Laboratoire de Radioécologie

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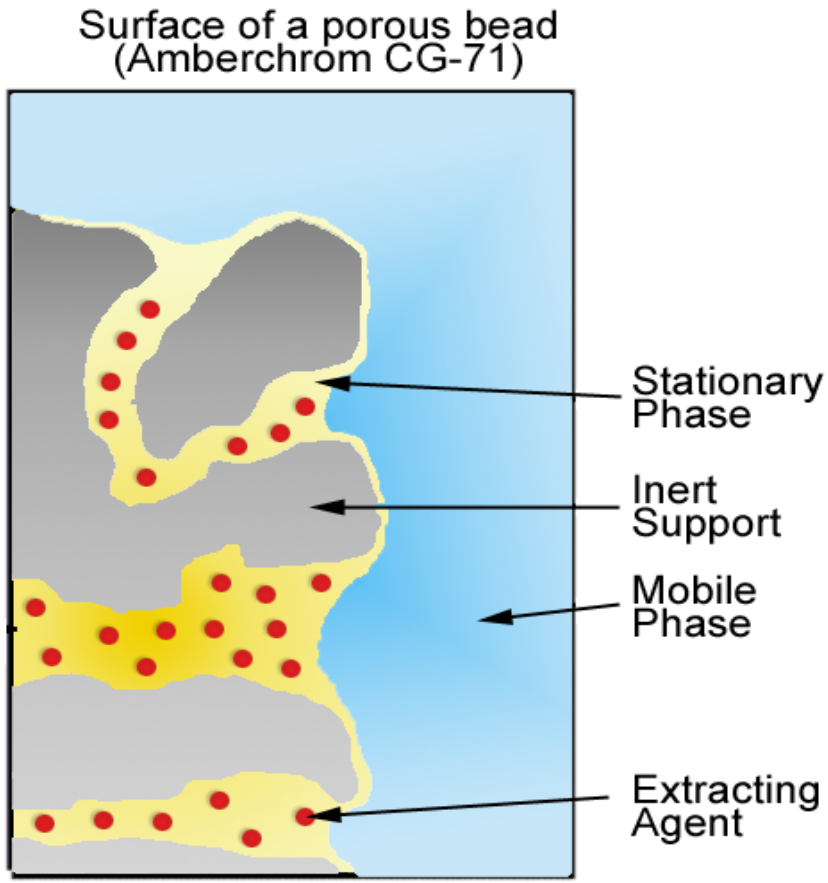
Improvements in separation performances for the measurement of long-lived radionuclides: new strategies using extraction chromatography

