

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

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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

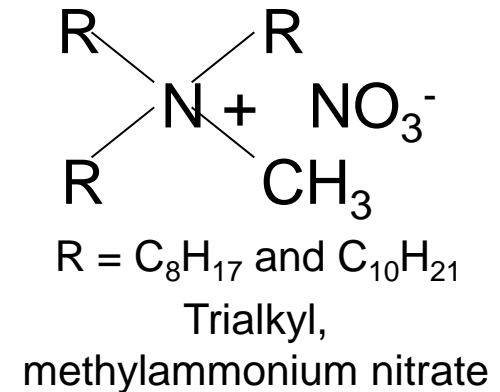
EXPERIMENTALS (1/3)

- 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

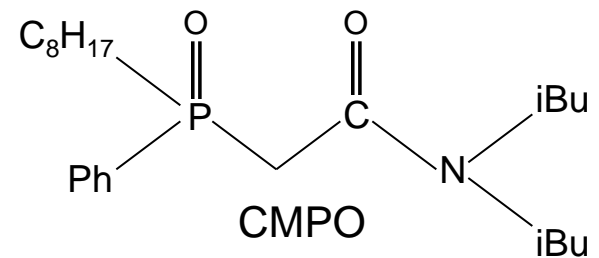
*Horwitz,E.P., Bloomquist, C.A.A., Orlandini, K.A., Henderson, D.J., Radiochim. Acta **8**, 127-32 (1967)

EXPERIMENTALS (2/3)

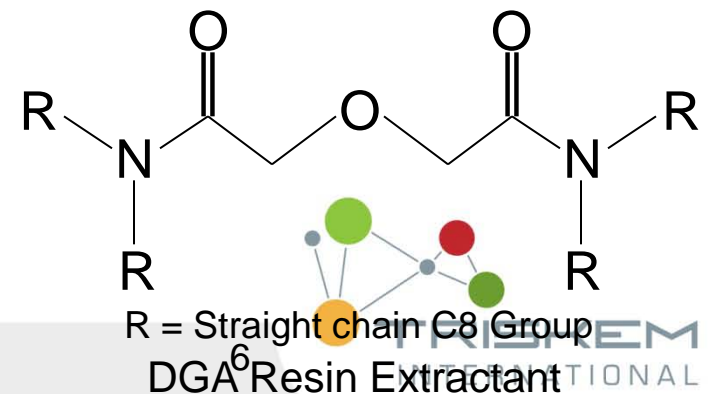
- TEVA Resin:
 - Active component = aliphatic quaternary amine (aliquat 336 nitrate)



- TRU Resin:
 - Active component = octylphenyl-N,N-di-isobutyl carbamoylphosphine oxide (CMPO) / TBP



- DGA N Resin:
 - Active component = N,N,N',N'-tetraoctyldiglycolamide



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

$$D_w = (A_r \times V_s) / (A_s \times m_r)$$

with V_s the volume of solution in contact with the mass m_r of resin

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

$$k' = D_w \times F$$

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

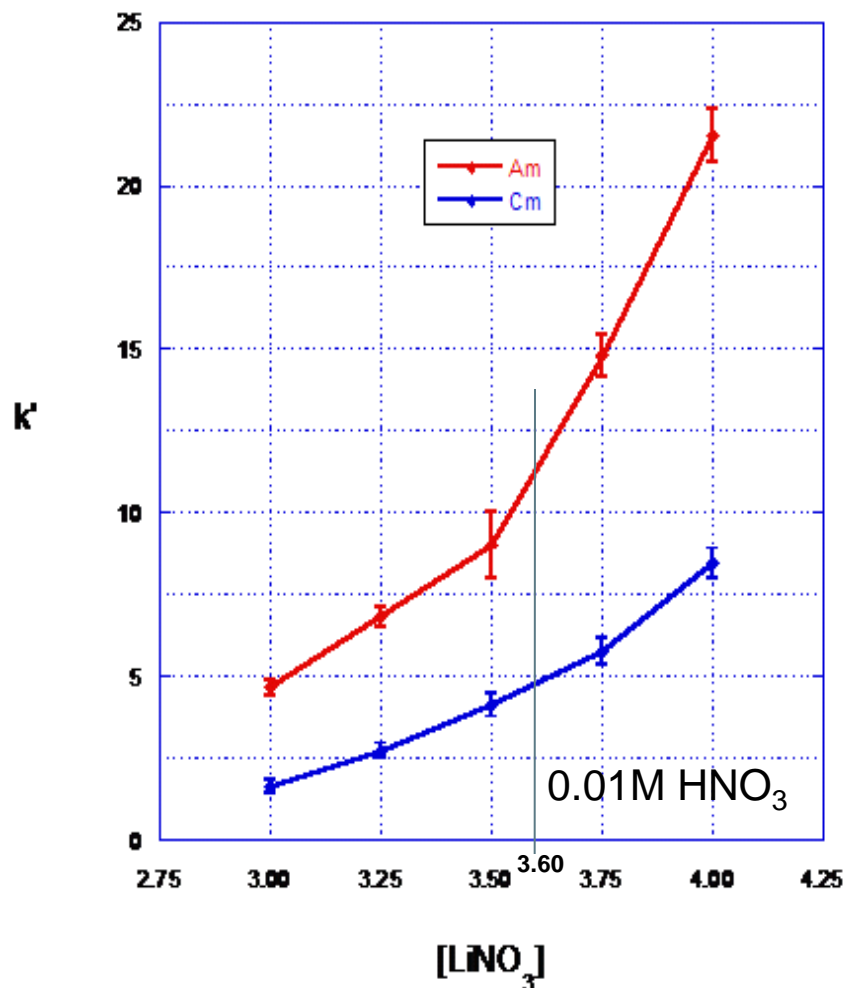
Resins	F
TEVA	0.53
TRU	0.56
DGA N	0.57

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

TEVA RESULTS

RESULTS - LiNO₃ system – UNLV (1/2)

