Absorption Study of Am and Cm to TEVA, TRU and DGA Resins

A. Crable[1], A. Capote[2], N. Gharibyan[1], S. Happel[3], G. Maddigan[4], R. Sudowe[5], A. Bombard[3]

[1] Radiochemistry PhD Program, University of Nevada, Las Vegas - USA
[2] IAEA, Vienna – AUSTRIA
[3] TrisKem International, Bruz - FRANCE
[4] Ortec/AMETEK, Oak Ridge – USA
[5] Department of Health Physics, University of Nevada, Las Vegas - USA

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OUTLINE

- Overview
- Experimentals
- Results
- Conclusions

OVERVIEW

- Problem: Am and Cm supposed to behave similarly.

  However, sometimes deviating behaviours are observed ?

  Overestimation of Cm yields when Am-243 used as tracer

- Need to know the real behaviour of Cm versus Am

- Collaboration with University of Las Vegas (UNLV), IAEA and University of Marburg (KCM)

OVERVIEW

- UNLV:
  - Need for Am/Cm separation
    - Bibliography search: TEVA Resin with $LiNO_3$ system
- IAEA
  - Several years of experience with Am and Cm yields for their method (QC samples):
    - Data show difference between Am and Cm yields
- TrisKem / KCM
  - Determination of k'(D_w) values for varying conditions taken from literature described methods

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EXPERIMENTALS (1/3)

- Experiments based on literature*:
  - Separation of Am/Cm on TEVA in 3.00-4.00M $LiNO_3$/0.01M HNO_3.

- Additional experiments:
  - Extent $LiNO_3$ experiments onto TRU and DGA Resins
  - Test Am/Cm separation on TEVA, TRU and DGA for 0.01M-10M HNO_3 and 0.01M-6M HCl
  - Test Am/Cm uptake under various conditions used in literature

*Horwitz,E.P., Bloomquist, C.A.A., Orlandini, K.A., Hendersonn, D.J., Radiochim. Acta **8**, 127-32 (1967)

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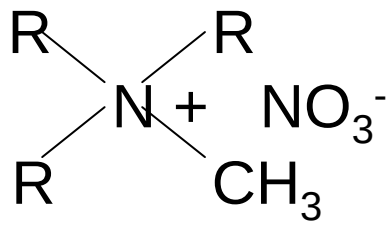
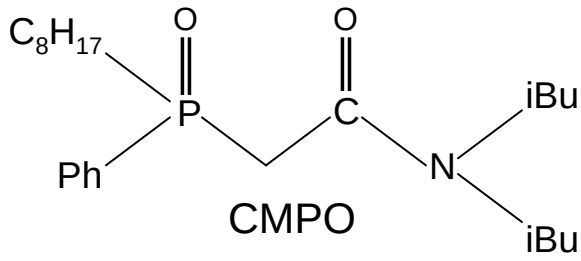
EXPERIMENTALS (2/3)

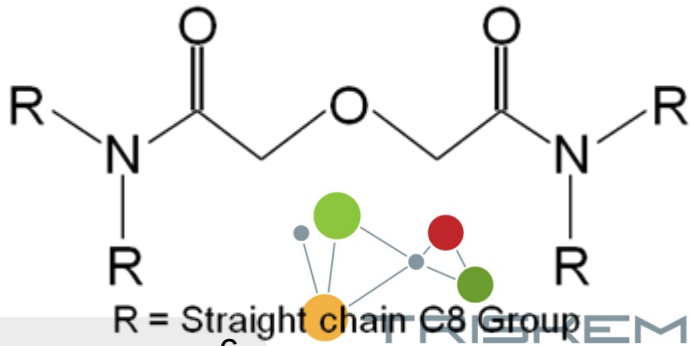
- TEVA Resin:
  - Active component = aliphatic quaternary amine (aliquat 336 nitrate)
- TRU Resin:
  - Active component = octylphenyl-N,N-di-isobutyl carbamoylphosphine oxyde (CMPO) / TBP
- DGA N Resin:
  - Active component = N,N,N',N'-tetraoctyldiglycolamide



R = C_8H_{17} and $C_{10}H_{21}$
Trialkyl,
methylammonium nitrate



CMPO



R = Straight chain C8 Group

DGA Resin Extractant

EXPERIMENTALS (3/3)

- Step 1: preconditionning of the resin
  - Known amount of resins
  - Known amount of solutions
- Step 2: addition of Am/Cm standards
  - Am-241
  - Cm-244
- Step 3: phase separation, sampling and activity determination
  - LSC counting

RESULTS

- $A_r = A_0 - A_s$ with A_r the activity on the resin
  A_0 the initial activity introduced in the sample
  A_s the activity in solution

- Weight distribution factor is obtained with

$D_w = (A_r x V_s)/(A_s x m_r)$ with V_s the volume of solution in contact with the mass m_r of resin

Resins	F
TEVA	0.53
TRU	0.56
DGA N	0.57

- k' can be calculated from D_W when correction factor F* of the resin is known

$k' = D_w x F$

- selectivity $\alpha_{Am/Cm} = k'_{Am}/k'_{Cm} = D_{wAm}/D_{wCm}$

*Eichrom Website: "Extraction Chromatography of Actinides and Selected Fission Products: Principles and Achievement of Selectivity" August 2008