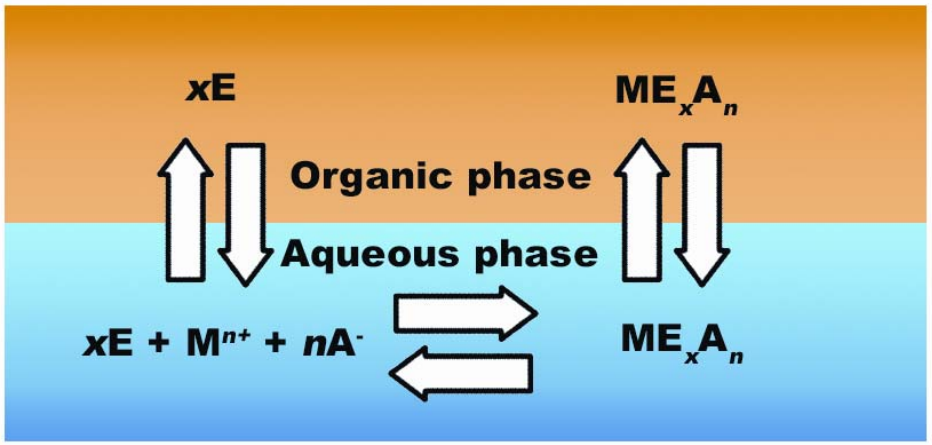
RRMC – February 2017 – Eichrom Workshop

UNIVERSITÉ LAVAL
Département de chimie

EXTRACTION CHROMATOGRAPHY

- Synergy between liquid chromatography and liquid-liquid extraction

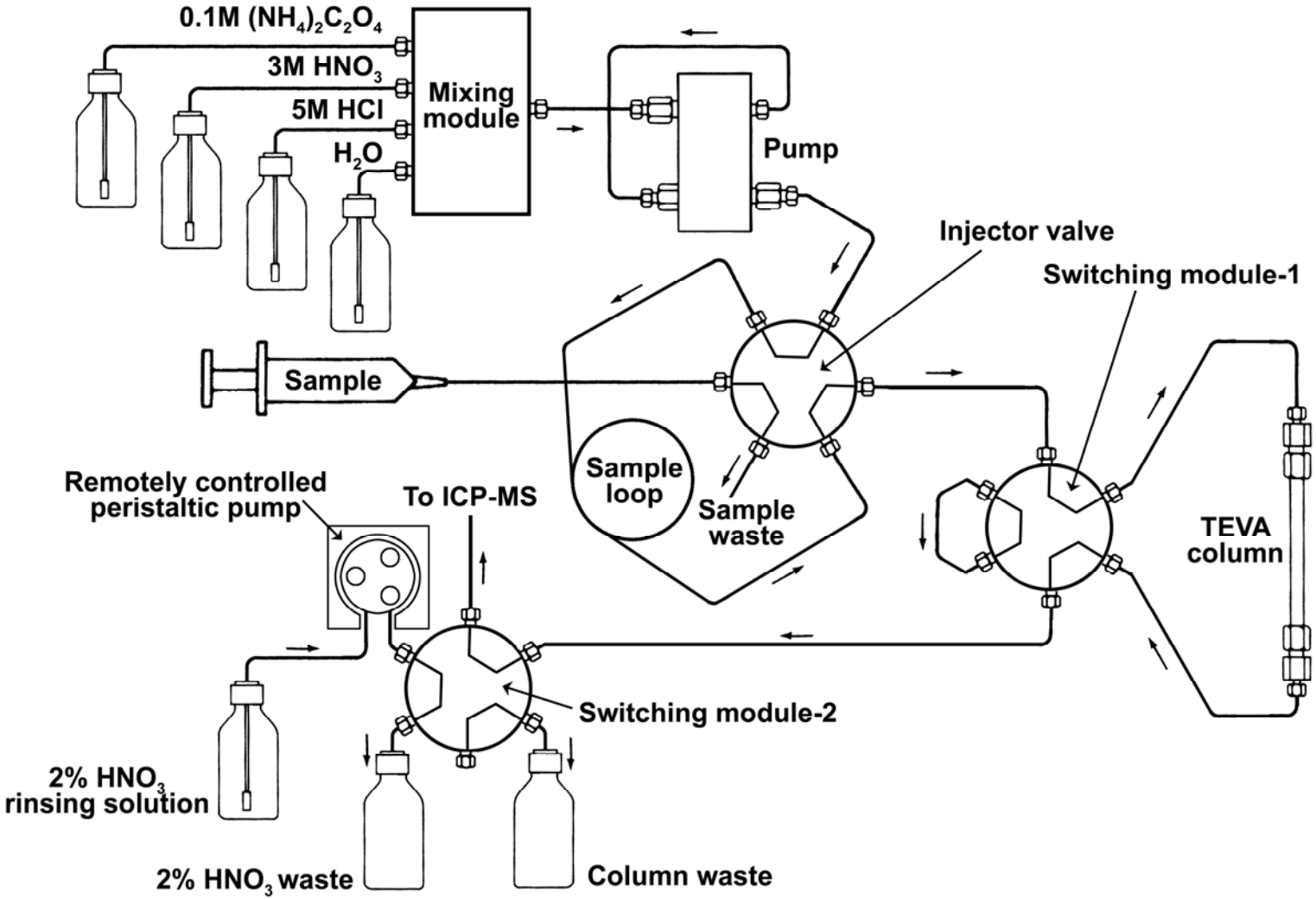




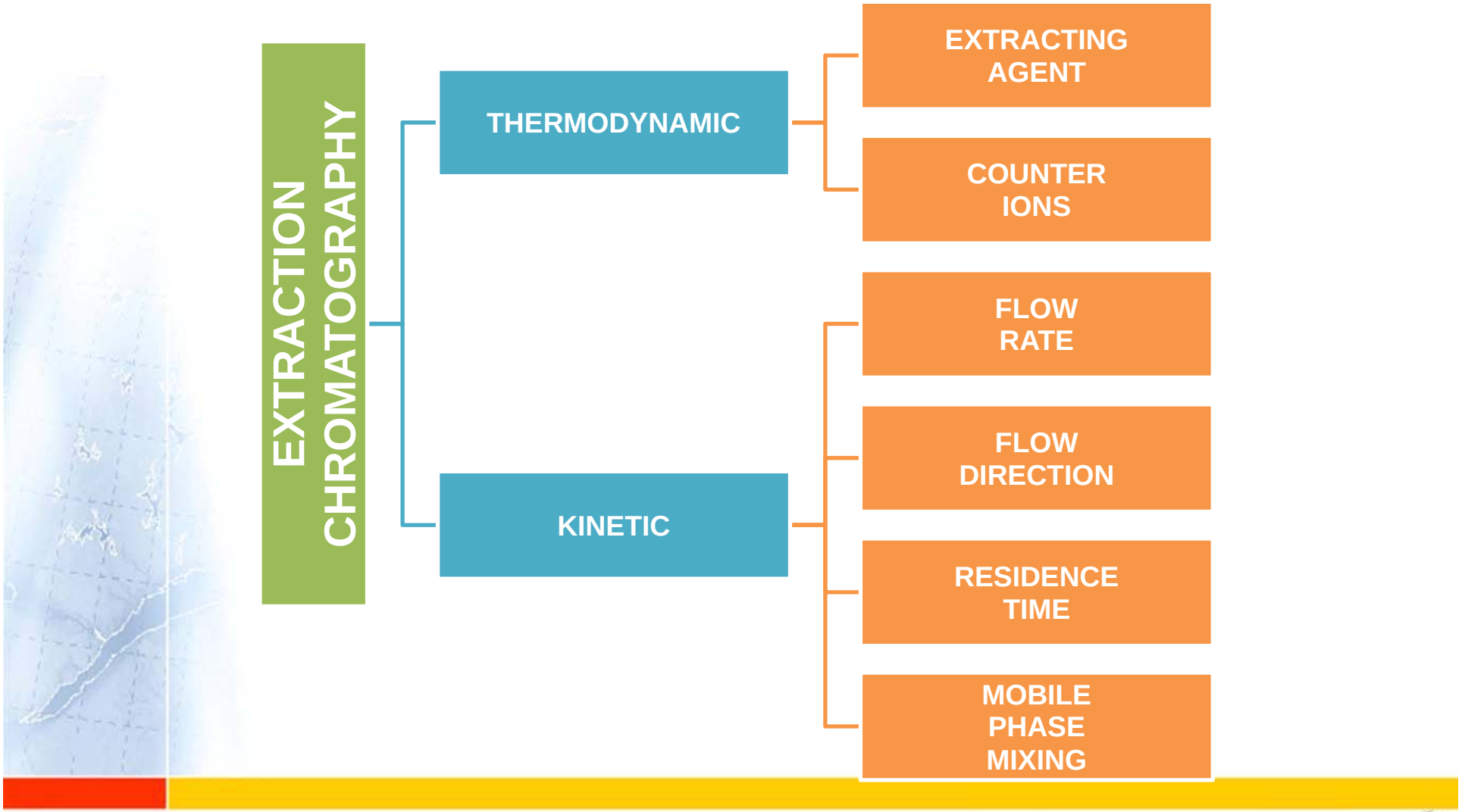
E = **Extracting agent**
M = **Metal**
A = **counter-ion**
n = **Ion charge**
x = **Number of molecules**

