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Title:	Introduction to Polymer Ligand Extractant Techniques
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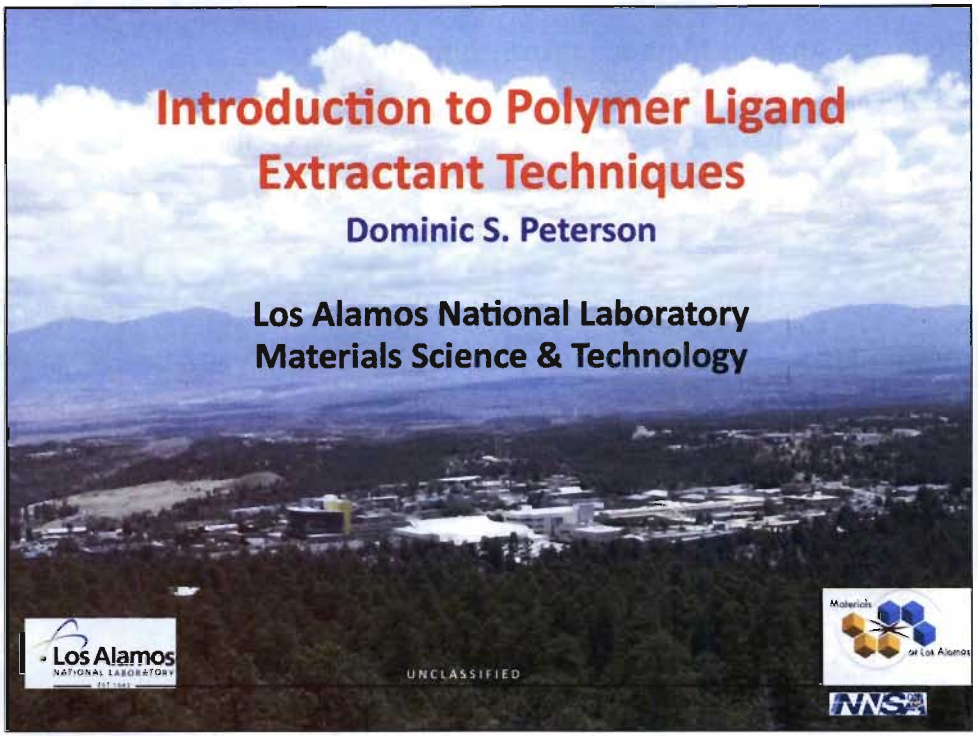
Form 836 (7/06)

Abstract

Introduction to Polymer Ligand Extractant Techniques

Dominic S. Peterson

Polymer ligand film extraction techniques have been shown to be useful for extraction and sample cleanup for use on radiochemical analytes. This presentation will give an overview of the state-of-the-art and the current system limitations and operational parameters. We will also discuss future work to be performed in a new ligand extraction project.



LANL Team / Development history

- Ed Gonzales – Chemistry/Counting expertise (Chemistry)
- Claudine Armenta – Chemistry expertise (Chemistry)
- Dom Peterson – Materials expertise (Materials Science)
- Jung Rim – Penn State PhD Student

- LANL emergency response
- CDC
- NA-22 – Pu Production Detection Portfolio

Classical Analysis Methods Take Significant Time

Analysis	Classical separation	Matrix	Analysis Time
Tritium	Distillation	Liquid/Solids	2 days
C-14	Wet / dry combustion	Liquid/Solids	2 days
Sr-90	Wet oxidation and chemical isolation and / or ion exchange	Liquids Solids	1 week 2 weeks
Pu/Am/U	Chemical isolation	Urine/Water	1 week
Pu/Am/U	Chemical isolation	Biological	1 week to 1 month
Pu/Am/U	Chemical isolation	Soil	1 to 2 weeks
Po-210	Chemical isolation	Urine	3 to 5 days
Gamma	Non destructive prep	Soil/Biol/Water	1 to 5 days

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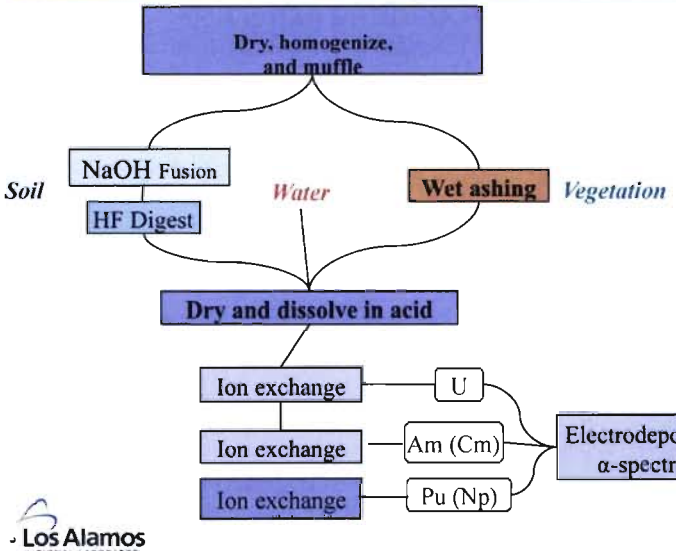
Standard radioanalytical procedure for alpha determination



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Advantages of PLE technology

- PLE enables rapid extraction/preparation of radioactive analyte
- Extraction is very rapid
- Chemistry can provide selection of specific analytes (reducing the need for column separations)
- PLE enables very high data quality (near electrodeposition for alpha spec)

Initial considerations for using polymer ligand thin film

- Emergency response situations
  - Screening of environmental samples
  - Field analysis situations
  - Rapid urine analysis
- Suitable media for rugged field deployed counting
- Process must be fast and easy
- Process must replace separation and plating

Initial analysis considerations

- Sample prepared using routine procedures
- Initial isotopes of interest – Am, Pu, U, and Po
- Method assumed in house analysis
- Sample treated as environmental
- Bioassay sample added

Initial analysis process

- Sample optimized for highest absorption
- Samples prepared with isotopes only – no matrix
- Sample volume is 100 mL or less
- PLE mechanically agitated
- Sample prepared in distilled H_2O and ICP grade acid

PLE media

- PLE on stainless steel backing
- PLE on plastic or Teflon backing
- PLE on GF filters for sample filtration
- PLE on resolve filter (Eichrom)
- Specialty materials (glass, rubber etc)

Preparation of polymer ligand extractants

- Initial PLE composition Dipex:Polystyrene (Dipex:PS)
- Polymer and ligand were dissolved in THF
- Initial concentration of the PLE in solution were 1:1, 1:5, and 1:10 (wt/wt)
- Initial PLE were air dried and weighed
- Different size and type of backings were tried
- Later different ligand polymers were tried

Dipex:PS polymer ligand extractants

- PLE chosen on bases of counting and analysis conditions (dipex:ps)
- 1:1 PLE – soft, hard to dry, foamed under vacuum
- 1:5 PLE –tended to be brittle and break under vacuum
- 1:10 PLE – more durable and stable under vacuum
- Stable surface provided better energy resolution
- High absorption coefficients