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TEVA RESULTS

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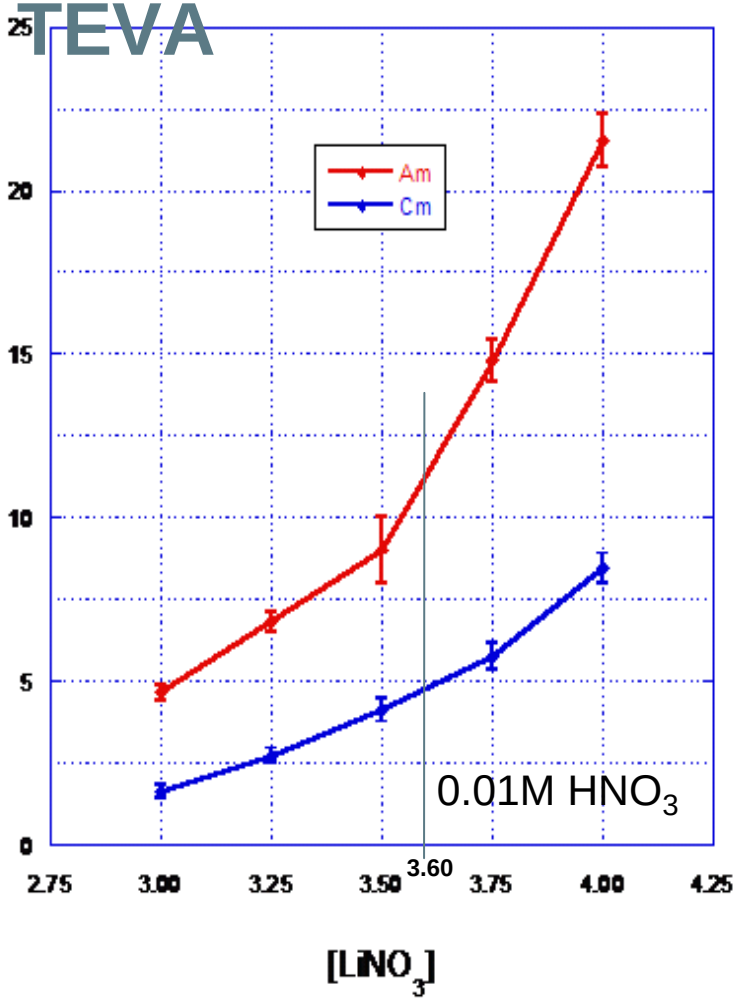
RESULTS - $LiNO_3$ system – UNLV (1/2)

Effects of $LiNO_3$ on Am and Cm uptake by TEVA



- Uptake: selectivity at 3.6M $LiNO_3$/0.01M HNO_3, $\alpha_{Am/Cm}$ =2.7-2.8
- maximum separation at 3.75M $LiNO_3$/0.01M HNO_3, $\alpha_{Am/Cm}$ ~ 2.58
- enhancement of separation at higher $LiNO_3$ concentration
- 4.00M $LiNO_3$ close to saturation point

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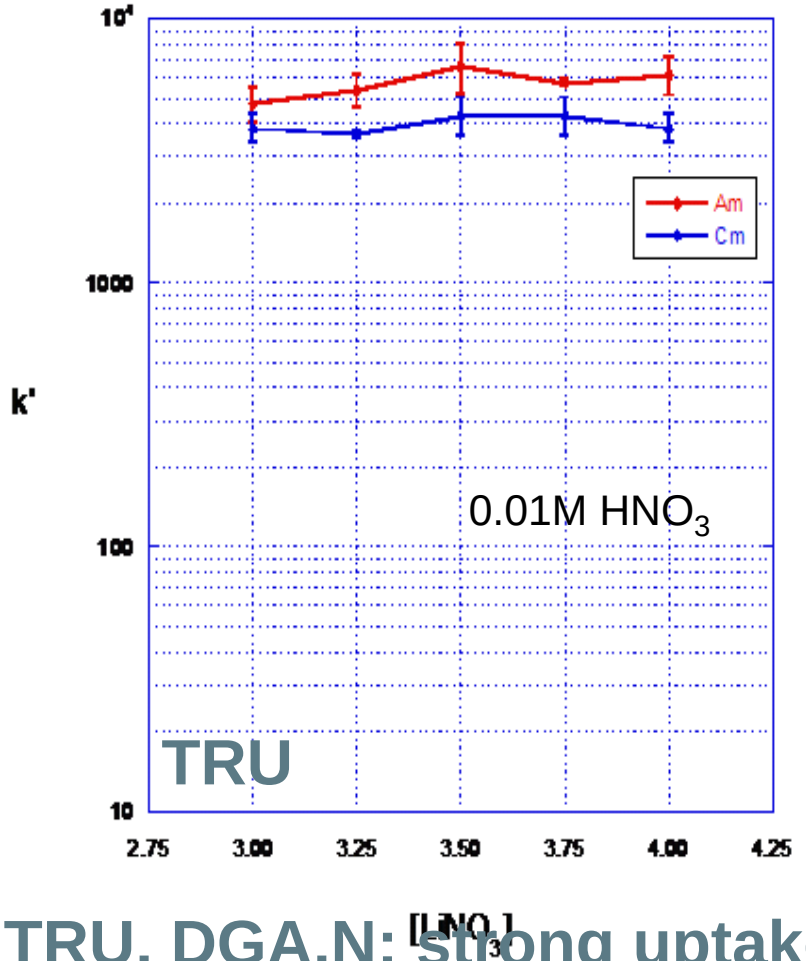
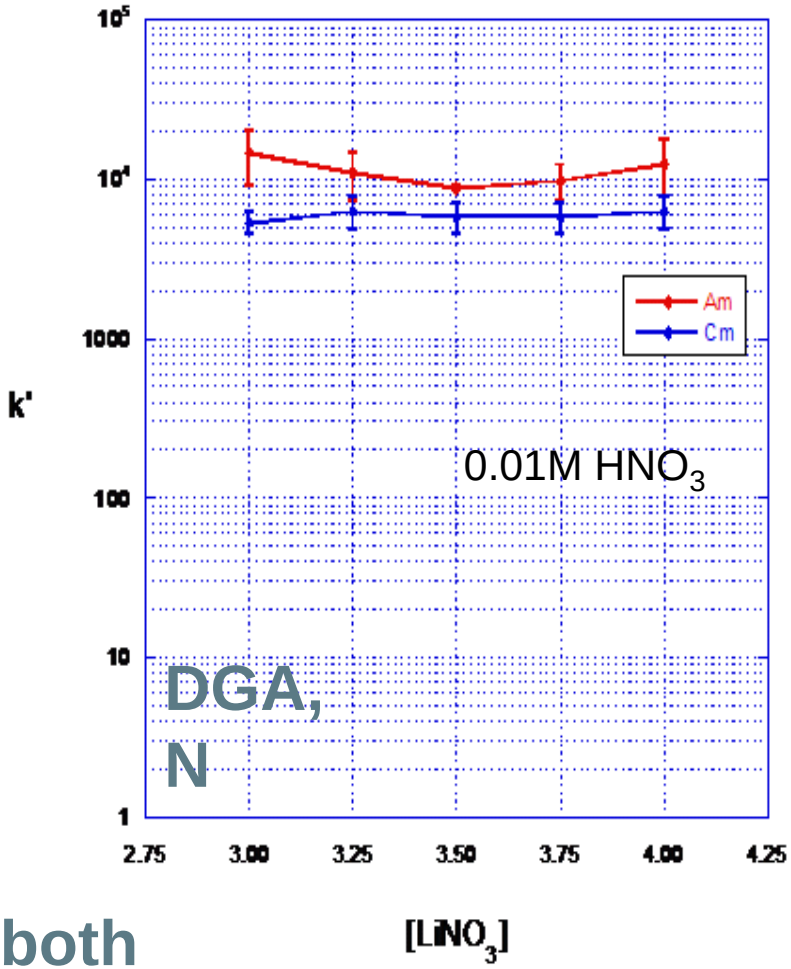
RESULTS - $LiNO_3$ system – UNLV

