90	94	92	63	100	82	3	0	2	0	54	27
	4	70	80	75	84	100	92	6	0	3	66	100	83
	6	66	70	68	100	100	100	4	0	2	59	100	80
	7	68	100	84	81	100	91	0	0	0	0	100	50
	8	100	81	91	100	100	100	3	0	2	24	100	62

Back extraction		U			Th			Po			Pb		
[PR4][Ant]	PH	Serie A	Serie B	Average	Serie A	Serie B	Average	Serie A	Serie B	Average	Serie A	Serie B	Average
	2	60	37	49	67	100	84	2	3	3	37	0	19
	4	28	43	36	0	65	33	3	4	4	96	100	98
	6	28	52	40	6	100	53	2	0	1	66	100	83
	7	33	37	35	12	75	44	3	3	3	100	100	100
	8	33	36	35	0	92	46	7	3	5	100	100	100

Back extraction		U			Th			Po			Pb		
[A336][HNBA]	PH	Serie A	Serie B	Average	Serie A	Serie B	Average	Serie A	Serie B	Average	Serie A	Serie B	Average
	2	13	18	16	0	0	0	0	0	0	0	0	0
	4	10	16	13	0	0	0	0	0	0	56	0	28
	6	13	15	14	0	0	0	0	0	0	100	22	61
	7	13	20	17	0	0	0	8	0	4	100	58	79
	8	15	23	19	0	0	0	0	0	0	100	74	87

Back extraction		U			Th			Po			Pb		
[PR4][HNBA]	PH	Serie A	Serie B	Average	Serie A	Serie B	Average	Serie A	Serie B	Average	Serie A	Serie B	Average
	2	4	0	2	0	0	0	0	0	0	0	0	0
	4	5	4	5	0	0	0	0	0	0	0	0	0
	6	5	4	5	0	4	2	0	0	0	0	0	0
	7	4	6	5	0	0	0	0	0	0	0	0	0
	8	5	5	5	0	0	0	0	0	0	0	0	0

Sorption of 1g AC +different µl U in 10 mL water		
Sorption	Desorption	µl U
100%	23%	5
100%	28%	10
100%	33%	15
100%	35%	20
100%	36%	25

Sorption of 1g AC+ 0.2 g IL+different µl U in 10 mL water		
Sorption	Desorption	µl U
100%	62%	5
100%	59%	10
100%	60%	15
100%	66%	20
100%	66%	25

Sorption of 0.1g AC +different µl U in 10 mL water		
Sorption	Desorption	µl U
74%	46%	10
98%	59%	20
92%	71%	50
71%	60%	100

Sorption of 0.1g AC+0.02 g IL +different µl U in 10 mL water		
Sorption	Desorption	µl U
78%	58%	10
97%	81%	20
96%	73%	50
85%	81%	100

Curriculum vitae

Marzieh Habibi

Born 04th April 1958 in Tehran; 2 children (1984, 1992)

Education

2012 – 2015	Chemistry, University of Vienna
2008 – 2010	Biomedical Engineering Sciences, FH Technikum Vienna
1976 – 1985	Chemistry, University of Al-Zahra/Tehran

Languages

Persian (mother tongue)

English (good)

German (good)