Initial Sample Processing Considerations

- PLE must be durable for rugged sample handling
- PLE must be able to withstand long immersion in water at variable pH
- PLE must minimize migration of analyte below surface
- Surface area must accommodate sufficient active sites

Alpha Counting Considerations

- PLE must be suitable for counting under vacuum
- PLE must hold analyte at surface
- PLE must not degrade for long count times
- PLE resolution must approach that of electroplated samples
- PLE must not decompose while counting

Data Considerations

- Yield must be consistent
- Data must be reproducible
- Detection limit will be based on lowest common denominator (in most cases this is yield)
- Sample counts must be discernable from sample noise

Data for Dipex:PS PLE

Composition	FWHM keV	Analyte	%Recovery
1:1	117	^{243}Am	20
1:10	36	^{243}Am	27

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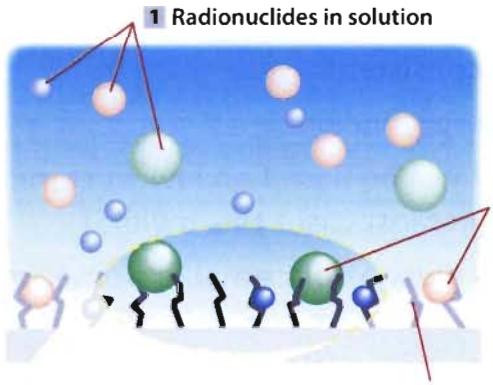
Thin film process



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Parameters to study

- Why incorporate extractant into polymer?
- What are the trade-offs in system optimization?
- Temperature conditions?
- Extraction conditions?
- Concentration of ligand in polymer system?

Parameters to study

- Extractive ligands – a variety are available commercially (relates to efficiency)
- Polymer support – initial work focused on those that are easily dispersible in organic solvents (relates to stability and data quality)
- Extraction efficiencies
- Data quality – particularly alpha spectrometry

Thin film comparison

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Preparation of polymer ligand extractants

- Polymer and ligand were dissolved in THF
- Total concentration of the PLE in solution was 1:5 (wt/wt)
- Concentration of the ligand to polymer were 1:10 (wt/wt)
- Solution was deposited using an automated pipette (1 mL)

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Solvent considered

- Ethanol
- Methanol
- Isopropanol
- Tetrahydrofuran (THF)

Polymers considered

- Poly vinyl acetate (PVA)
- Poly methyl methacrylate (PMMA)
- Poly vinyl pyrrolidone (PVP)
- Poly vinyl butryal (PVB)
- Polystyrene (PS)
- THF used as solvent

Fabrication of Thin Film

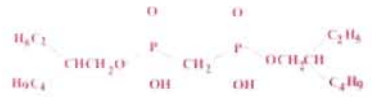
- Simply involves mixing an extractive resin with a polymer
  - Poly(styrene) dissolved in Tetrahydrofuran (THF) with DIPEX extractant
- Solution is placed on collection plate and dried
- Thin film forms from the polymer/extractant solution

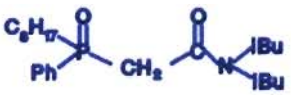
Experimental Setup

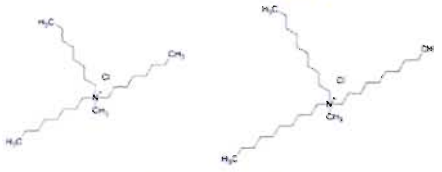
- Involves preparation of thin film on support plate
- Thin film is introduced into analysis solution (dipping, mixing, etc)
- After a certain amount of time, thin film is removed from solution and dried
- Thin film plate is then directly placed into alpha spectrometer and counted

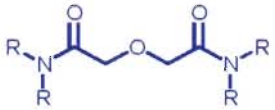
Ligand Study

- Dipex®
- CMPO
- Aliquat 336
- DGA Branched









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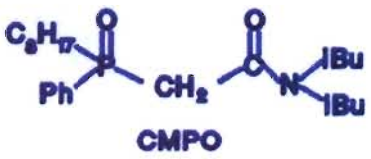
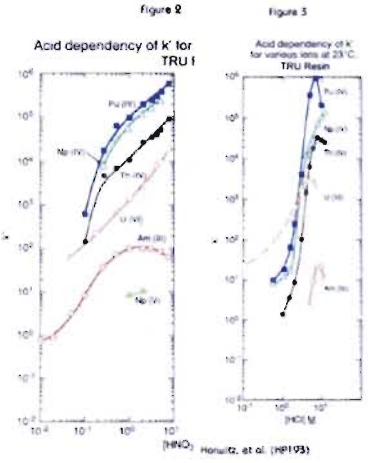
Extractants used: CMPO



octylphenyl-N,N-di-isobutyl carbamoylphosphine oxide (**CMPO**)

- Binds Actinides strongly (esp. Pu, Np)
- Releases actinides in more neutral solutions
- Sold as TRU resin
- http://www.eichrom.com



Horwitz, E. P., *et al.*, Solvent Extraction and Ion Exchange, 14, **1996**, 13-33.

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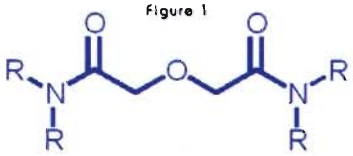
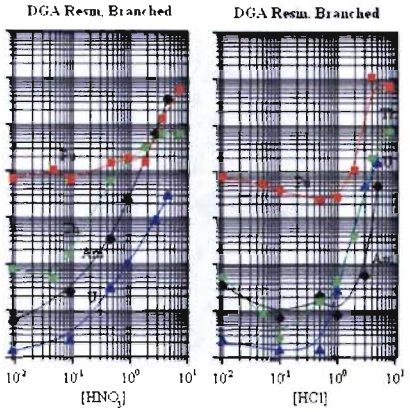
Extractants used: B-DGA



N,N,N',N'-tetrakis-2-ethylhexyldiglycolamide

- Binds Actinides strongly (esp. Pu, Am)
- Releases actinides in more neutral solutions
- http://www.eichrom.com



Horwitz, E. P., *et al.*, Solvent Extraction and Ion Exchange, 23, **2005**, 319-344.