Effects of $LiNO_3$ on Am and Cm uptake by **TRU** and **DGA** (2/2)





TRU, DGA,N: strong uptake of both RN

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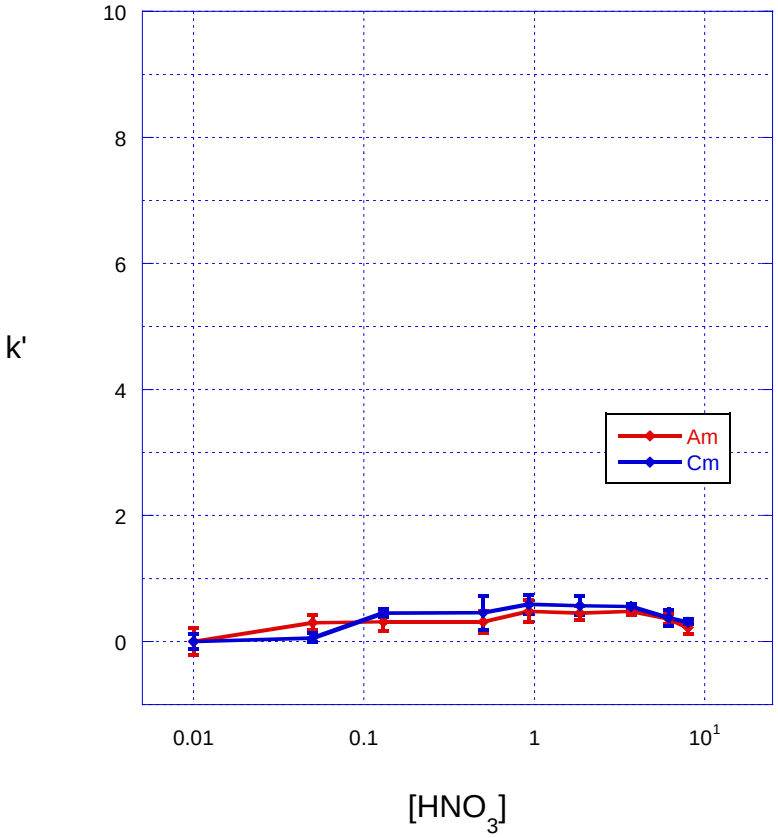
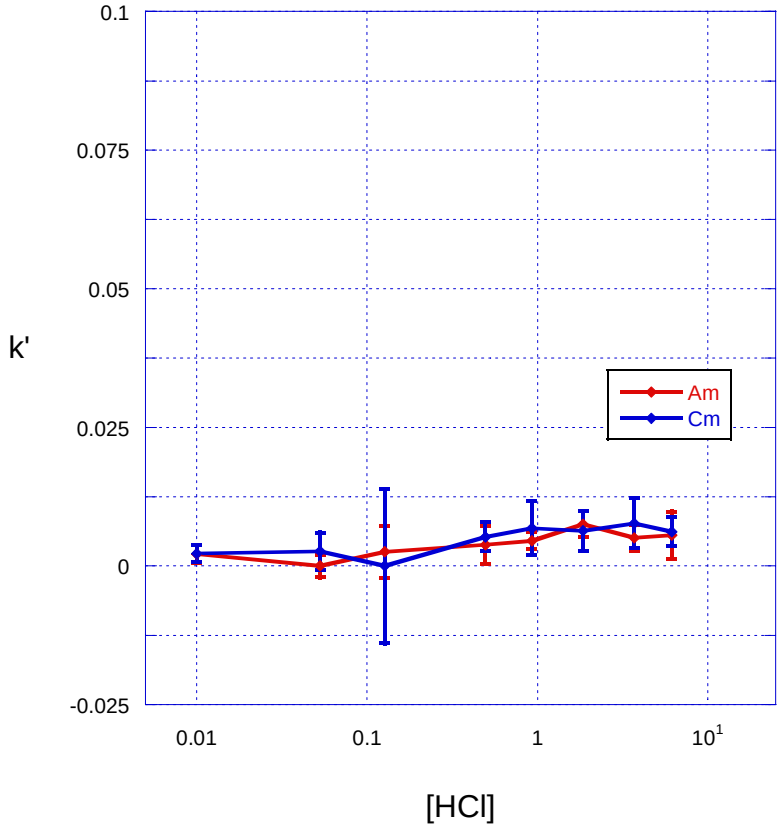
RESULTS: TEVA Resin - UNVL