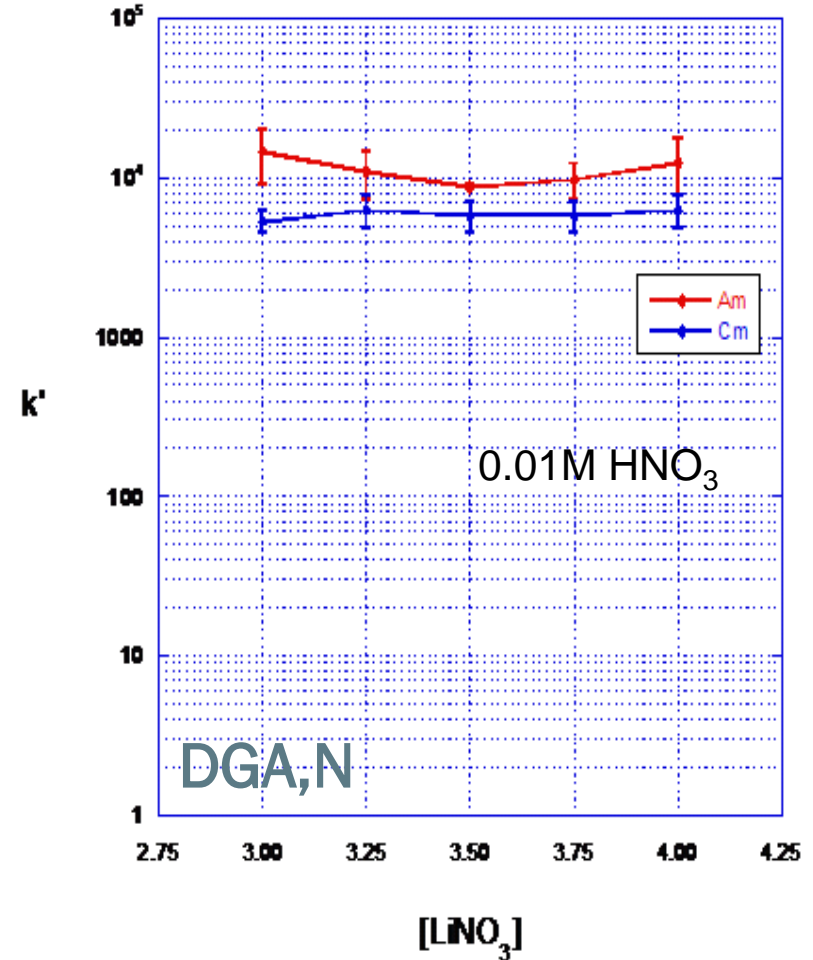
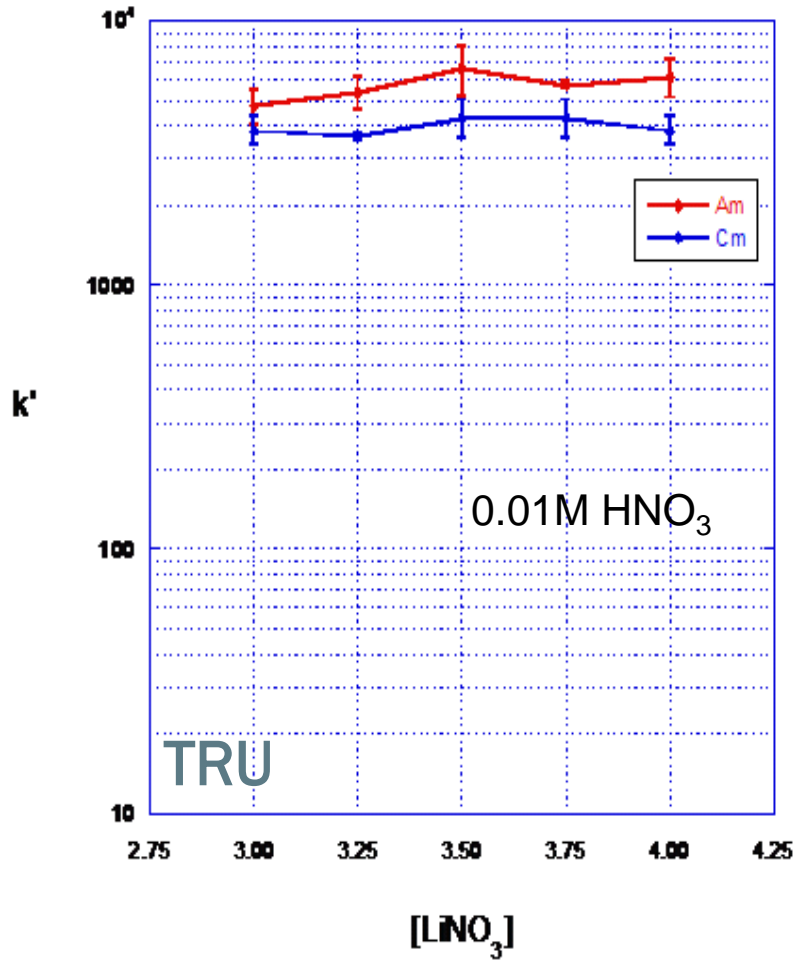
Effects of LiNO₃ on Am and Cm uptake by TEVA



- Literature: best selectivity at 3.6M LiNO₃/0.01M HNO₃, $\alpha_{Am/Cm} = 2.7-2.8$
- maximum separation at 3.75M LiNO₃/0.01M HNO₃, $\alpha_{Am/Cm} \sim 2.58$
- enhancement of separation at higher LiNO₃ concentration
- 4.00M LiNO₃ close to saturation point

RESULTS - LiNO₃ system – UNLV (2/2)