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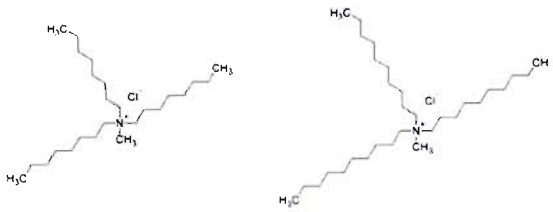
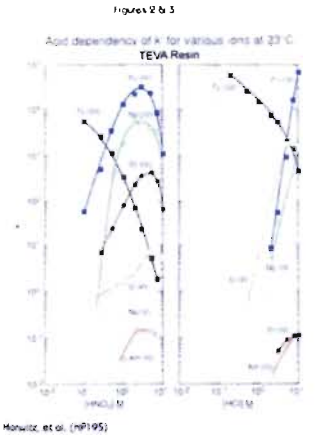
Extractants used: Aliquat 336





- Binds Pu(IV) & Np(IV) strongly; other actinides less strongly, all better at higher acid concentrations
- Soluble in many organic solvents
- Sold as TEVA resin
- http://www.eichrom.com

Horwitz, E. P., *et al.*, Solvent Extraction and Ion Exchange, 13, **1995**, 615-645

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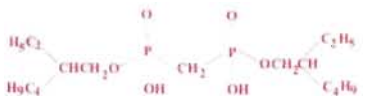
Extractants used: Dipex®

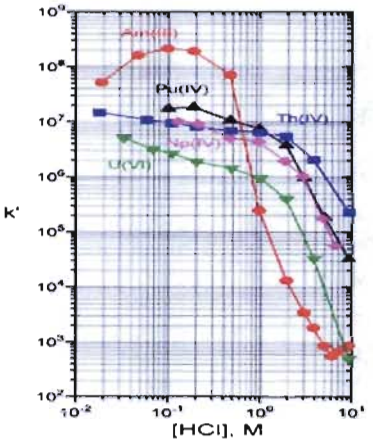
DIPEX® Extractant

P,P'- di(2-ethylhexyl)methanediphosphonic acid



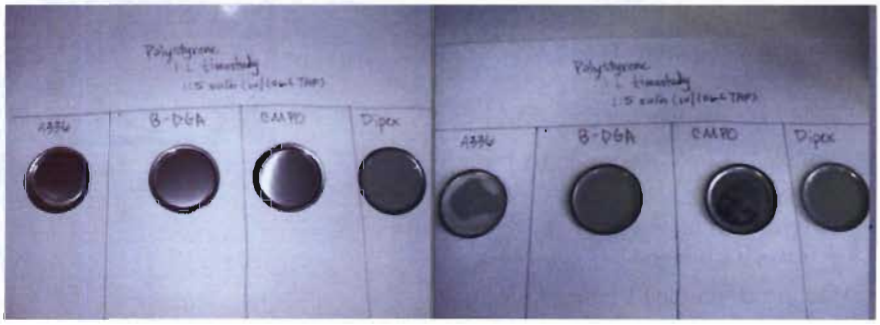
$H_2DEH[MDP]$

- Binds Actinides very strongly
- Soluble in many organic solvents
- Sold as Actinide resin
- Best spot for Pu(IV) ~0.1M HNO_3
- http://www.eichrom.com



Horwitz, E. P., *et al.*, Reactive & Functional Polymers, 33, **1997**, 25-36

Polymer & ligand study



Before and After: different ligands with polystyrene

Percent recovery and FWHM for samples prepared

Extractant	polymer	% recovery	FWHM (keV)	Comments
DIPEX	Poly(styrene)	53%	30 keV	
DIPEX	nitrocellulose	55%	80 keV	
DIPEX	Poly(methyl methacrylate)	24%	35 keV	Issues with Prep
DIPEX	Poly(carbonate) (Filter)	27%	251 keV	
B-DGA	Poly(styrene)	48%	50 keV	
B-DGA	nitrocellulose	65%	300 keV	
B-DGA	Poly(methyl methacrylate)	11%	50 keV	Issues with prep
CMPO	Poly(styrene)	16%	200 keV	
CMPO	nitrocellulose	45%	320 keV	
A-336	Poly(styrene)	-	-	Degraded – couldn't be counted
A-336	nitrocellulose	12%	600 keV	A-336 Degrades

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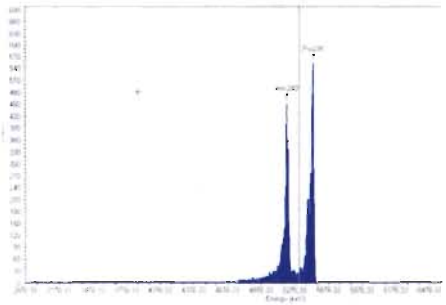
Thin Film

- Chemistry on the surface
- Place in sample and stir
- 2 hour stirring yields up to 57% yield for actinides.
- Sample contains low molarity HCl or HNO3
- Different acid allows control of actinide exchanged
- Fast prep – liquids 1 hour
  - Solids with fusion 2 hours
- Count directly



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Variety of supports

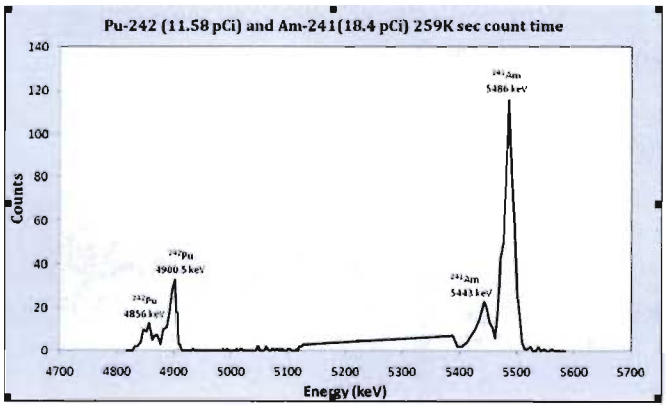
Poly(styrene) dissolved in Tetrahydrofuran (THF) with DIPEX extractant

Nitrocellulose dissolved in isoamyl acetate with DIPEX extractant

Poly(vinylpyrrolidone) dissolved in isopropyl alcohol with DIPEX and placed on filter

Poly(styrene)/DIPEX PLE

- Recovery of Pu – 8%
- Recovery of Am – 53%
- FWHM Pu – 25 keV
- FWHM Am – 34 keV



Poly(styrene)/B-DGA PLE

Poly(styrene)/b-DGA

- Recovery of Pu – 15-48%
- FWHM Pu – 21-51 keV

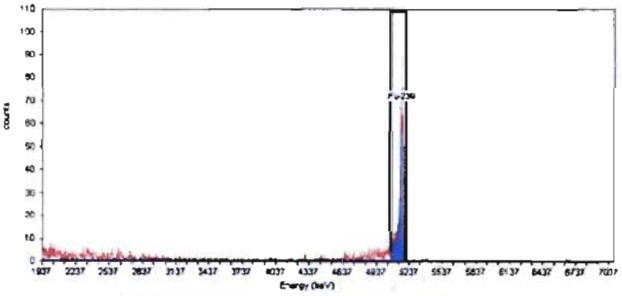
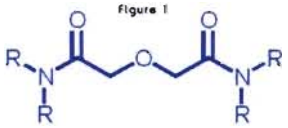
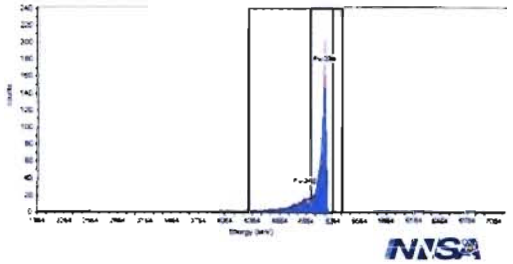