Acid dependency, HNO_3 and HCl, of k' for Am and Cm





No Am/Cm uptake over the domain of concentration for both acids

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TRU RESULTS

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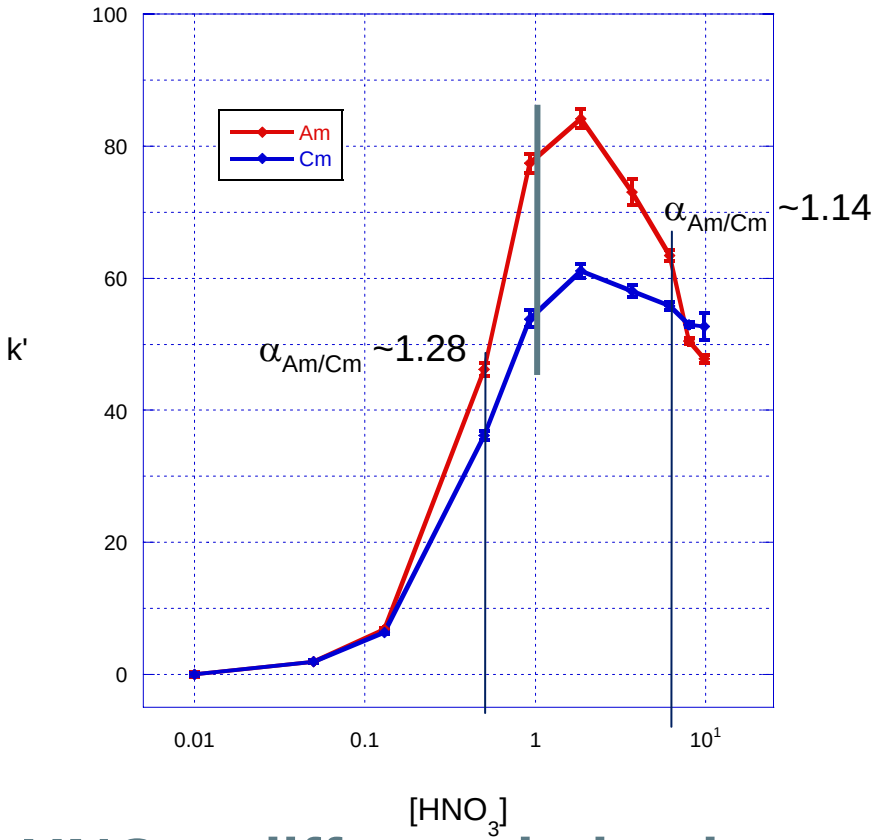
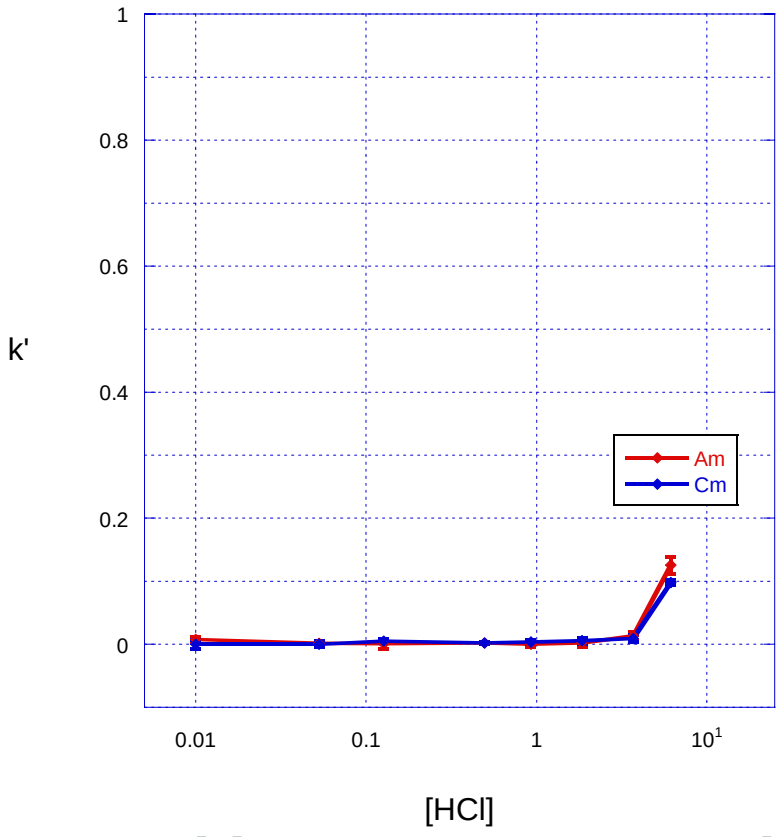
RESULTS: TRU Resin (1/7) - UNVL

Acid dependency, HNO_3 and HCl, of k' for Am and Cm





- **HNO_3 : different behaviour observed between 0.5M and 6M HNO_3. Maximum selectivity at 1M HNO_3: $\alpha_{Am/Cm}$ ~1.43**
- **HCl: No uptake**

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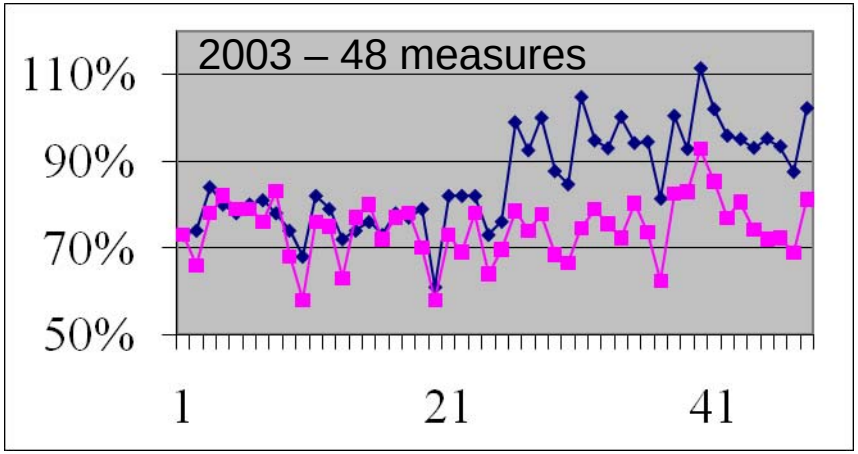
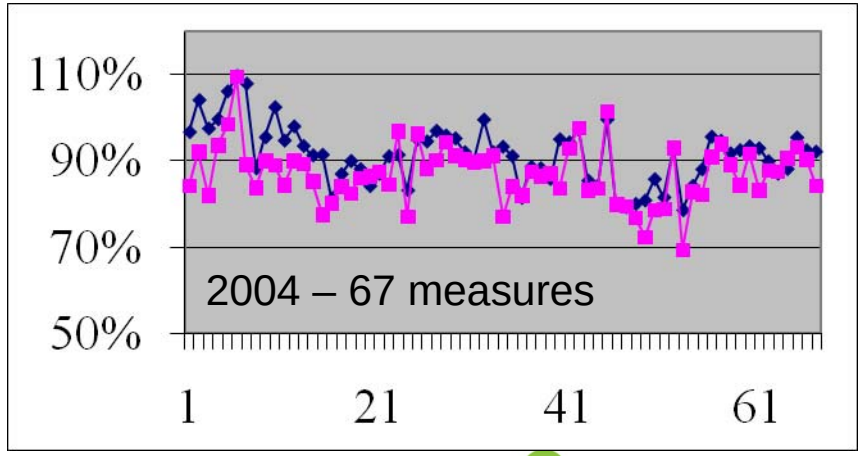
RESULTS: TRU Resin (2/7) - IAEA

Chemical yields obtained in Am and Cm from urine samples from 2003 to 2007.

Conditions of separation on TRU resin:

- Load: 2.5M HNO_3/0.5M $Al(NO_3)_3$,
- Rinse: 1M HNO_3,
- Elution: Ammonium bioxalate solution.