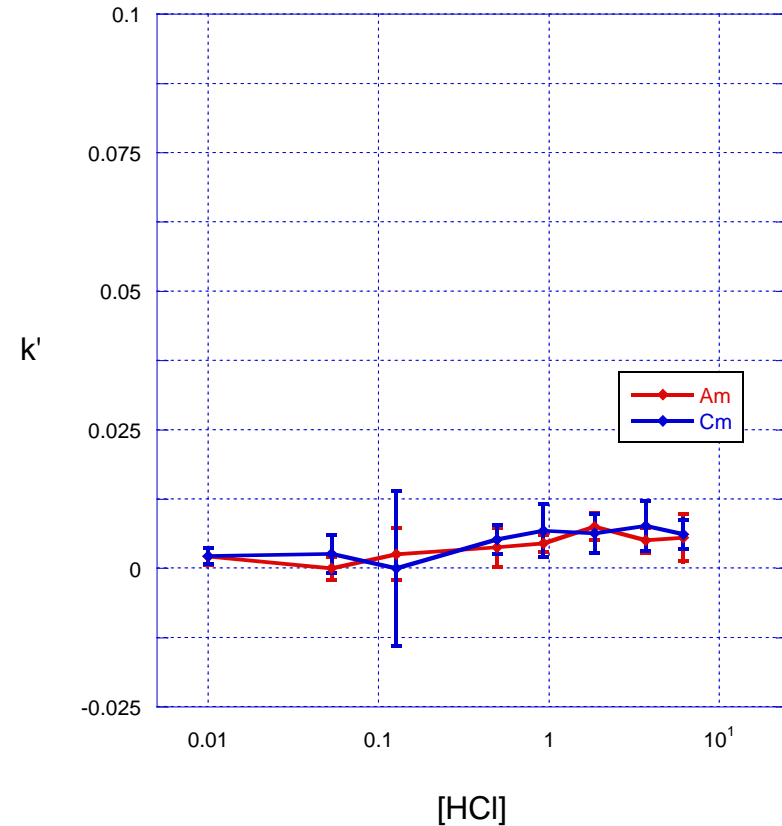
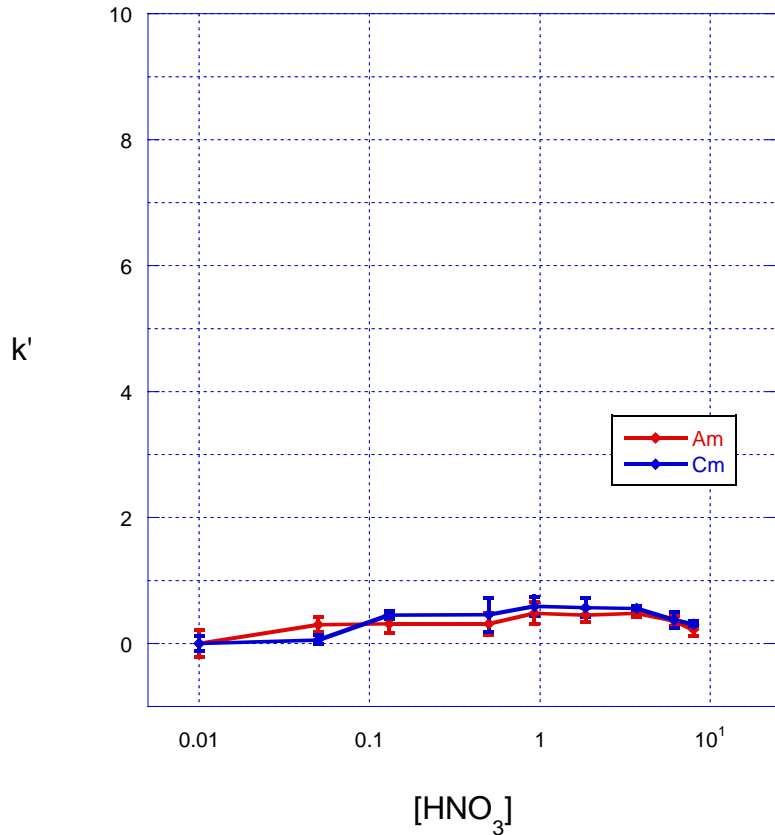
Effects of LiNO₃ on Am and Cm uptake by TRU and DGA