Figure 1





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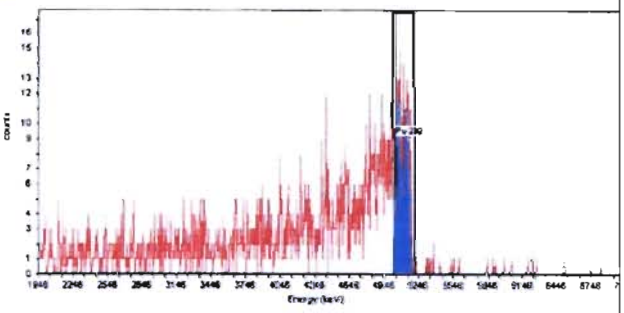
Poly(styrene)/CMPO PLE

Poly(styrene)/CMPO

- Recovery of Pu – 6-16%
- FWHM Pu – 250+ keV



octylphenyl-N,N-di-isobutyl carbamoylphosphine oxide (abbreviated **CMPO**)

CMPO

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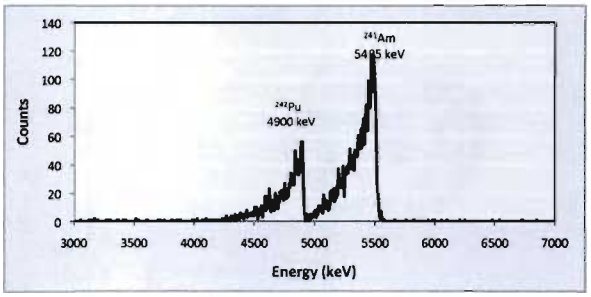
Nitrocellulose/DIPEX PLE



- Recovery of Pu – 36%
- Recovery of Am – 54%
- FWHM Pu –60 keV
- FWHM Am – 54 keV

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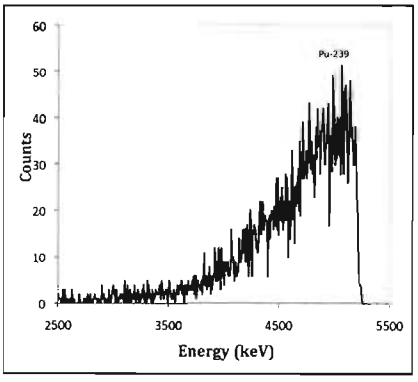
Nitrocellulose/CMPO PLE



- Recovery of Pu – 36%
- Recovery of Am – 54%
- FWHM Pu –60 keV
- FWHM Am – 54 keV

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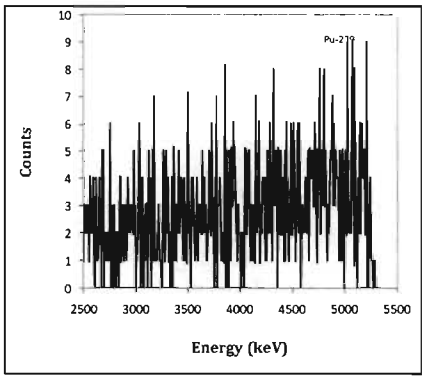
Nitrocellulose/Aliquot 336 PLE



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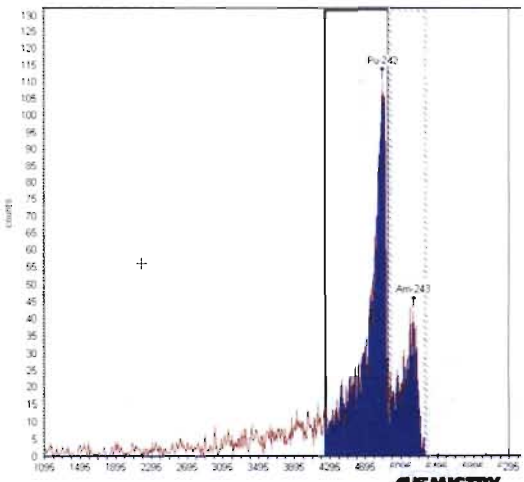
Thin Film on Resolve Filter

TF on Resolve filter – dip filter into TF polymer extractant.

TF weight – 0.0092g

Pour 50 mL sample through Millipore setup

^{243}Am – 29% recovery
^{238}Pu – 98% recovery
Total recovery ~80% with indication of some migration into filter resulting in scatter.



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CHEMISTRY

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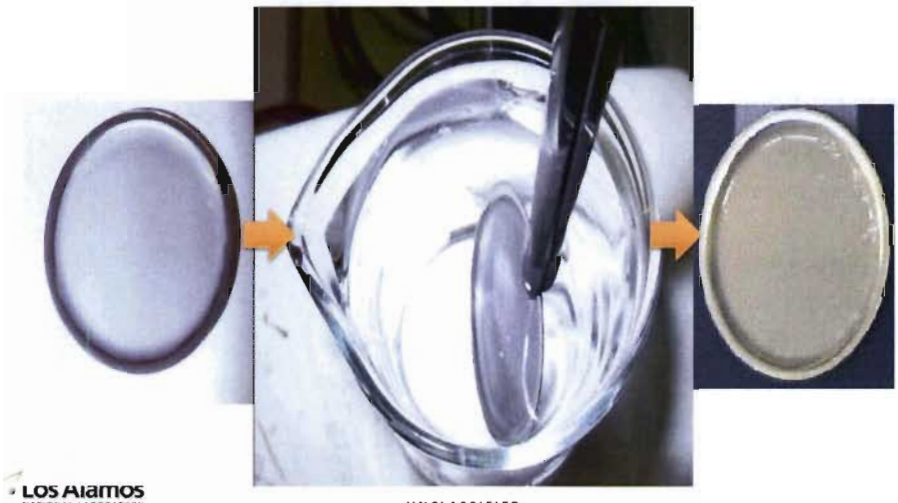
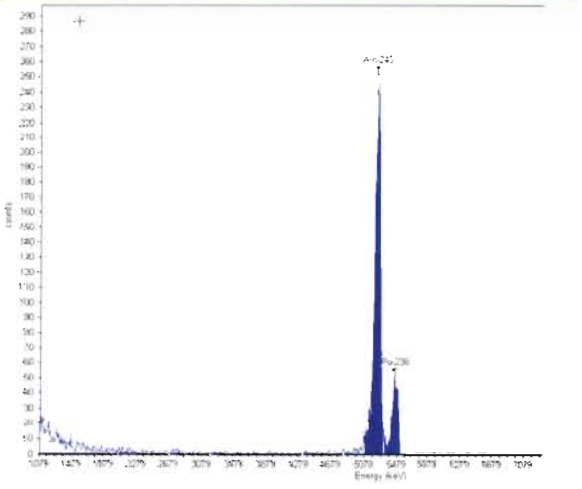
Thin film process



Extraction of Actinides Onto Thin Film

Weight – 0.113
100 ml 0.04 M HNO3
Mixing time 1 hour
^{243}Am – 3.9% recovery
^{238}Pu – 0.6% recovery