♦ Am-243
■ Cm-244

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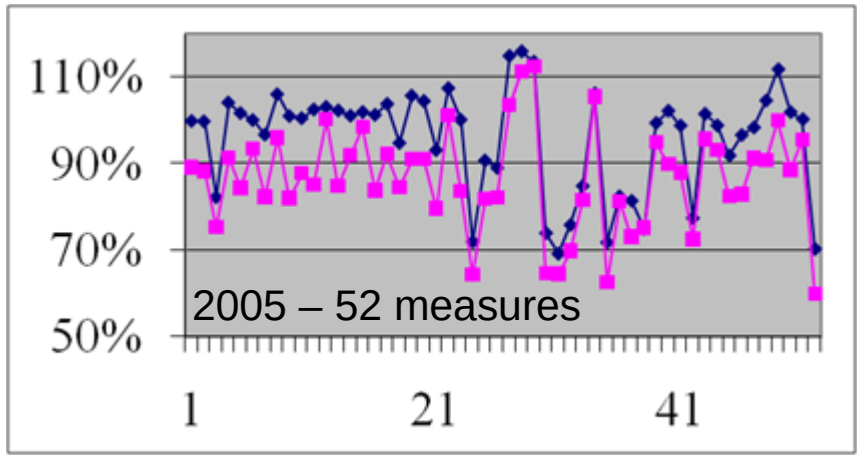
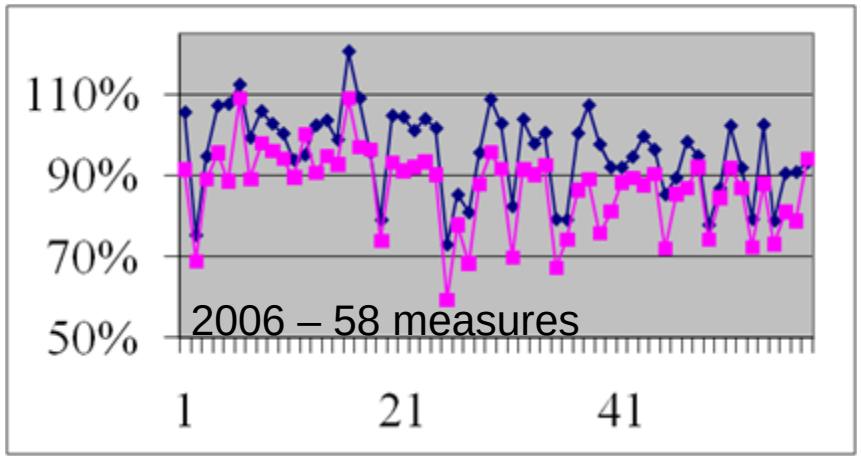
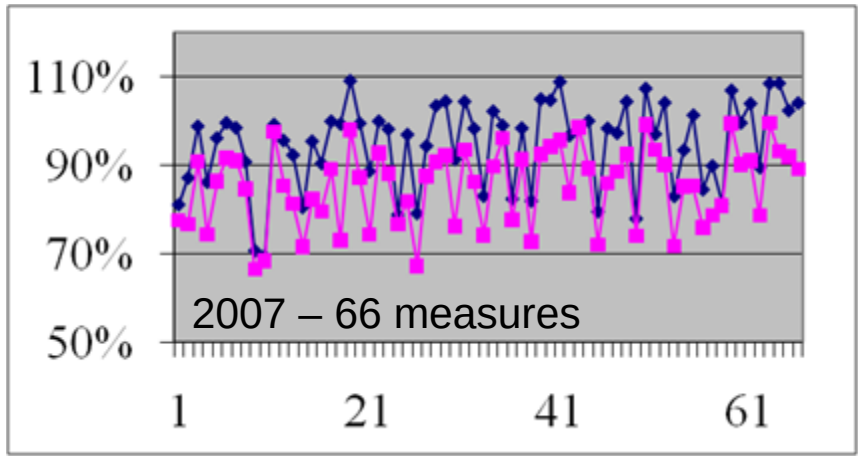
RESULTS: TRU Resin (3/7) - IAEA

- Am-243
- Cm-244







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RESULTS: TRU Resin (4/7) - IAEA

Years	Number of measures	Average chemical recoveries (%)		Average Deviation of Cm vs Am (%)
		Am-243	Cm-244	
2003	48	86 %	74 %	-11 %
2004	67	92%	87%	-5 %
2005	52	96%	86%	-9 %
2006	58	96%	87%	-9 %
2007	66	95%	85%	-10 %

If Am and Cm recoveries are supposed similar, Cm chemical recovery is overestimated by about 10% compared to « real » value observed.
Where is the Cm gone ?