TRU, DGA,N: strong uptake of both RN

RESULTS: TEVA Resin - UNVL

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

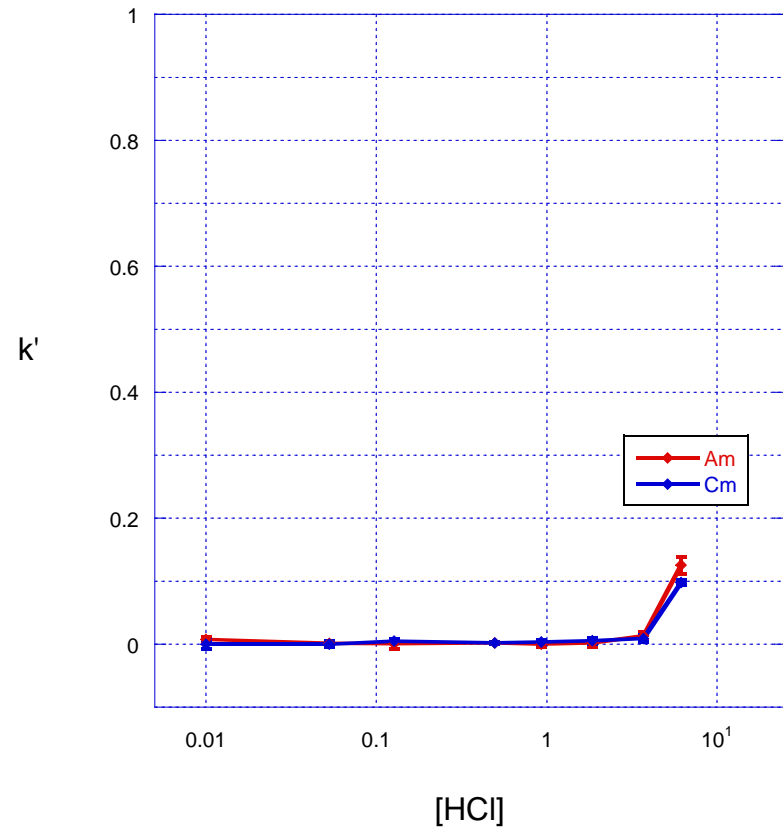
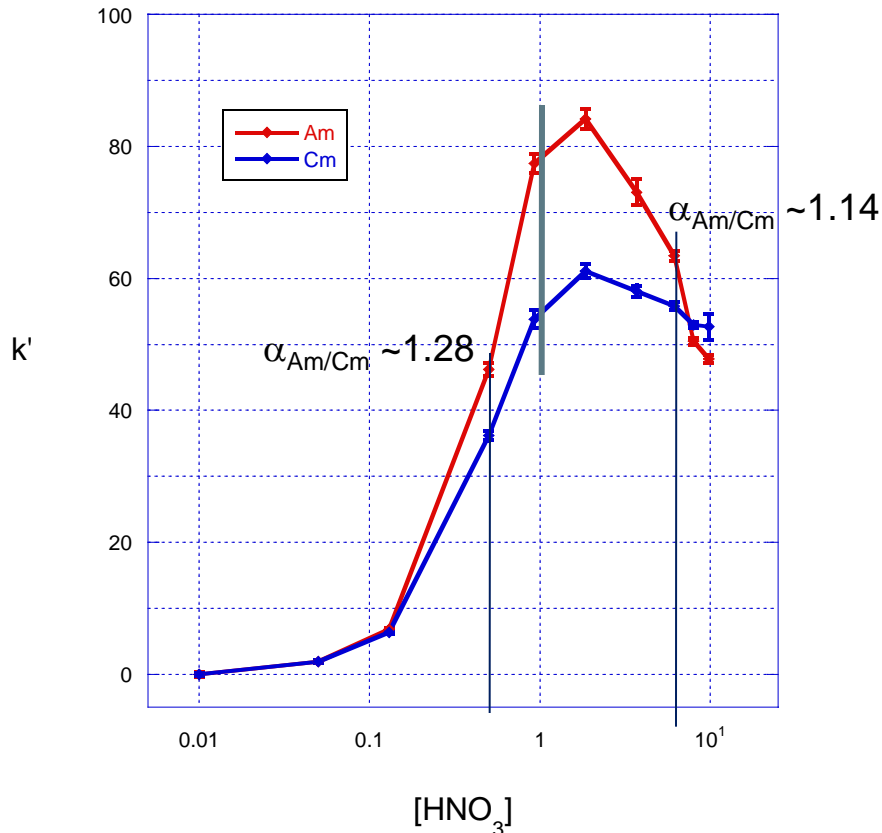


No Am/Cm uptake over the domain of concentration for both acids

TRU RESULTS

RESULTS: TRU Resin (1/8) - 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 : $\alpha_{\text{Am/Cm}} \sim 1.43$

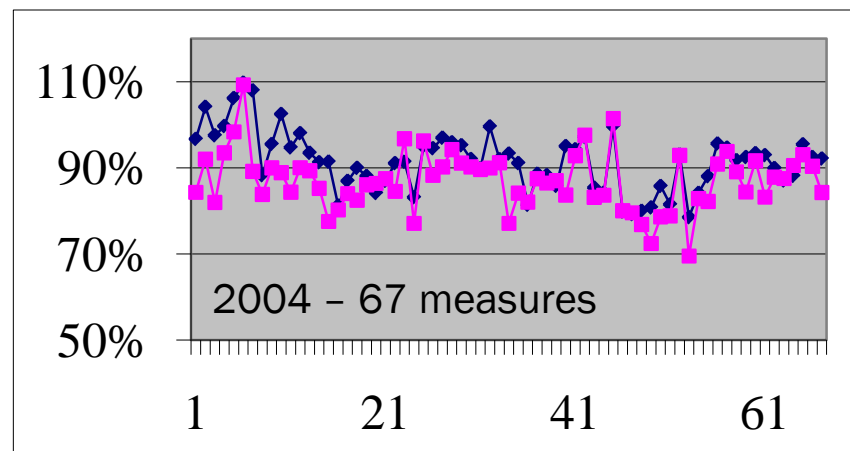
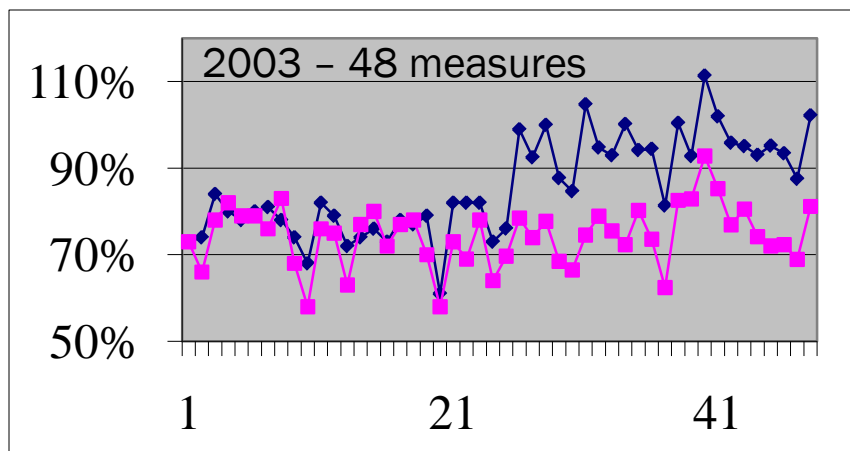
• HCl : No uptake

RESULTS: TRU Resin (2/8) - IAEA

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

Conditions of separation on TRU resin:

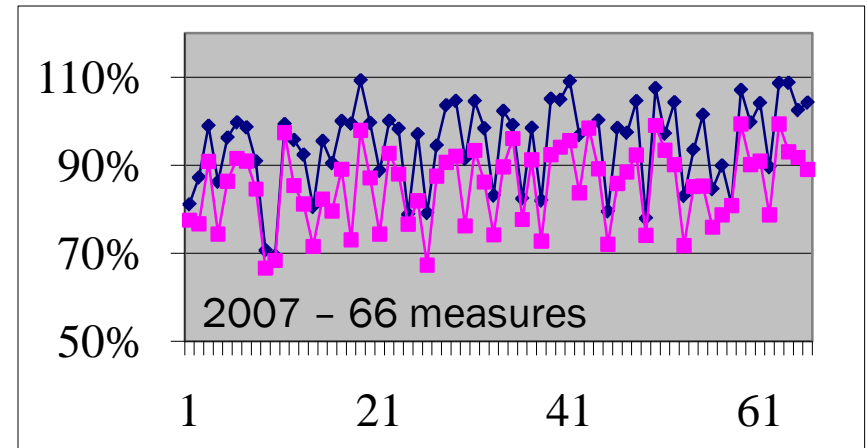
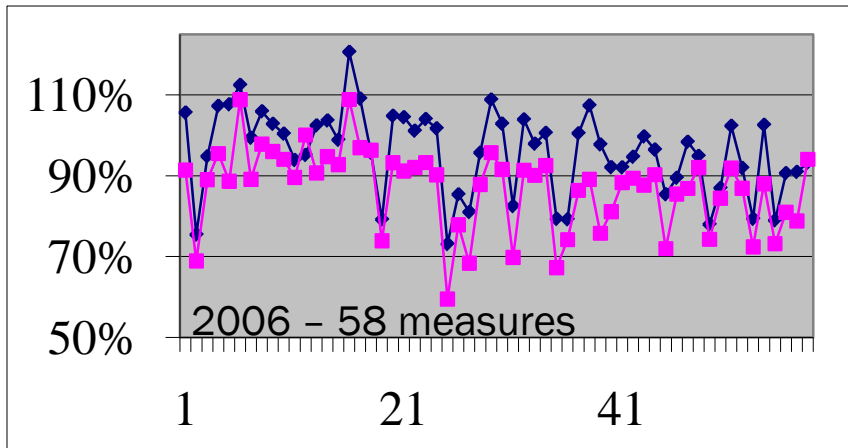
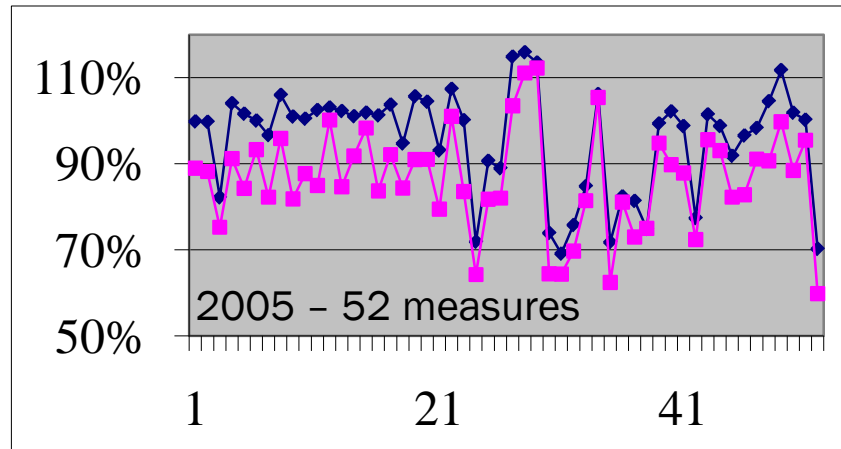
- Load: 2.5M HNO_3 /0.5M $\text{Al}(\text{NO}_3)_3$,
- Rinse: 1M HNO_3 ,
- Elution: Ammonium bioxalate solution.



- ◆ Am-243
- Cm-244

RESULTS: TRU Resin (3/8) - IAEA

◆ Am-243
■ Cm-244



RESULTS: TRU Resin (4/8) - 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 %