M.L. Dietz et E.P. Horwitz, *LC GC*, 11 (**1993**) 424-436

AUTOMATED SYSTEM



STRATEGIES STUDIED



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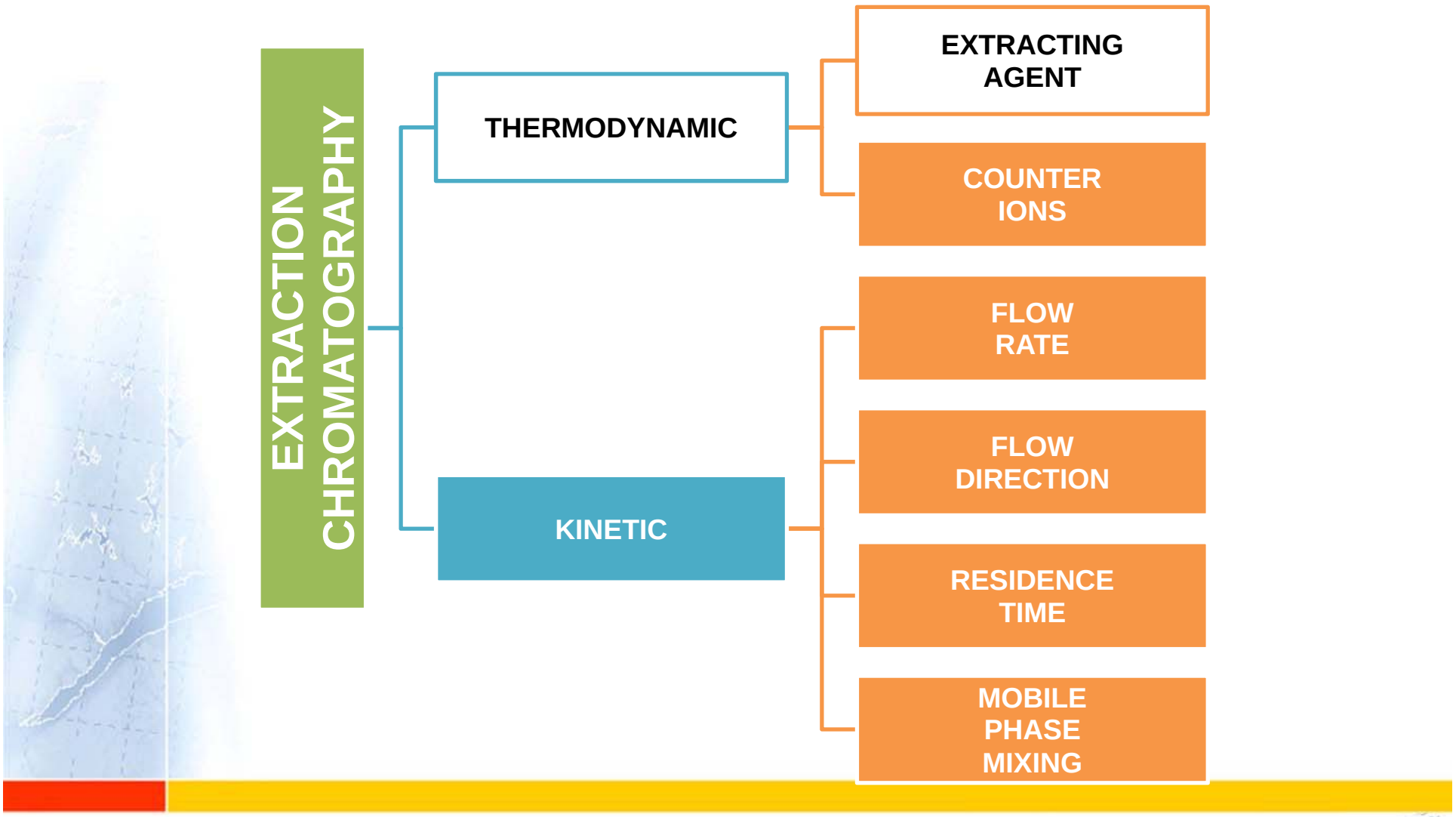
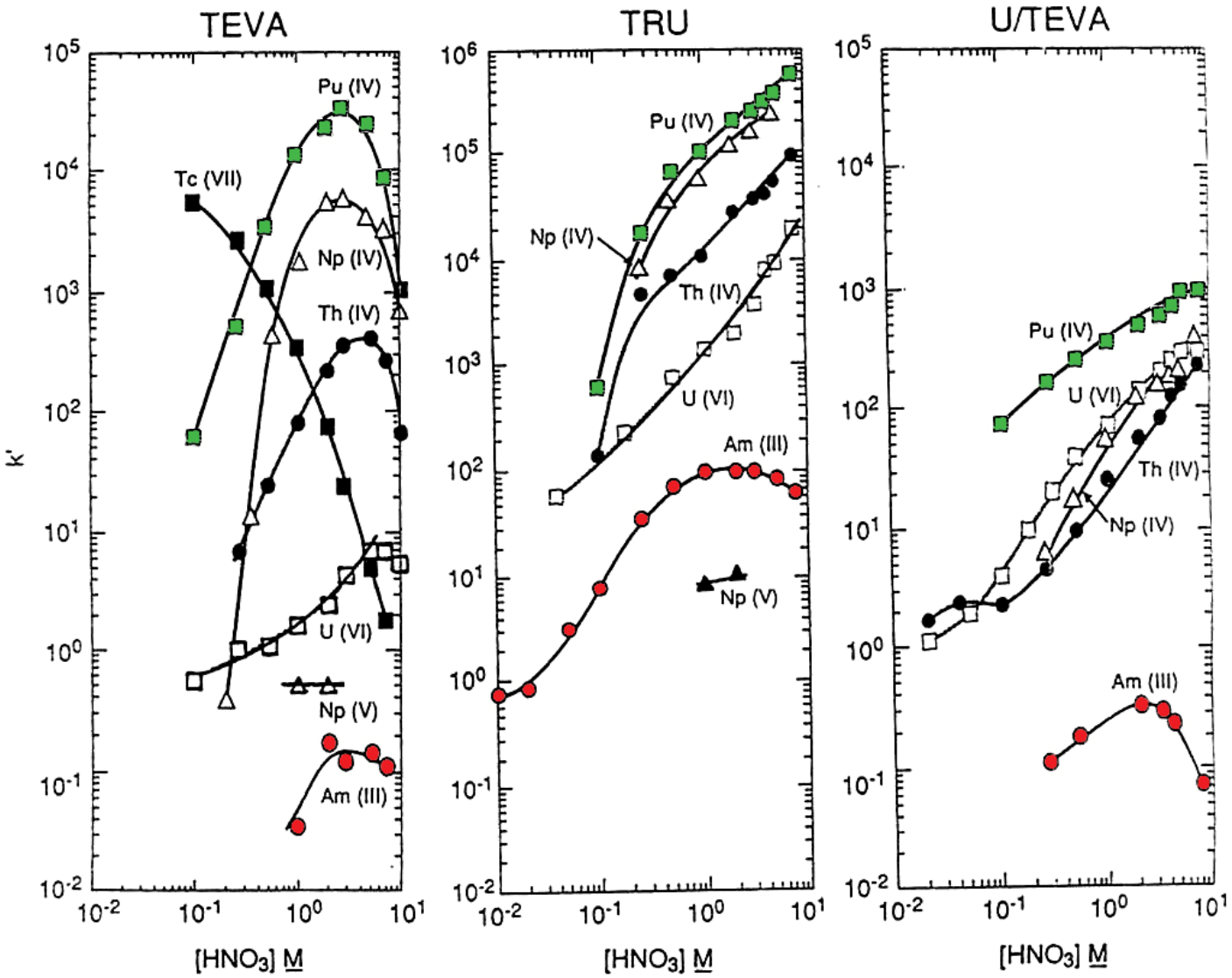