Reverse Side of Thin Film

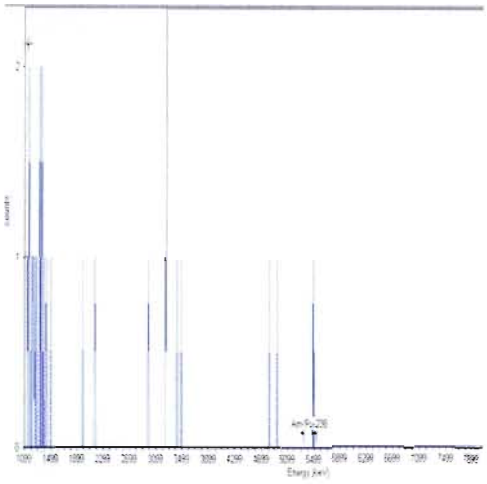
Thin Film 3 removed from support

Placed backside up

Counted by alpha spec

Determine migration through TF

No migration detected



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Thin film Analyzed by Traditional Methods

TF 3 removed and dissolved

Traced with Pu-242

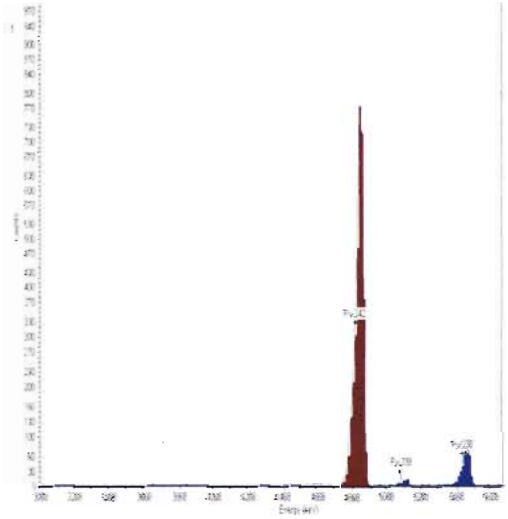
Electroplated

Compared to Direct count of TF

^{238}Pu TF direct count -0.67 ± 0.06 dpm

^{238}Pu electroplate count -0.58 ± 0.07 dpm

Thin film provides reasonable agreement with traditional method – analytes are captured on surface



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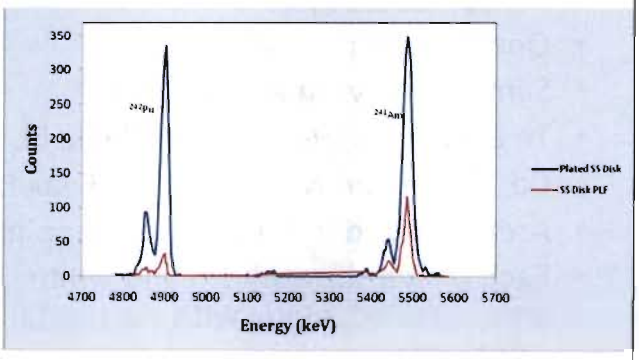
Comparison of polymer & ligand

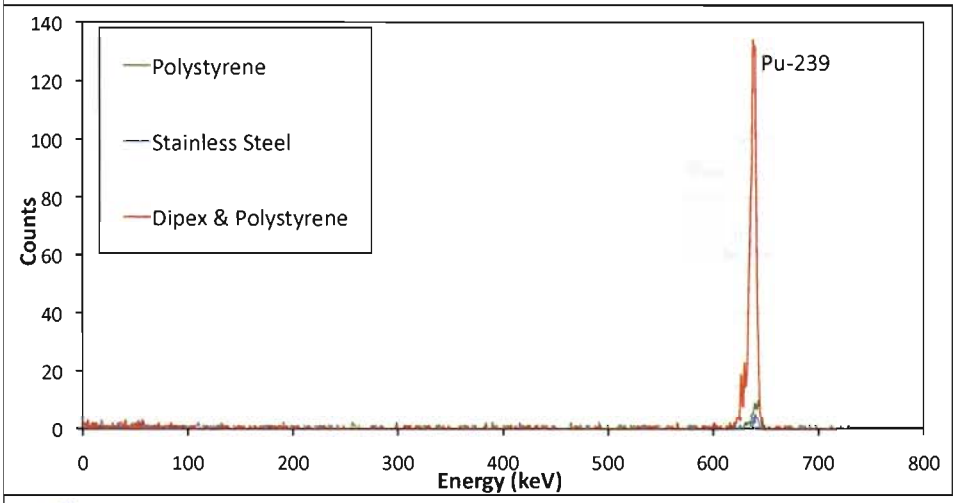
No polymer or ligand | Polymer only | Polymer & ligand

Comparison between plated and PLE Sample

- Recovery of Pu – 8%
- Recovery of Am – 53%
- FWHM Pu – 25 keV
- FWHM Am – 34 keV



Electrostatic vs. ligand attraction



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XRF Experimental

- Substrate exposed to analyte (1000 ug/ml in 4% HNO3) for 2 days
- One analyte per slide
- Sample analyzed as received
- Th and U analyzed by Edax Eagle III.
- Co, Cu, Fe and Ni analyzed by Edax Eagle II.
- Area selected for elemental mapping
- Each image show photo and white light image of area scanned, along with elemental images of the same area

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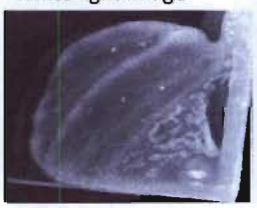
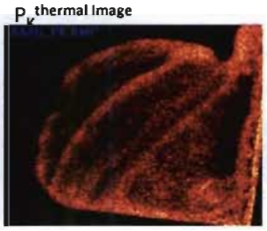
Elemental Images
Ligand with Uranium extracted

White light image

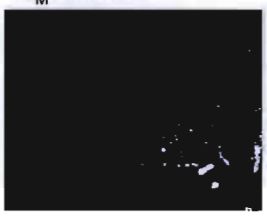


P_K psuedo image

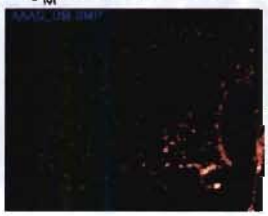
P_K thermal image



U_M psuedo image



U_M thermal image



Scan Distance (mm)
8 x 7
Beam Spacing (μm)
71 x 74
30 kV, 300 μA

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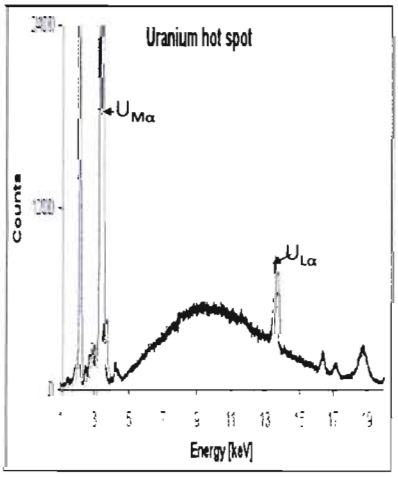
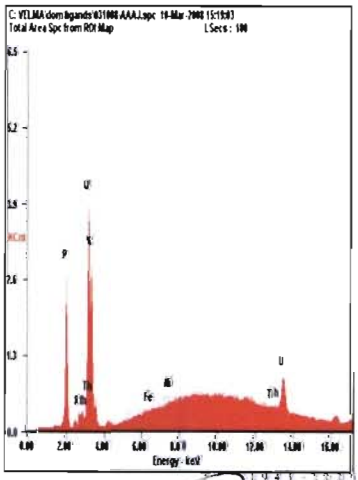
Spectrum
Ligand with Uranium extracted