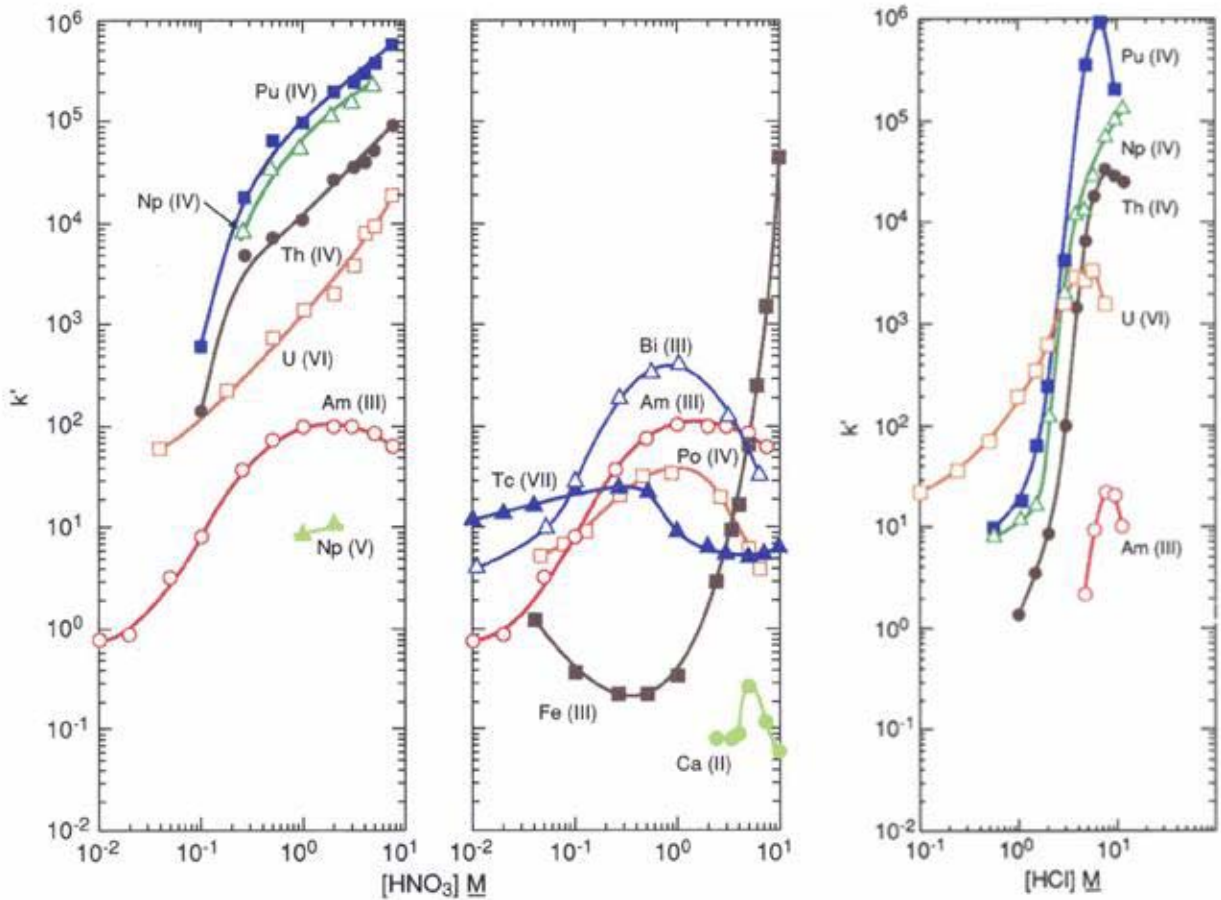
If Am and Cm recoveries are supposed similar, Cm chemical recovery is overestimated by about 10% compared to « real » value observed.

Where is the Cm gone ?

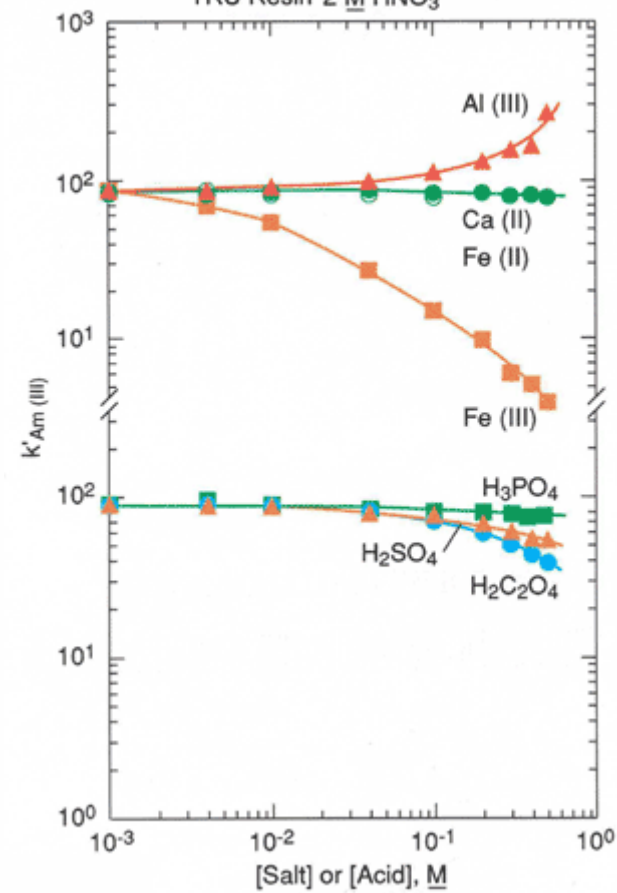
RESULTS: TRU Resin (5/8) - KCM

Acid dependency of k' for various ions at 23-25°C.

TRU Resin



Effect of Matrix Constituents on Americium Retention
TRU Resin 2 M HNO_3



Horwitz, et al. (HP193)

RESULTS: TRU Resin (6/8) - 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 ₃ PO ₄	Conditions testing the presence of phosphate
3M HNO ₃ , 0.1M Ca(NO ₃) ₂ , 0.1M Na ₃ PO 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 ₄ HC ₂ O ₄	Elution conditions
4M HCl-0.1M HF (ACW04)	

RESULTS: TRU Resin (7/8) - KCM

Tested conditions	$k'_{Am} \pm \text{STD}$		$k'_{Cm} \pm \text{STD}$		$\alpha^* \pm \text{STD}$	
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 ₃ PO ₄	126	3	109	10	1,16	0,09
3M HNO ₃ , 0.1M Ca(NO ₃) ₂ , 0.1M Na ₃ PO 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 ₄ HC ₂ O ₄	0	0	0	0	-	-
4M HCl-0.1M HF (ACW04)	0,39	0,08	0,62	0,02	0,62	0,21