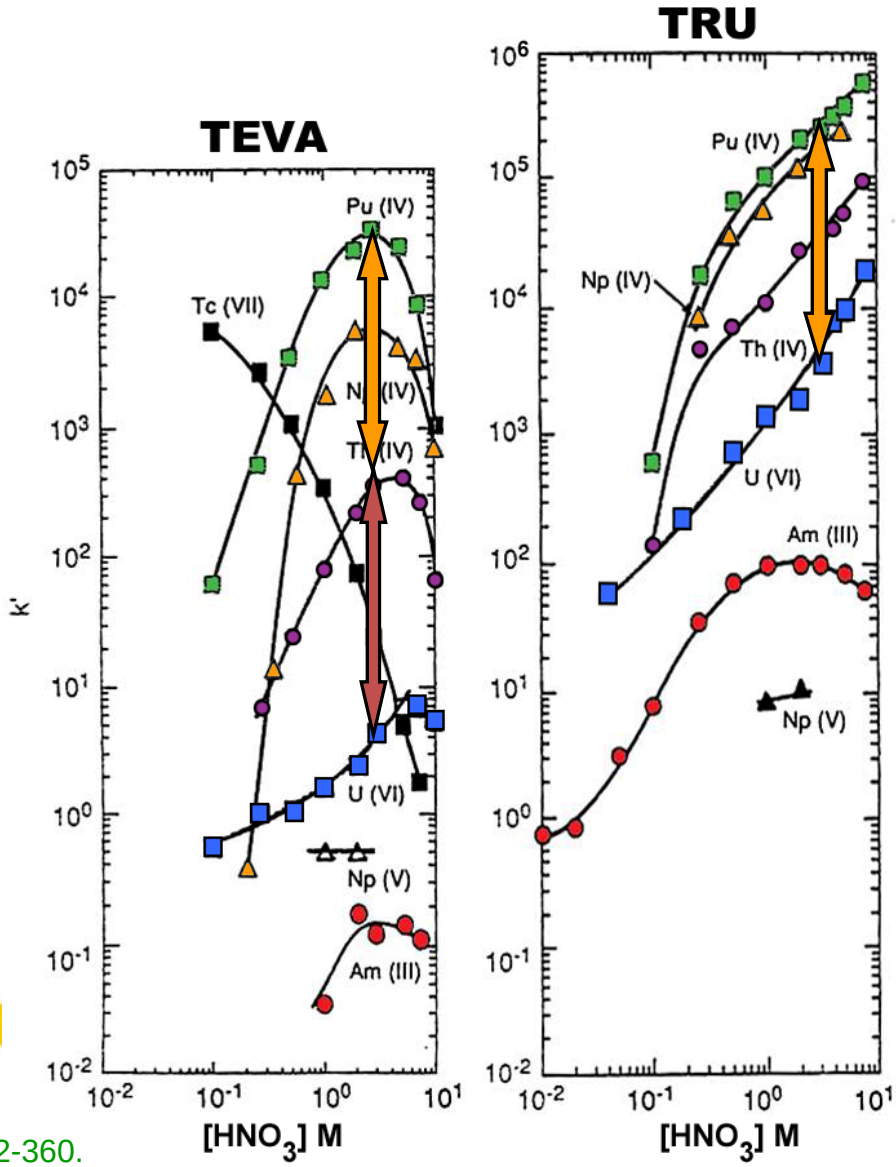
MODIFYING THE EXTRACTING AGENT



E. P. Horwitz et al, *Anal. Chim. Acta*, 310 (**1995**) 63-78

MODIFYING THE EXTRACTING AGENT

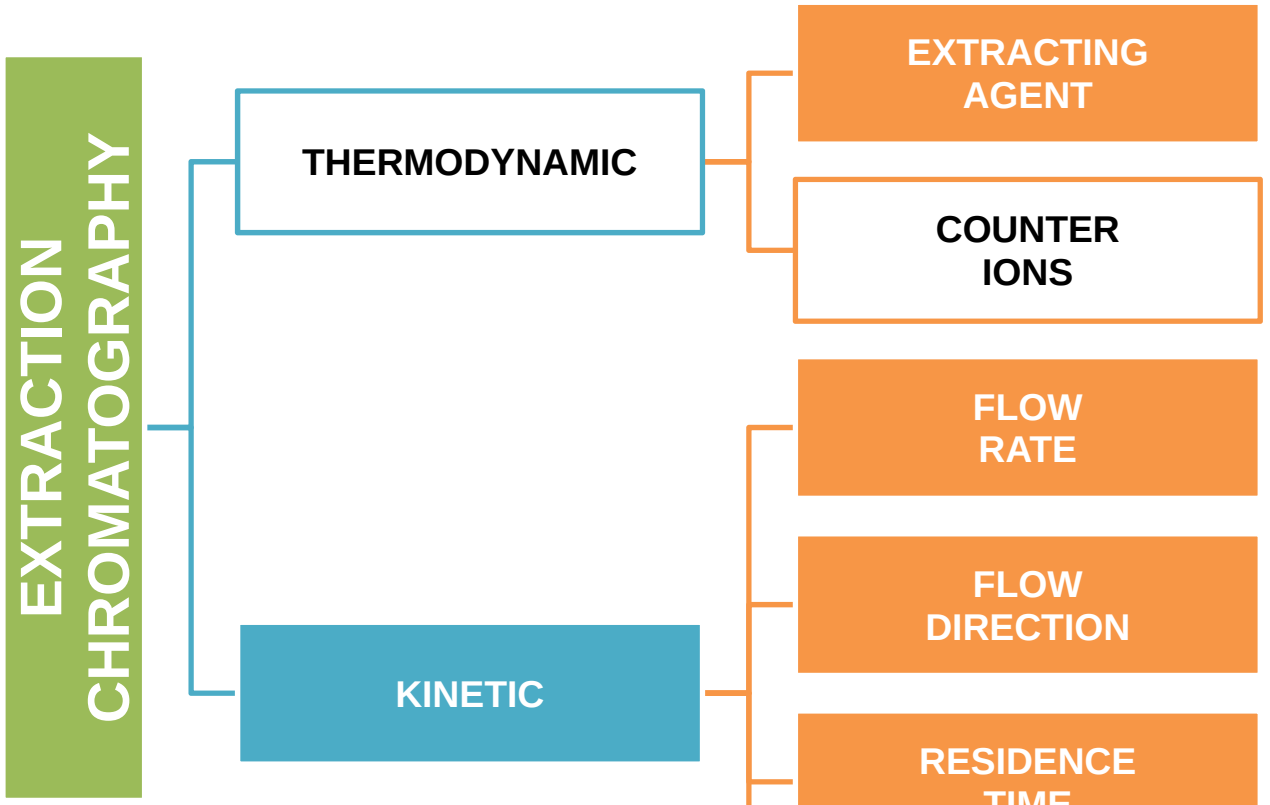
Resin	Decontamination Factor (U)
U/TEVA (Calc.)[1]	3.3×10^{-1}
TRU (Calc.)[1]	3.3×10^{-2}
TEVA (Calc.)[1]	2.6×10^{-4}
TEVA (Exp.)[2]	1.4×10^{-4}



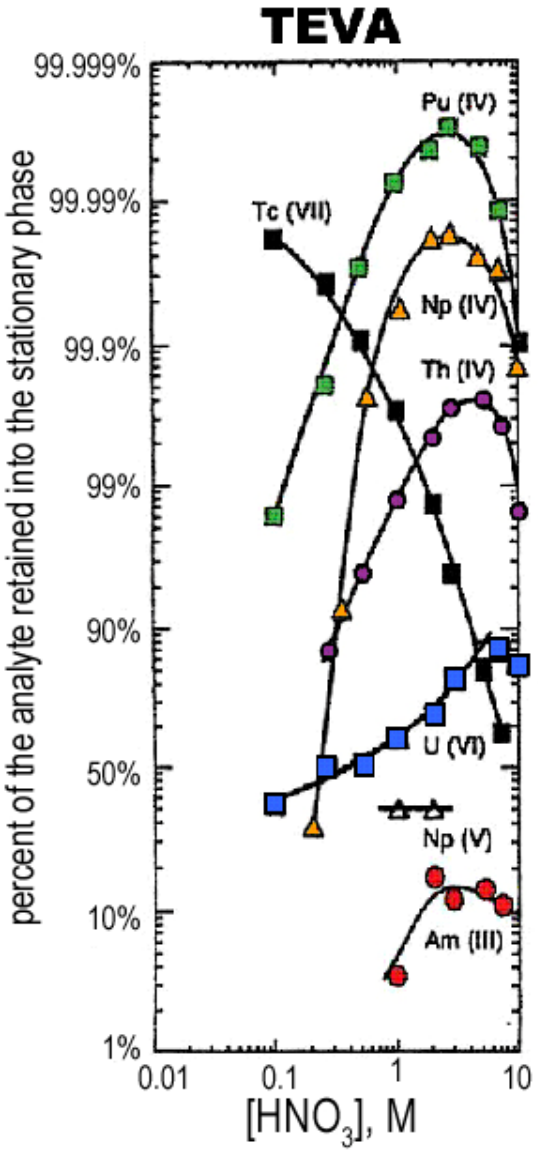
E. P. Horwitz *et al.*, *Anal. Chim. Acta*, 310 (1995) 63-78

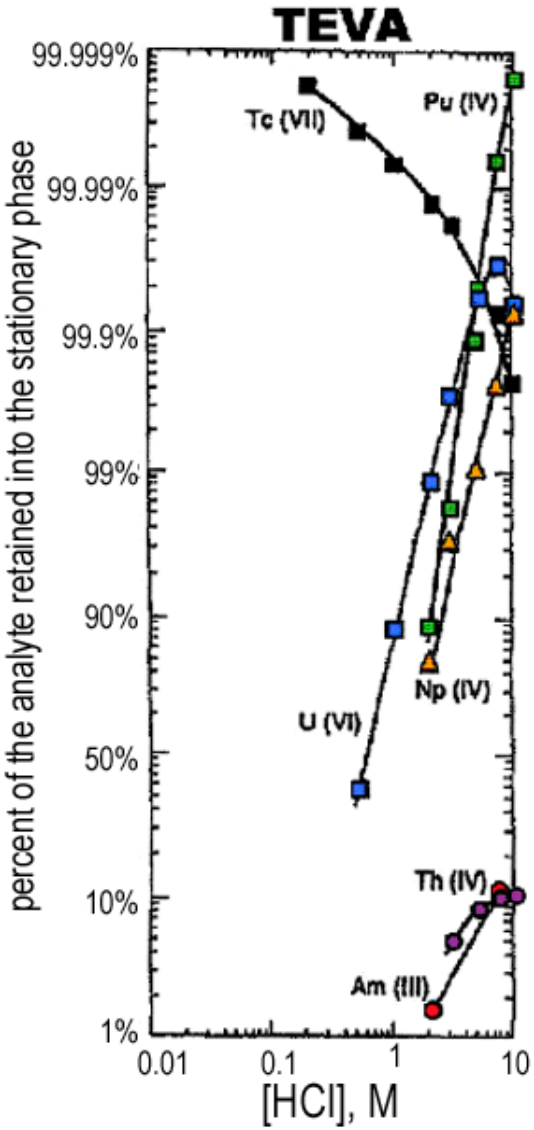
D. Lariviere *et al.*, *J. Anal. Atom. Spectrom.,* 23 (2008) , 352-360.