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CHEMISTRY

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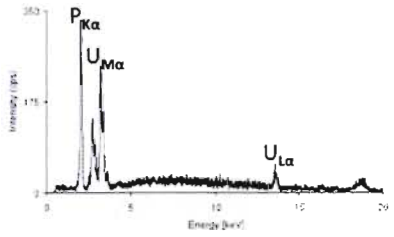
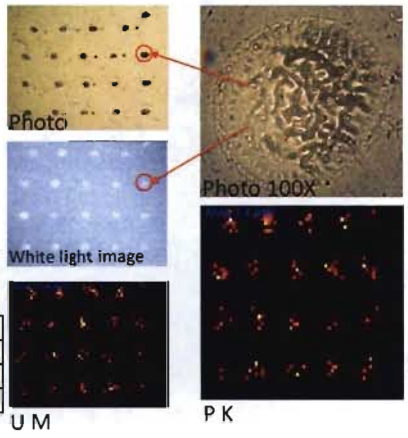
Ideas That Change the World

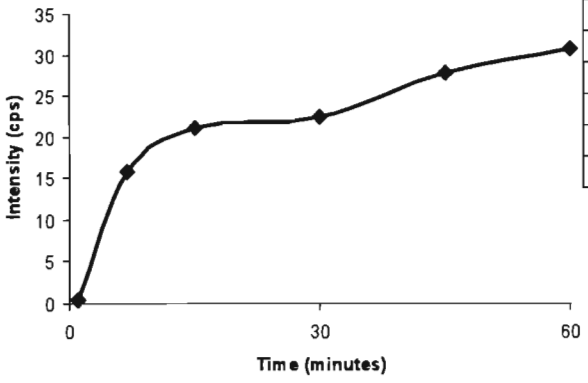
MXRF Spectra and elemental images
35 pL DIPEX deposits exposed for 7 minutes with 1 mg/mL Uranium



NET INTENSITY											
Elem	1	2	3	4	5	6	7	8	9	10	11
P K	18.0	35.7	11.3	30.5	19.4	3.4	32.6	25.8	19.3	18.7	23.9
U M	11.5	28.5	6.9	23.1	13.1	1.7	25.2	19.4	14.2	12.7	17.6



XRF Extraction Summary



Time (min.)	Ave U M counts (m=11)	Std Dev
1	1	0.1
7	16	3
15	21	12
30	22	14
45	28	15
60	31	11

Extraction mechanisms

- Three methods of mixing were used to determine if mixing effected the amount of radionuclides extracted. All had the same Pu-239 concentrations.

Extraction Comparison

- Stir and Non-stir methods
- 1L sample (tap water)
- Pu-239 (300 dpm)

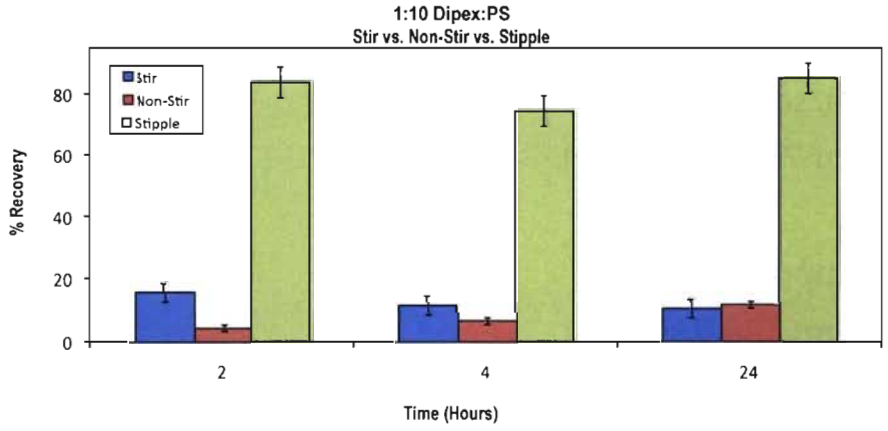
- Stipple method
- 3mL (Pu-239)
- Pu-239 (300 dpm)

Extraction mechanisms

a)  b)  c) 

Mechanisms a) stir b) non-stir c) drip

Extraction comparison



Stir

- Stir plate
- Stir rod
- 100 mL tap water
- 0.1 M HNO_3
- Pu-239 (15 dpm)
- 1:10 Dipex : PS thin film
- 45 degree angle

Non-stir

- No external supplies needed
- 100 mL tap water
- 0.1 M HNO_3
- Pu-239 (15 dpm)
- 1:10 Dipex : PS thin film
- Thin film face up

Drip

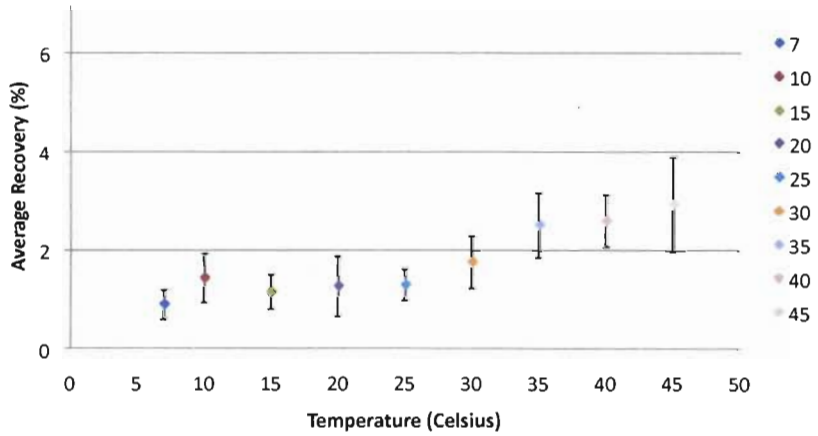
- 60 mL Syringe
- 100 mL tap water
- 0.1 M HNO_3
- Pu-239 (15 dpm)
- 1:10 Dipex : PS thin film
- Rinse with DI H_2O

Temperature study

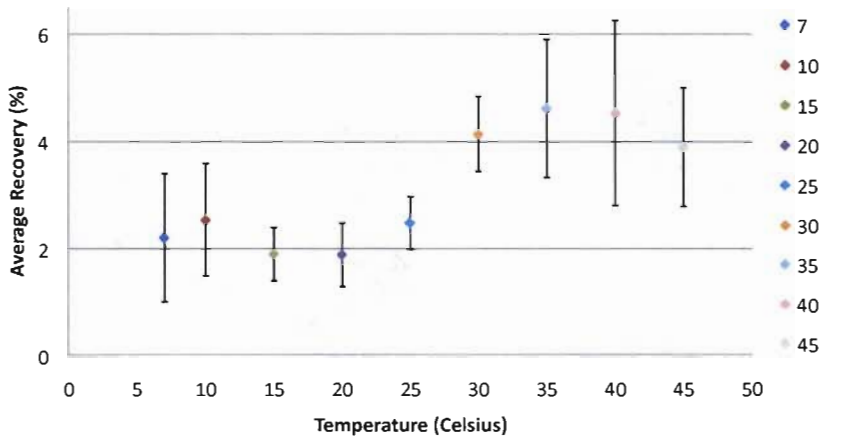
- A temperature study was conducted comparing the recovery and temperature variance. The samples were 1M using 100 mL (DI H_2O) spiked with 1mL of 15 dpm, Pu-239. Polystyrene was the polymer used for two extractants: Dipex and BDGA to create the PLE.