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

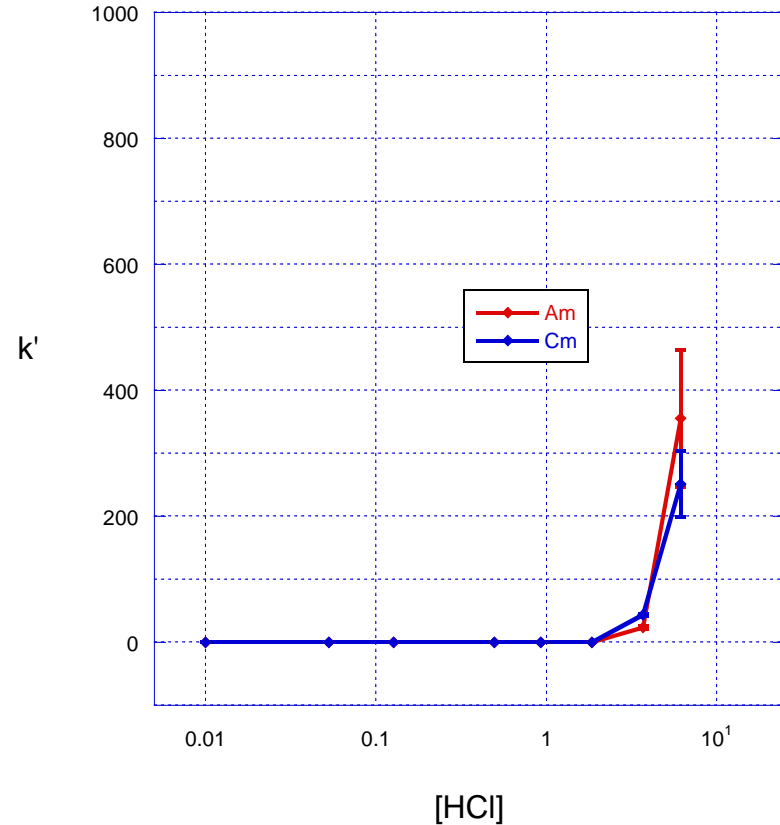
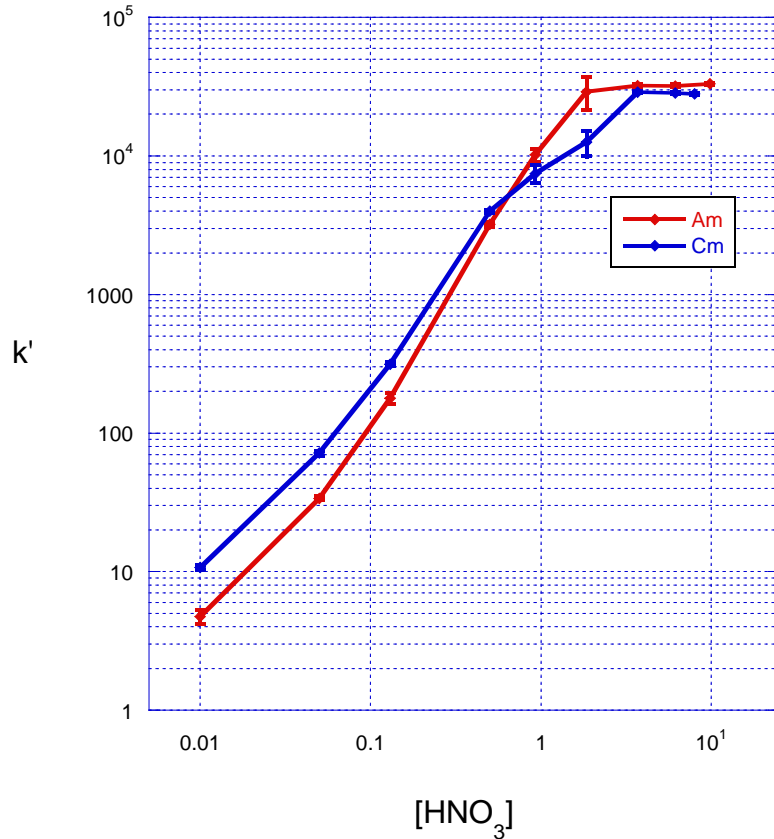
Results KCM (8/8)

- For most conditions tested, uptake of Am is 1.2 to 2 times higher than Cm (coherent with UNVL results).
- Presence of Al(III) alone or with EDTA increase the retention of Am and Cm by a factor 1.5 to 3.
- Phosphates, EDTA and amidosulfonique acid do not interfere Am and Cm retention.
- Fe(III) and Fe(II) interfere Am and Cm retention.
- No uptake at all of Am and Cm with ammonium bioxalate solution and HCl 4M-HF 0.1M: these conditions ensure 100% recovery of Am/Cm from the resin.
 - The loss of Cm happens prior the elution step