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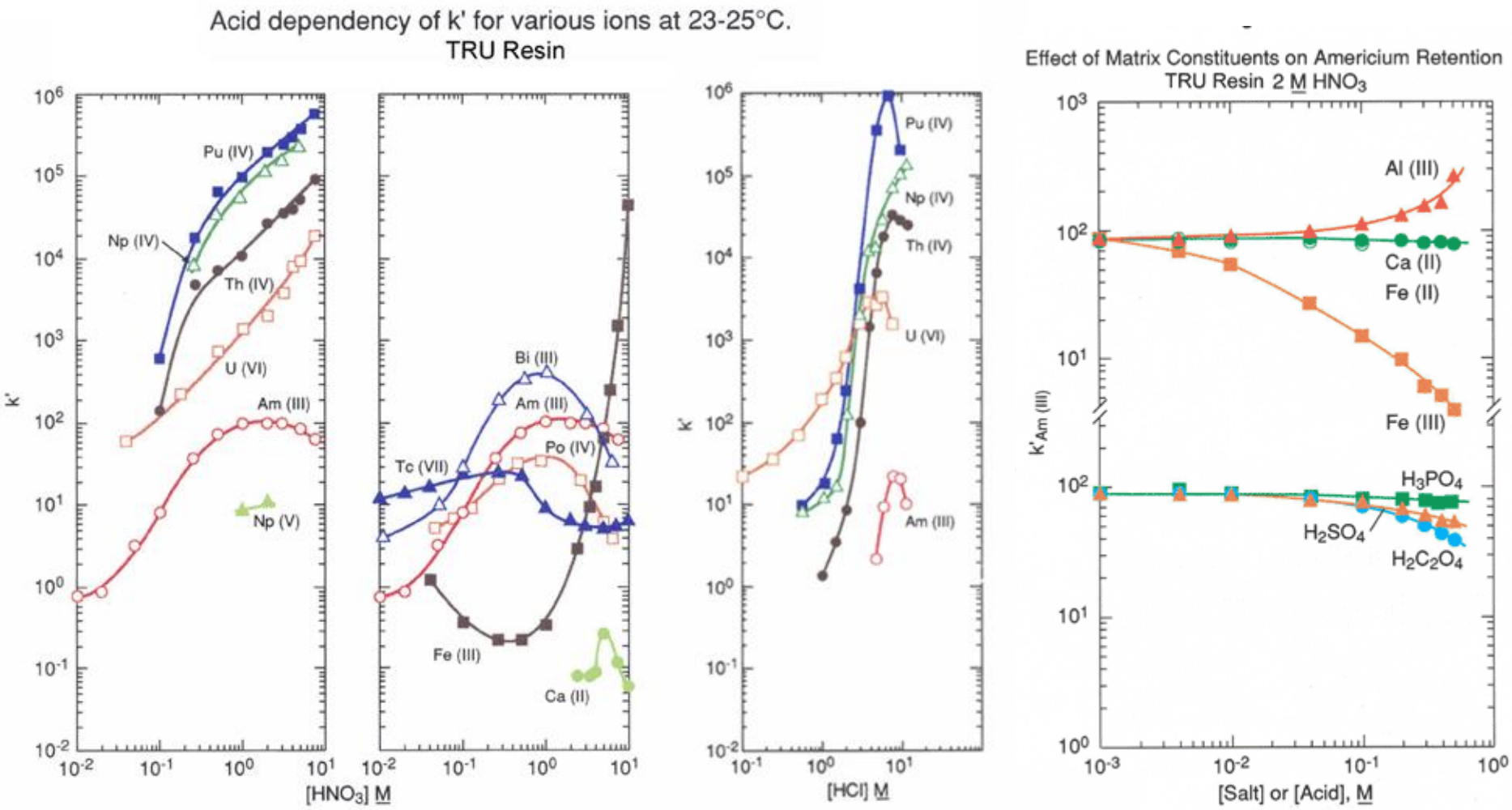
RESULTS: TRU Resin (5/7) - KCM



Horwitz, et al. (HP193)

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RESULTS: TRU Resin (6/7) - KCM

Tested conditions	
3M HNO_3	Standard loading conditions
3M HNO_3, 1M $Al(NO_3)_3$	
2M HNO_3, EDTA, 1M $Al(NO_3)_3$	
3M HNO_3, 1M $Al(NO_3)_3$, 0.1M $Ca(NO_3)_2$, 0.1M Na_3PO_4	Conditions testing the presence of phosphate
3M HNO_3, 0.1M $Ca(NO_3)_2$, 0.1M Na_3PO_4	
3M HNO_3, 0,5mg Fe(III),	Condition testing Fe(III) impact
3M HNO_3, 0,5mg EDTA,	Condition testing EDTA impact
3M HNO_3, 1M $Al(NO_3)_3$, Fe(II)sulfoxylate (‘rongalite’)	Reduction conditions for Fe(III) to Fe(II)
3M HNO_3 / 0.05M Fe(II)sulfamate	
3M HNO_3 / 0.1M Fe(II)sulfamate	
3M HNO_3 / 0.05M amidosulfonic acid	Condition testing sulfamic acid impact without Fe
3M HNO_3 / 0.1M amidosulfonic acid	
0.1M ammonium bioxalate, $NH_4HC_2O_4$	Elution conditions
4M HCl-0.1M HF (ACW04)	

RESULTS: TRU Resin (7/7) - KCM

Tested conditions	k'_{Am} ± STD		k'_{Cm} ± STD		α* ± STD	
3M HNO_3	86,2	2,1	60,5	1,0	1,42	0,03
3M HNO_3, 1M $Al(NO_3)_3$	133	16	101	4	1,31	0,13
2M HNO_3, EDTA, 1M $Al(NO_3)_3$	217	12	176	7	1,23	0,07
3M HNO_3, 1M $Al(NO_3)_3$, 0.1M $Ca(NO_3)_2$, 0.1M Na_3PO_4	126	3	109	10	1,16	0,09
3M HNO_3, 0.1M $Ca(NO_3)_2$, 0.1M Na_3PO_4,	95,8	0,2	63,9	1,1	1,50	0,02
3M HNO_3, 0,5mg Fe(III),	42,4	1,5	30,1	0,9	1,41	0,05
3M HNO_3, 0,5mg EDTA,	90,4	3,4	61,4	0,6	1,47	0,04
3M HNO_3, 1M $Al(NO_3)_3$, Fe(II)sulfoxylate ('rongalite')	6,16	0,17	5,97	0,50	1,03	0,09
3M HNO_3 / 0.05M Fe(II)sulfamate	55,3	0,8	27,5	0,3	2,01	0,02
3M HNO_3 / 0.1M Fe(II)sulfamate	28,9	0,7	20,3	1,4	1,42	0,07
3M HNO_3 / 0.05M amidosulfonic acid	90,0	0,5	60,649	0,001	1,48	0,01
3M HNO_3 / 0.1M amidosulfonic acid	90,1	0,4	58,0	0,8	1,55	0,02
0.1M ammonium bioxalate, $NH_4HC_2O_4$	0	0	0	0	-	-
4M HCl-0.1M HF (ACW04)	0,39	0,08	0,62	0,02	0,62	0,21

- **For most conditions tested, uptake of Am is 1.2 to 2 times higher than Cm.**
- **No uptake at all of Am and Cm with ammonium bioxalate solution.**