Temperature study

1 HR, Dipex:PS Temp Bath



2 HRS, Dipex:PS Temp Bath



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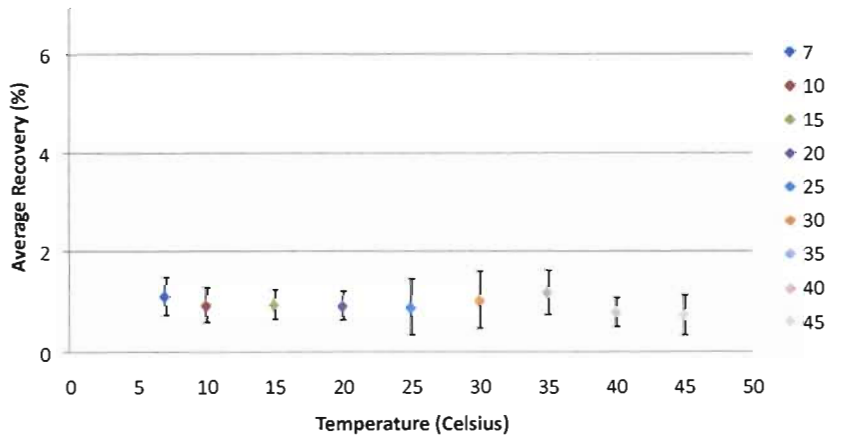
1 HR, BDGA:PS Temp Bath



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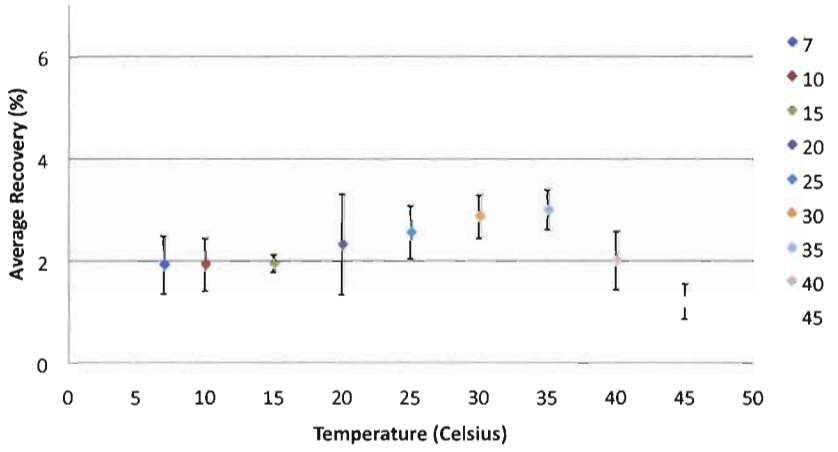
2 HRS BDGA:PS Temp Bath



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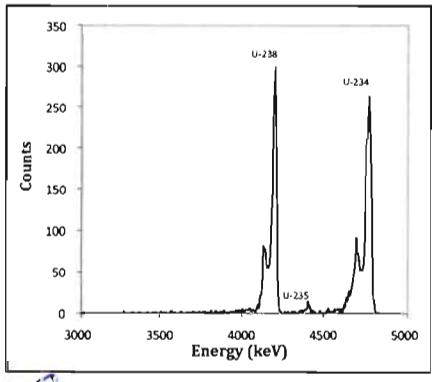
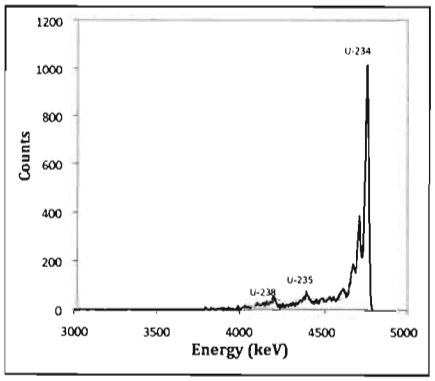
Application: Determination of Uranium Enrichment

Poly(styrene)/Dipex®

Natural Uranium



20% Enriched Uranium



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Application: Analysis of a soil sample

- 1 g soil sample prepared by NaOH fusion
  - 1g soil & 6g NaOH liquefied over flame
  - Sample cooled and dissolved in 50 mL water
  - Iron oxide precipitate filtered under vacuum
  - Solid dissolved in dilute nitric acid solution with 0.1 mL saturated sodium nitrite
  - Placed on hot plate until dry
- Solid residue dissolved in 10 mL of 0.08 M nitric acid
- Resulting solution analyzed with poly(styrene) and nitrocellulose polymer ligand films

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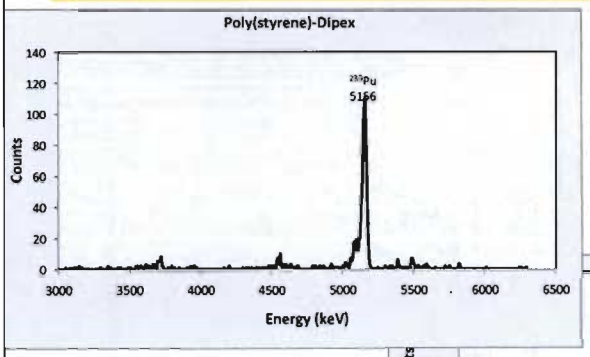
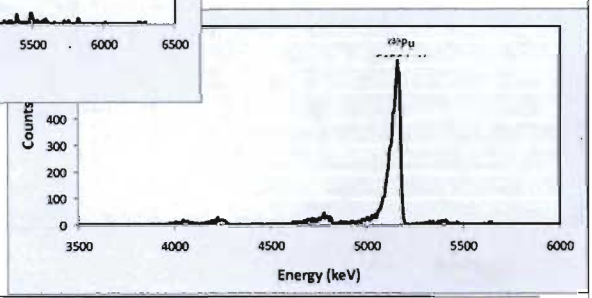
Soil Sample



Poly(styrene) PLF
- 5% extraction
- 20 keV FWHM



Nitrocellulose PLF
- 7% extraction
- 60 keV FWHM

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Application: Extraction of actinides from urine

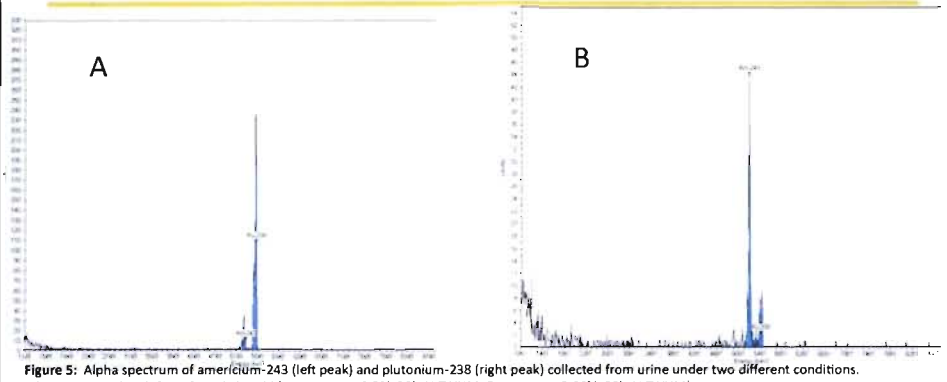

Figure 5: Alpha spectrum of americium-243 (left peak) and plutonium-238 (right peak) collected from urine under two different conditions.
A) urine treated with 2 mL 8 M nitric acid (Am recovery 9.5%, 30keV FWHM, Pu recovery 0.66%, 30keV FWHM),
B) urine treated with 1 mL saturated sodium nitrite (Am recovery 0.9%, 28 keV FWHM, Pu recovery 5.5%, 45 keV FWHM).