DGA RESULTS

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

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

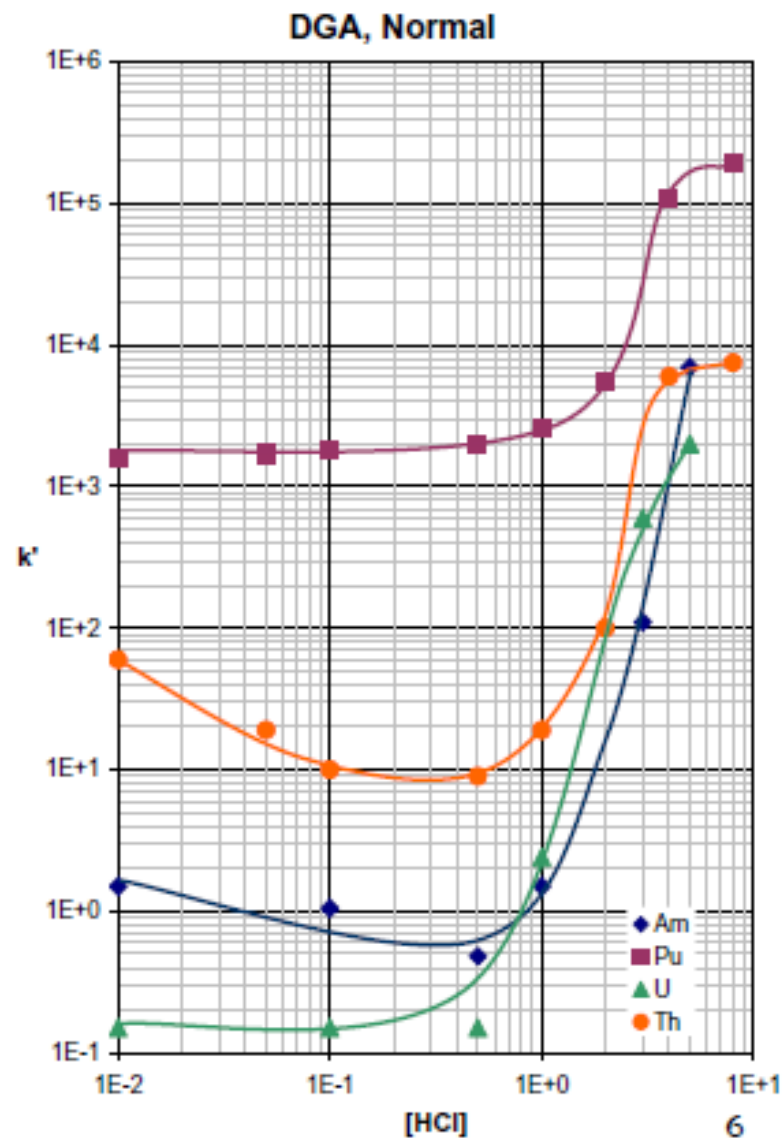
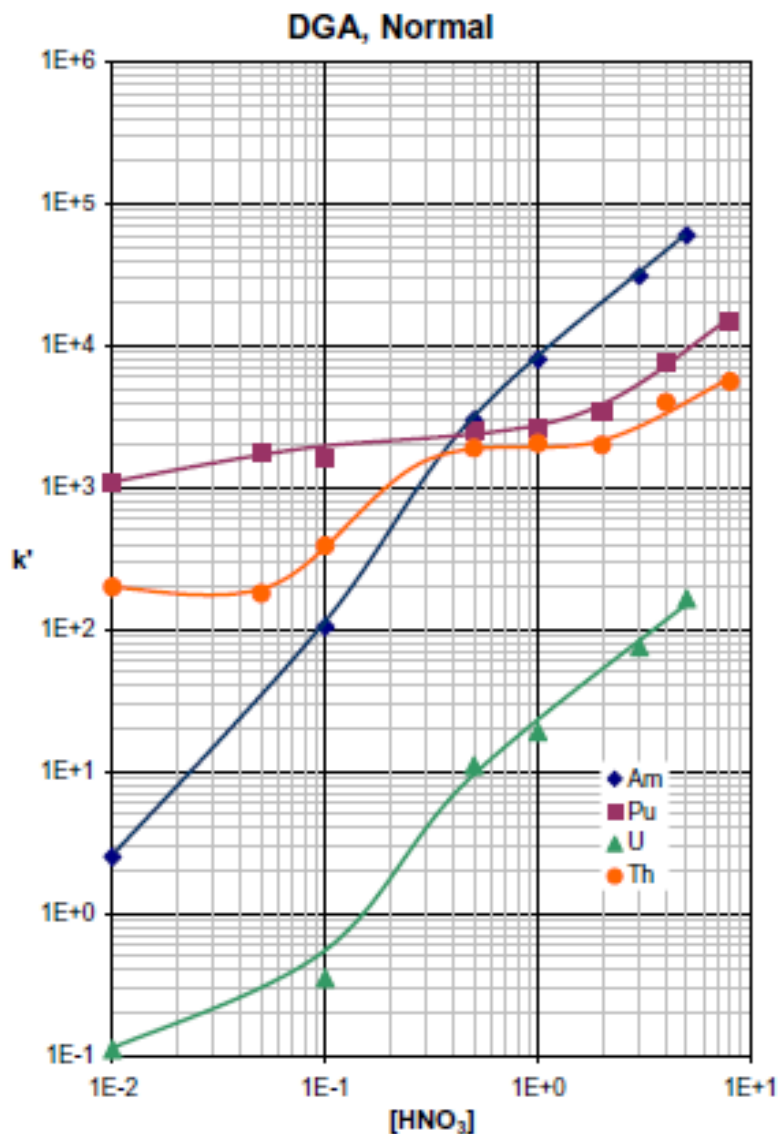


- HNO_3 : uptake of Am/Cm increases with increasing concentration.

Similar uptake of Am/Cm; $k'_{\text{Cm}} > k'_{\text{Am}}$ from 0.01M to 1M HNO_3 .

- HCl : uptake at high HCl concentrations. Similar uptake of Am/Cm.

RESULTS: DGA Resin (2/4) - KCM



RESULTS: DGA Resin (3/4) - KCM

Tested conditions	$k'_{Am} \pm \text{STD}$		$k'_{Cm} \pm \text{STD}$		$\alpha^* \pm \text{STD}$	
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 ₃ PO ₄	1669	164	2225	9	0,750	0,098
3M HNO ₃ , 0.1M Ca(NO ₃) ₂ , 0.1M Na ₃ PO 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 ₄ HC ₂ O ₄	0	0	0	0	-	-

RESULTS: DGA Resin (4/4) - KCM

- For most conditions tested, retention of Am and Cm is so high that it is not possible to elute one against the other even with a good selectivity Am/Cm or Cm/Am. Results are in accordance with those of UNVL for retention.
- Presence of Al(III) increase by a factor ~ 10 Am and Cm retention.
- Phosphates « interfere » Am/Cm retention especially in the absence of Al(III).
- Fe(III), Fe(II) and EDTA have little or no effect on Am/Cm retention.
- Ammonium bioxalate solution allows 100% recovery of Am/Cm present on the resin (same as TRU resin).

CONCLUSIONS

- Co-separation/elution/determination of Am/Cm
 - DGA resin looks more robust than TRU regarding potential interferents: retention coefficients greater by at least a factor 10.
 - Elution step with ammonium bioxalate. Diluted HCl medium is another option for elution.
 - To be tested on « real » samples
- Am/Cm Separation
 - Possibility on $\text{LiNO}_3/\text{HNO}_3$ 0.01M system
 - Under research

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Thank you
Questions