* Selectivity factor
$\alpha_{Am/Cm}=(Dw_{Am}/Dw_{Cm})$

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DGA RESULTS

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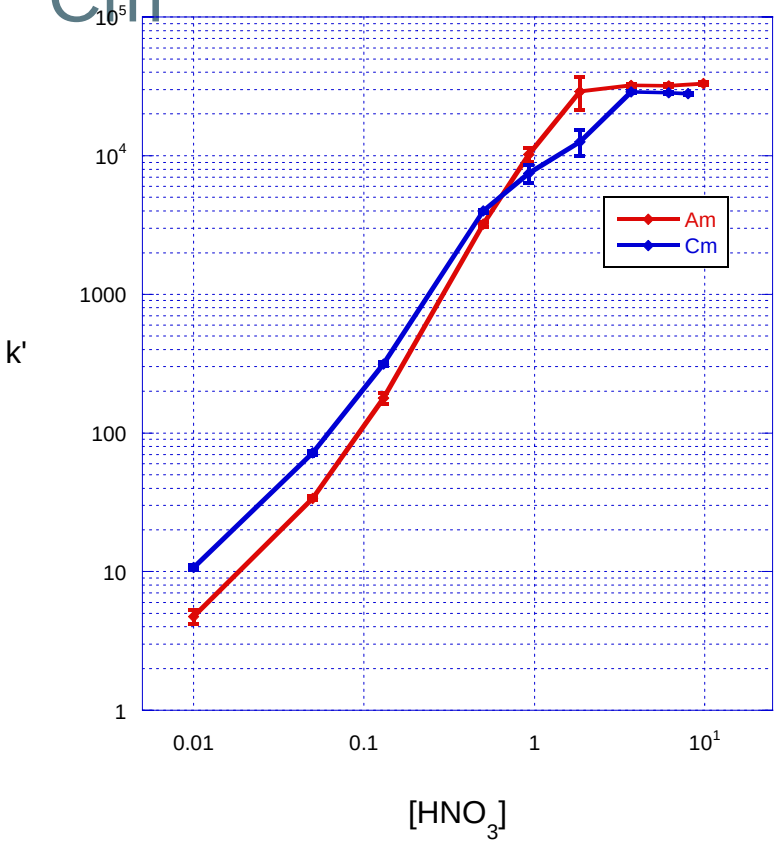
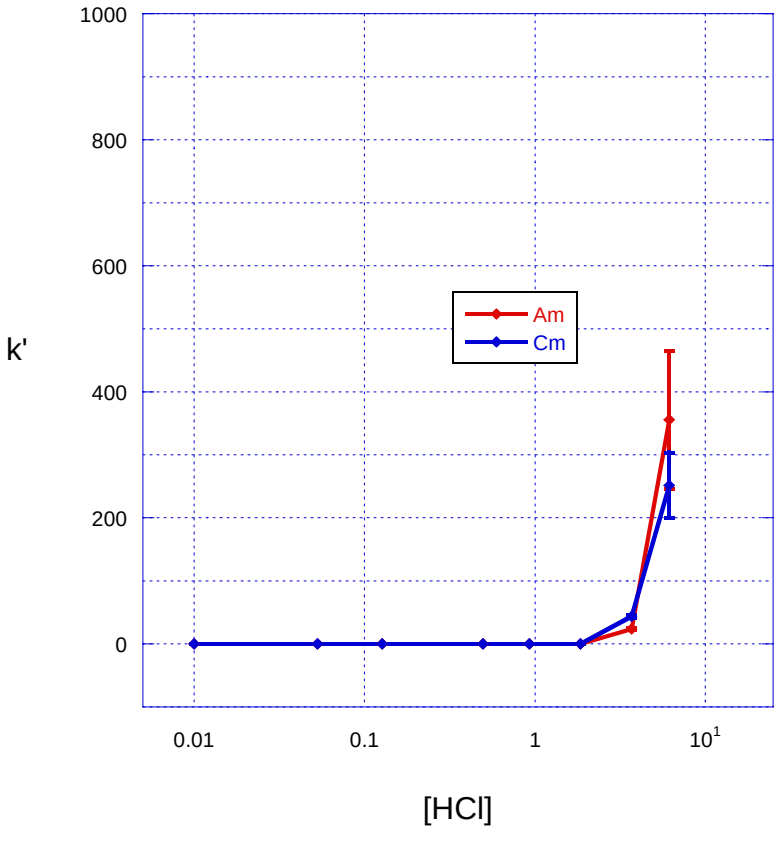
RESULTS: DGA,N Resin (1/4) - UNLV

Acid dependency, HNO_3 and HCl, of k' for Am and Cm





- **HNO_3 : uptake of Am/Cm increases with increasing concentration. Similar uptake of Am/Cm; $k'_{Cm} > k'_{Am}$ from 0.01M to 1M HNO_3.**
- **HCl: uptake at high HCl concentrations. Similar uptake of Am/Cm.**