Gonzales & Peterson, Journal of Radioanalytical and Nuclear Chemistry, 282:543-547 (2009)

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Materials at Los Alamos

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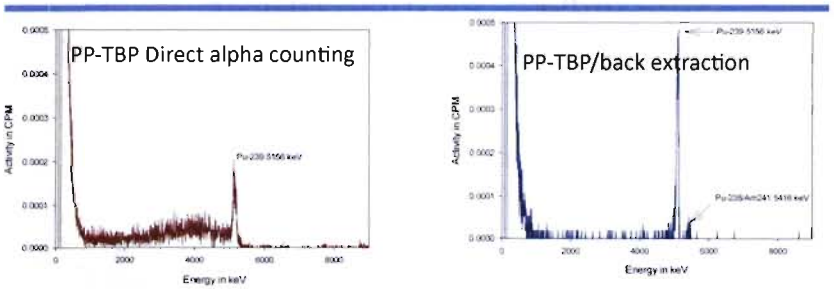
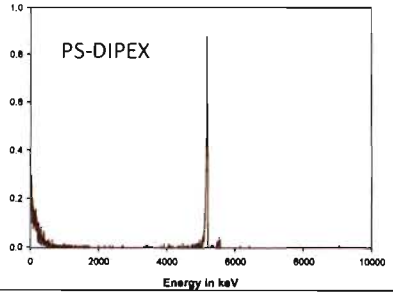
Comparative Alpha Spectrometry Analysis of Pu solution



Direct counting of the PP-TBP filters is not sufficient to resolve the different radionuclides present in solution.
Back extraction of the radionuclides into Decane enhances the resolution of the spectrum

Analysis of a pure Pu-239 stock solution on the PS-DIPEX membranes is sufficent to resolve the different radionuclides extracted onto the thin film.



Final comments on applications/PLEs

- pH effects are very important
- Speciation can be important (especially for Pu samples)
- Colloids
- Sampling results & parameters
- Lower levels of detection
- Operational considerations

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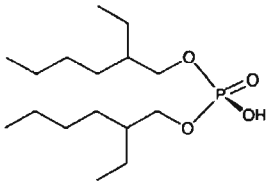
Extractants to be tried: HDEHP

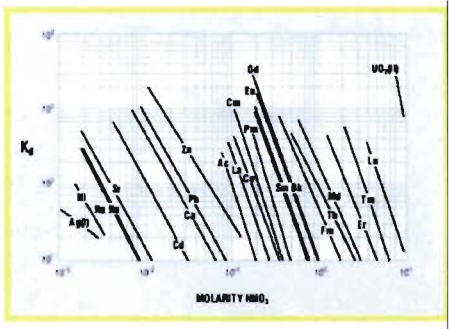


2-ethylhexylphosphoric acid

- Developed as an extractant for Ln series; sold by eichrom as their "Lanthanide" extractant

Figure 1

Uptake of Various Elements by Ln Resin



Horwitz et. al (1975)

Horwitz, E. P., *Bloomquist, C. A. A.*, J Inorg. Nucl. Chem, 37, **1997**, 425-434.

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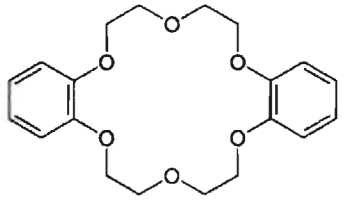
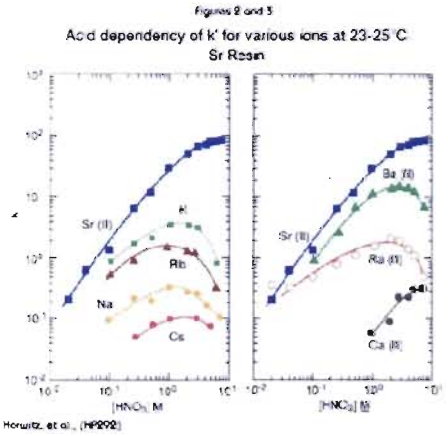
Extractants to be tried: Crown Ether



Dibenzo-18-crown-6



- Crown ethers are known to extract ions from solution
- Eichrom utilizes a similar concept in their Strontium resin
- http://www.eichrom.com

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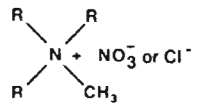
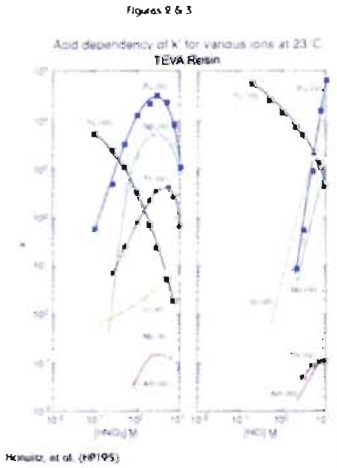
Extractants to be tried: TEVA

Figure 1

Trialkyl, methylammonium nitrate (or chloride)



R = C_8H_{17} and $C_{10}H_{21}$



- Used for the analysis of a wide range of analytes; from tetravalent actinides to lanthanides

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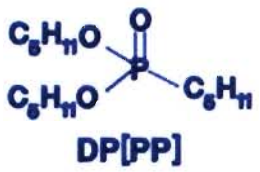
Extractants to be tried: U-TEVA

Figure 1



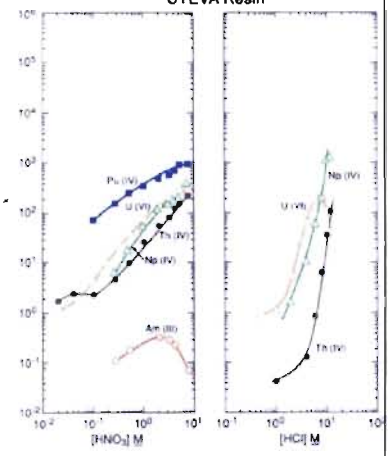
DP[PP]

Dipentyl, pentylphosphonate
(or Diamyl, amylphosphonate – DAAP)

- Used commercially for high uranium content materials

Figures 2 and 3

Acid dependency of k' for various ions at 23-25 C
UTEVA Resin



Horwitz, et al. (HP392)

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