STRATEGIES STUDIED



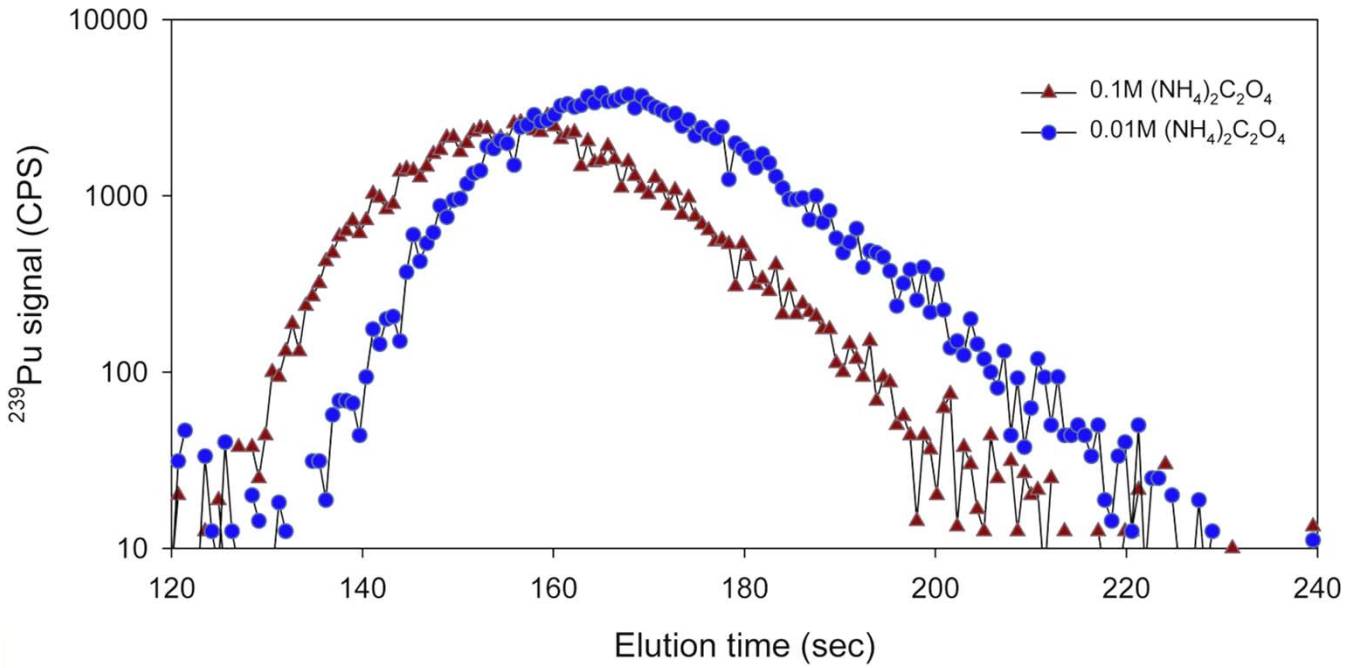
MODIFYING THE COUNTER IONS





E. P. Horwitz et al, *Anal. Chim. Acta*, 310 (**1995**) 63-78

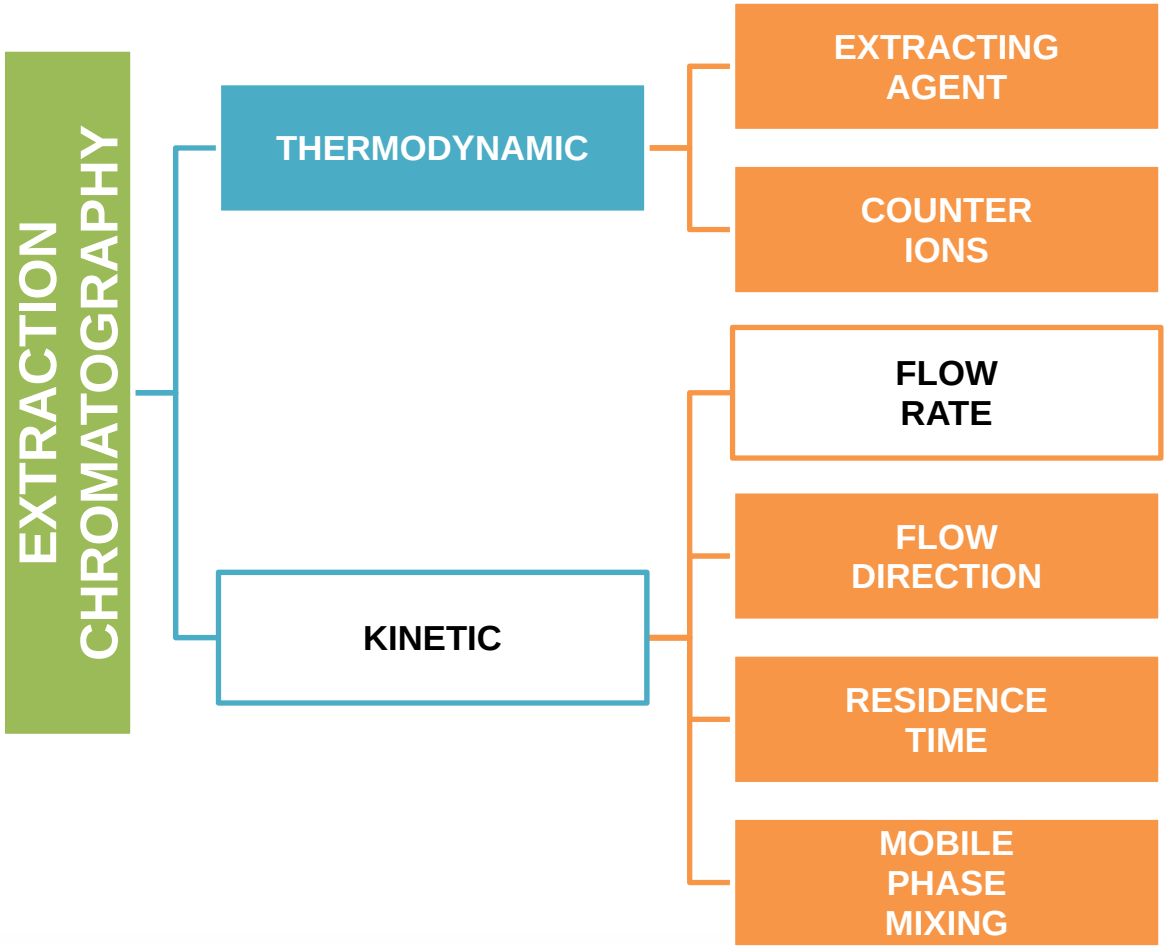
MODIFYING THE COUNTER IONS



Eluent	Time (sec)	FWHM (sec)	FW 5%M (sec)	Integrated signal (CPS)
0.1M $(NH_4)_2C_2O_4$	156 ± 3	22.9 ±0.4	57.4 ± 0.8	99 908 ± 2 688
0.01M $(NH_4)_2C_2O_4$	164 ± 3	25.0 ± 0.8	60 ± 1	158 219 ± 7 519