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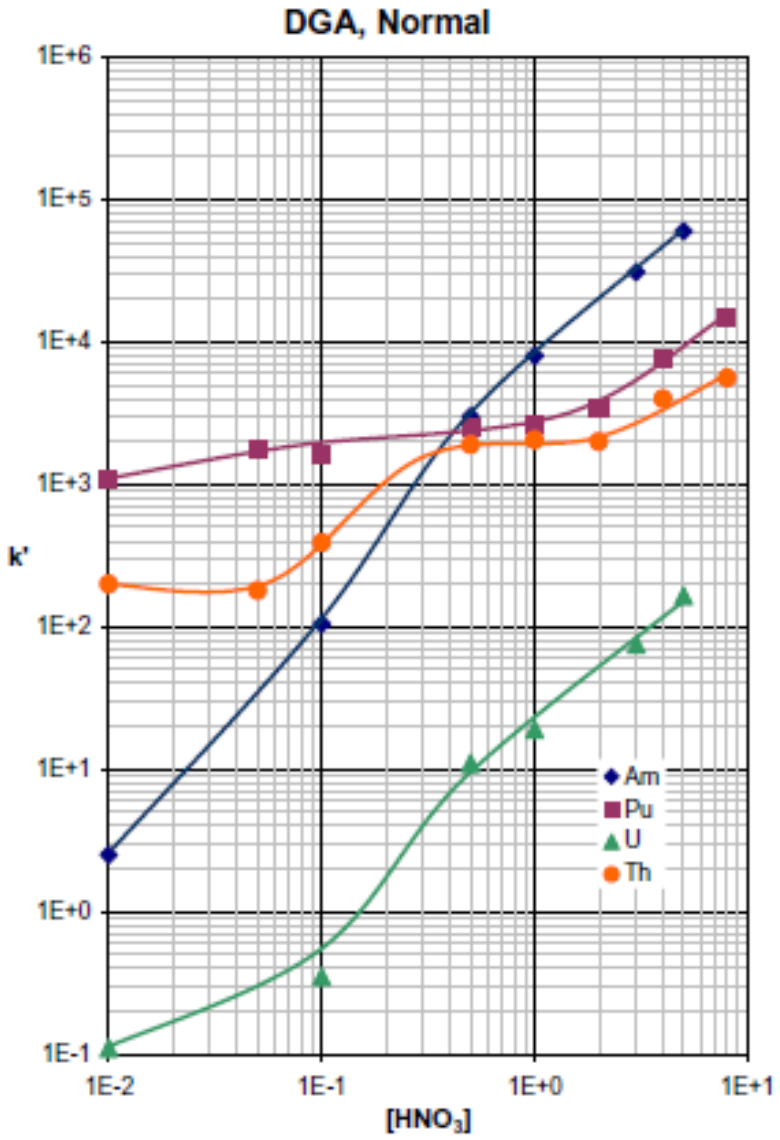
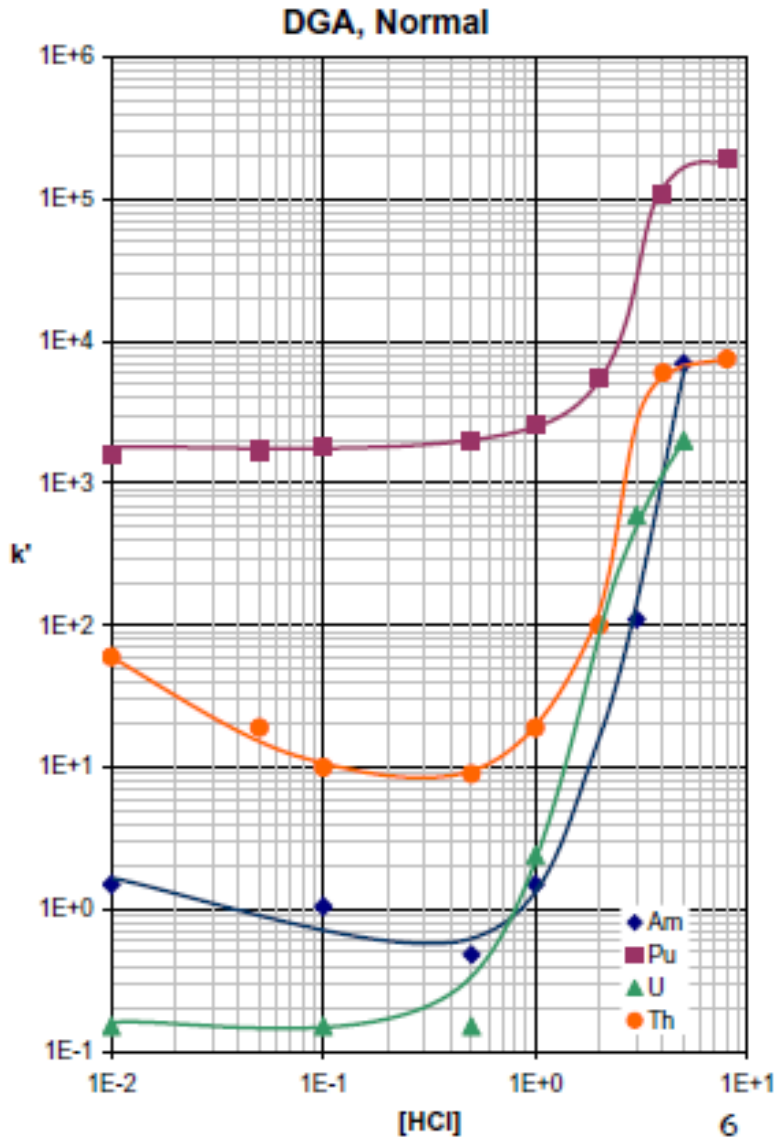
RESULTS: DGA Resin (2/4) - KCM





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RESULTS: DGA Resin (3/4) - KCM

Tested conditions	k'_{Am} ± STD		k'_{Cm} ± STD		α* ± STD	
3M HNO_3	>5000	-	4033	147	>1	-
3M HNO_3, 1M $Al(NO_3)_3$	>5000	-	>5000	-	NA	-
2M HNO_3, EDTA, 1M $Al(NO_3)_3$	>5000	-	4826	1264	>1	-
3M HNO_3, 1M $Al(NO_3)_3$, 0.1M $Ca(NO_3)_2$, 0.1M Na_3PO_4	1669	164	2225	9	0,750	0,098
3M HNO_3, 0.1M $Ca(NO_3)_2$, 0.1M Na_3PO_4,	147	4	249	8	0,589	0,042
3M HNO_3, 0,5mg Fe(III),	>5000	-	>5000	-	NA	-
3M HNO_3, 0,5mg EDTA,	>5000	-	>5000	-	NA	-
3M HNO_3, 1M $Al(NO_3)_3$, Fe(II)sulfoxylate (‘rongalite’)	>5000	-	2626	128	>1	-
3M HNO_3 / 0.05M Fe(II)sulfamate	>5000	-	>5000	-	NA	-
3M HNO_3 / 0.1M Fe(II)sulfamate	>5000	-	>5000	-	NA	-
3M HNO_3 / 0.05M amidosulfonic acid	>5000	-	3816	162	>1	-
3M HNO_3 / 0.1M amidosulfonic acid	>5000	-	4452	182	>1	-
0.1M ammonium bioxalate, $NH_4HC_2O_4$	0	0	0	0	-	-

RESULTS: DGA Resin (4/4) - KCM

- **For most of the conditions tested, the retention of both Am and Cm is so high that it would be difficult to recover one or the other even with a high selectivity value.**
- **Like for TRU, neither Am nor Cm are fixed on resin in ammonium bioxalate solution.**
- **For some conditions, $k'_{Cm} > k'_{Am}$.**

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CONCLUSIONS

- TEVA
  - Am and Cm behave differently in $LiNO_3$ /0.01 HNO_3 systems: possible separation
  - No Am/Cm uptake in HNO_3, HCl media

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CONCLUSIONS

- TRU
  - High uptake in $LiNO_3$ system, in the order of 10^3.
  - No Am/Cm uptake in HCl media.
  - In HNO_3, k'_{Am} differs from k'_{Cm} between 0.5M and 6M: $k'_{Am} > k'_{Cm}$.
  - Am and Cm recovered in the same fraction
  - For certain conditions, Cm starts eluting while Am remains on column
  - Ammonium bioxalate solution elutes completely Am/Cm-> Cm is lost in previous fractions

CONCLUSIONS

- DGA,N
  - High uptake in $LiNO_3$ system, in the order of 10^4
  - In HCl, Am/Cm uptake at high concentrations
  - In HNO_3, uptake of Am/Cm increases with increasing HNO_3 concentration, k'_{Am} and k'_{Cm} remaining similar over the whole domain of concentrations.
  - Very high uptake for almost all conditions tested:
    - Even high Am/Cm selectivity would not allow any breakthrough
    - Ammonium bioxalate solution for complete elution

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Thank you

Questions

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