D. Lariviere *et al.*, *J. Anal. Atom. Spectrom.,* 23 (2008) , 352-360.

STRATEGIES STUDIED



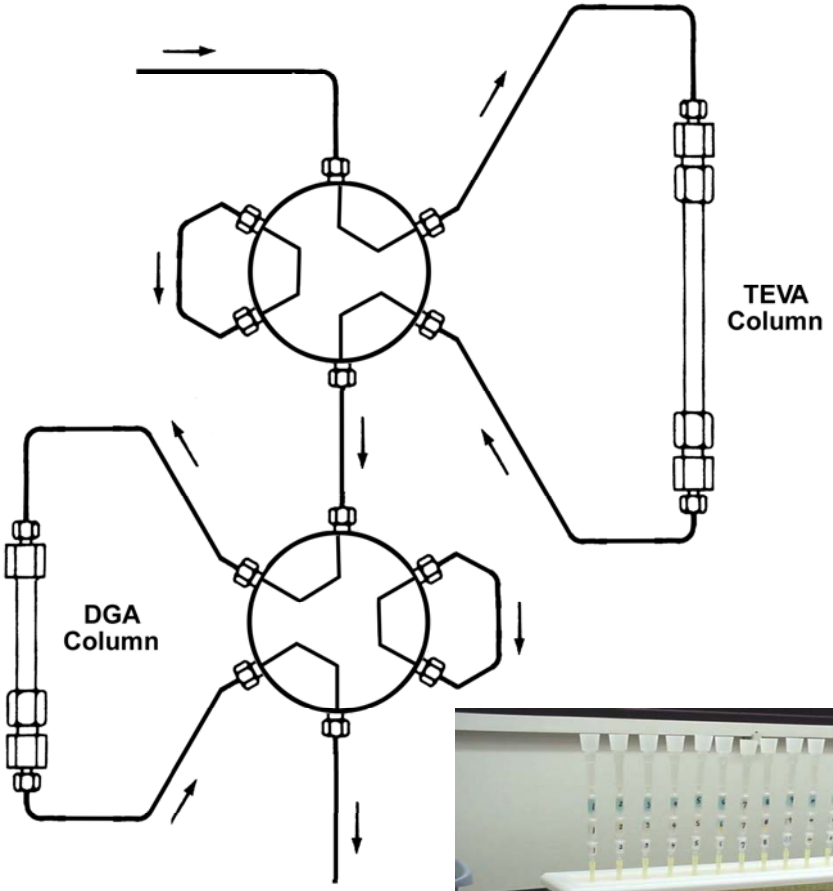
MODIFYING THE FLOW RATE

Loading:

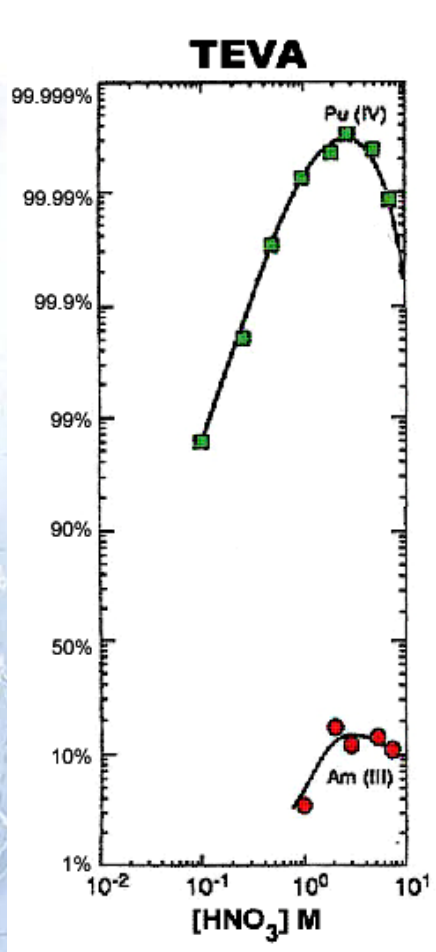
- Pu and Am loaded onto TEVA and DGA (3M HNO_3)

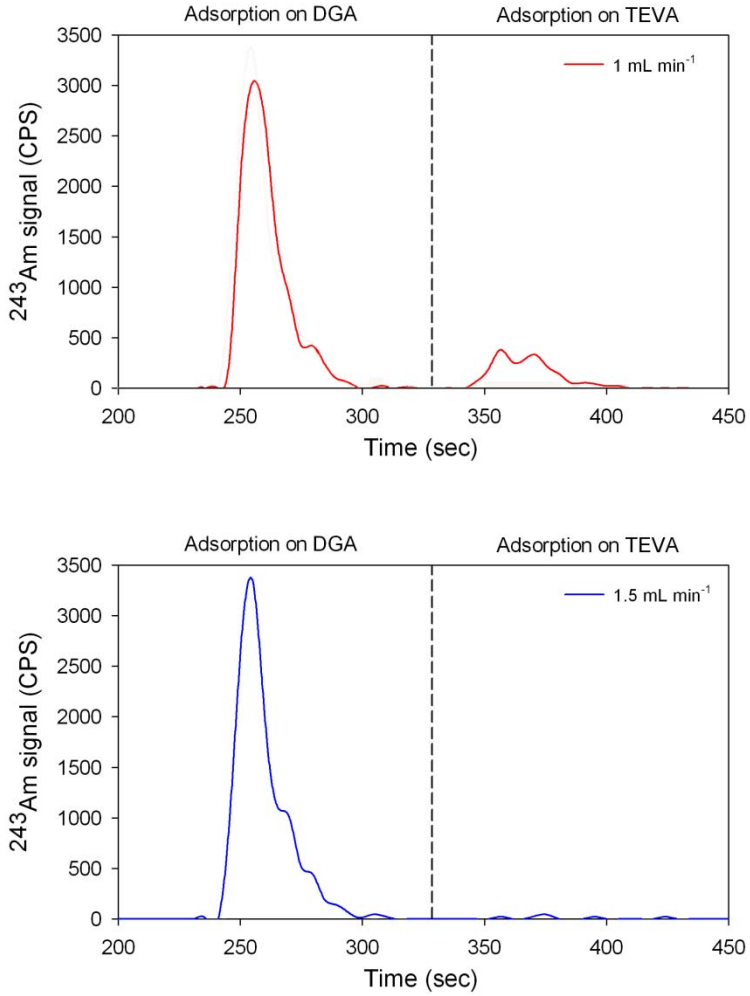
Eluting:

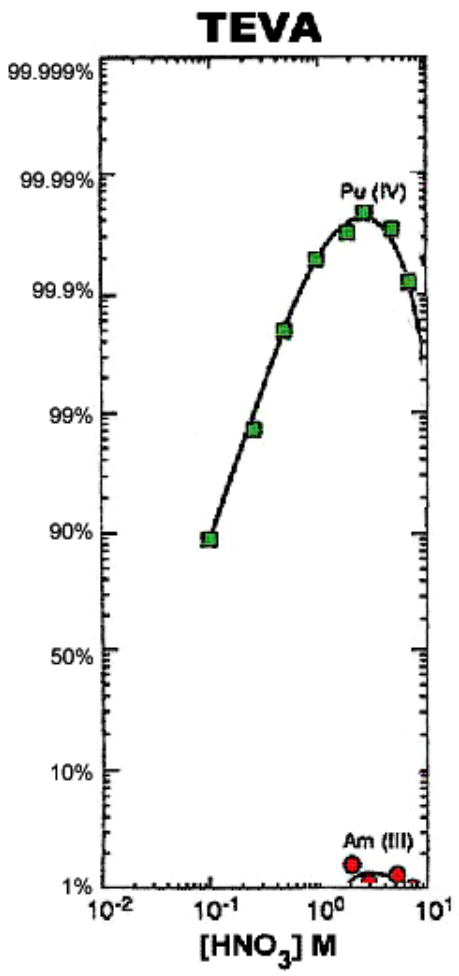
- DGA stripped from its Am (0.01M $(NH_4)_2C_2O_4$)
- TEVA stripped from its Pu (0.01M $(NH_4)_2C_2O_4$)



MODIFYING THE FLOW RATE

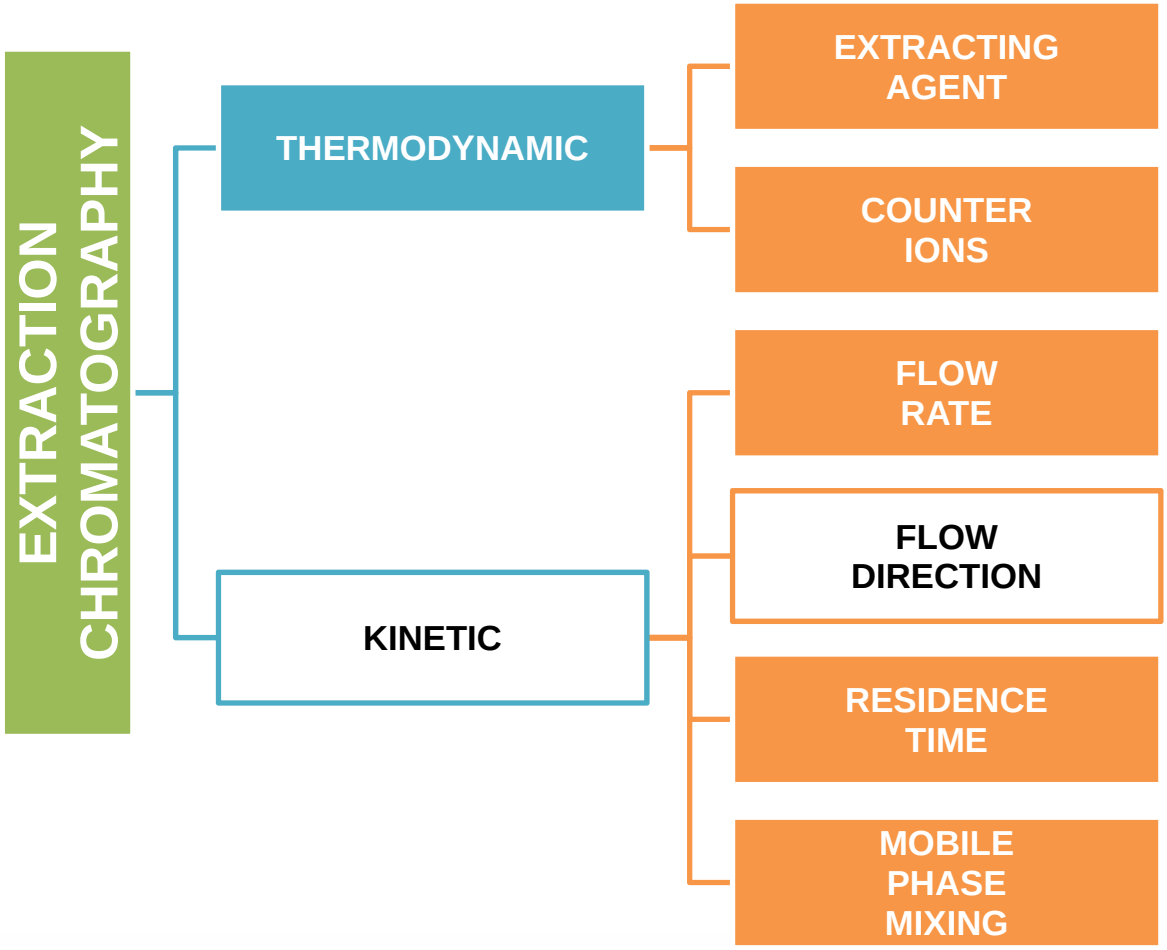






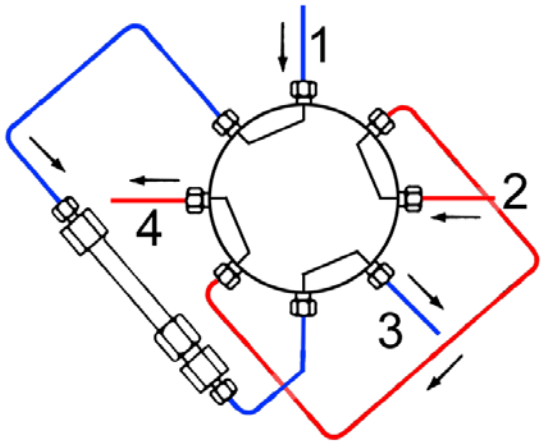
E. P. Horwitz et al, *Anal. Chim. Acta*, 310 (**1995**) 63-78

STRATEGIES STUDIED

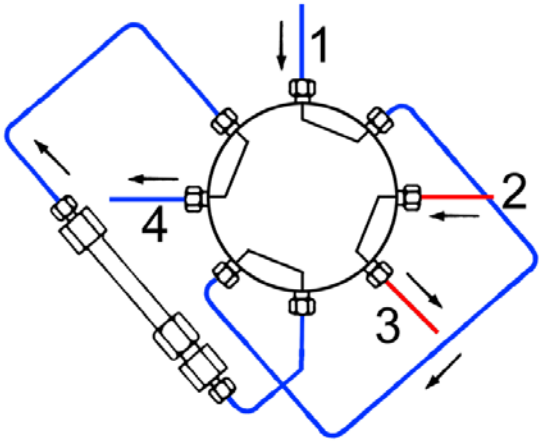


MODIYING THE DIRECTION OF THE FLOW

Loading

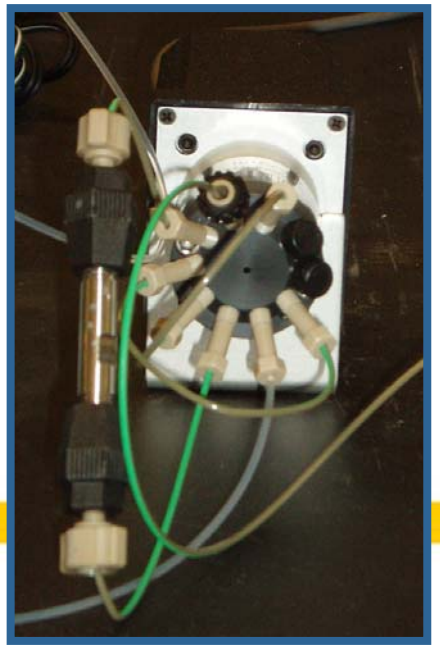


Elution



Possible advantages:

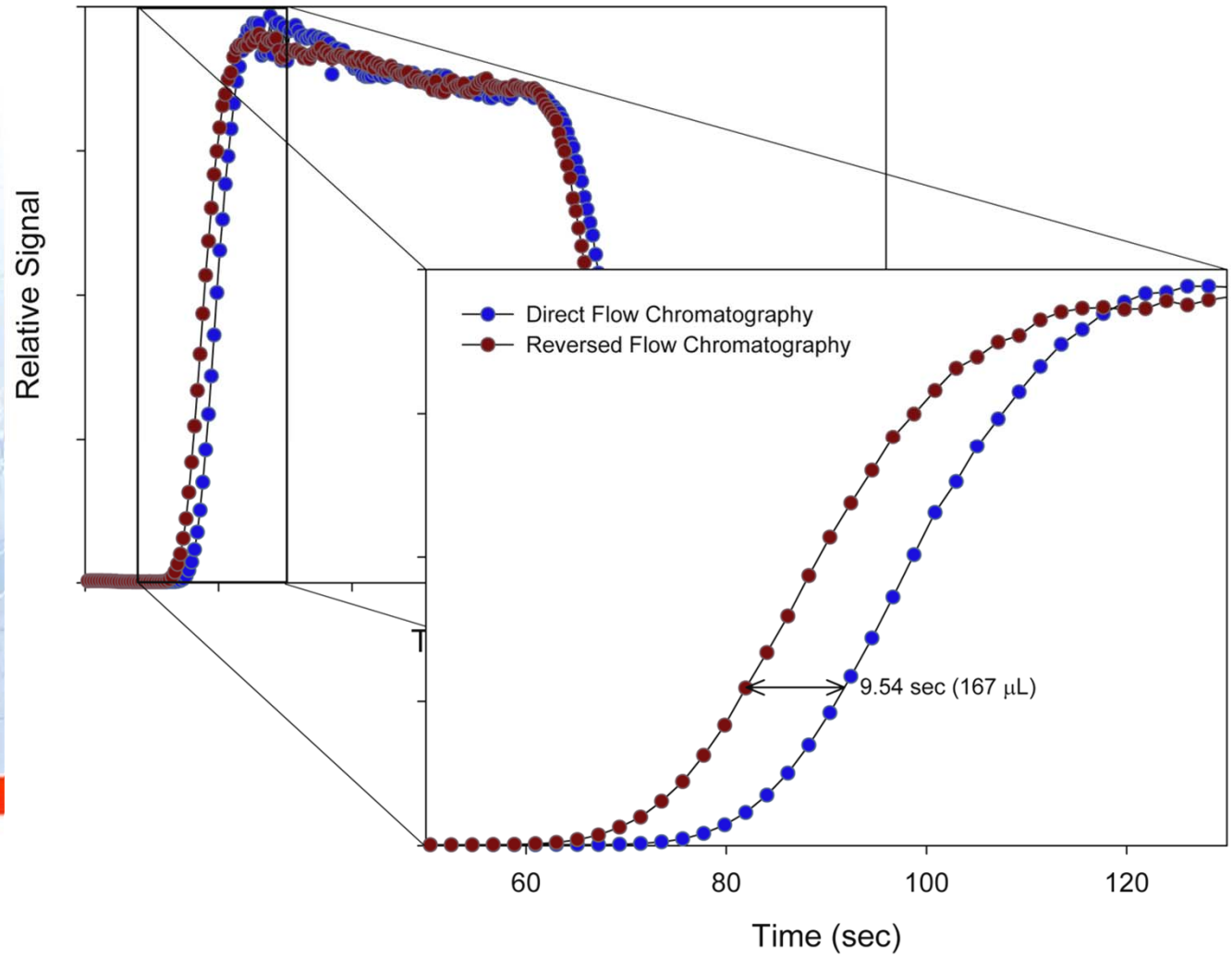
- Reduction in contact time between resin and analyte.
- Reduction in Eddy diffusion



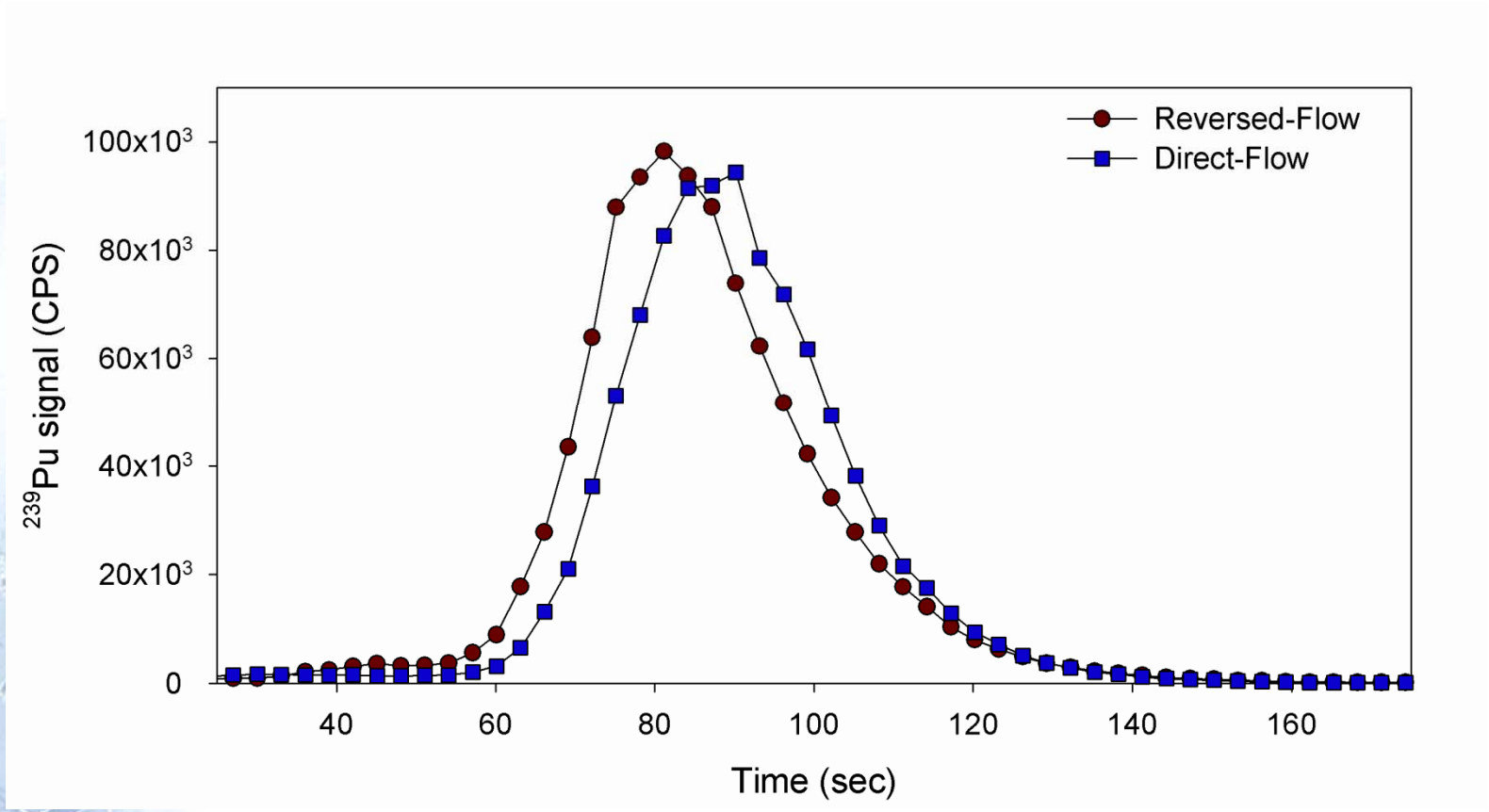
1. from SDU
2. rinse
3. to waste
4. to detector

MODIYING THE DIRECTION OF THE FLOW

Cs

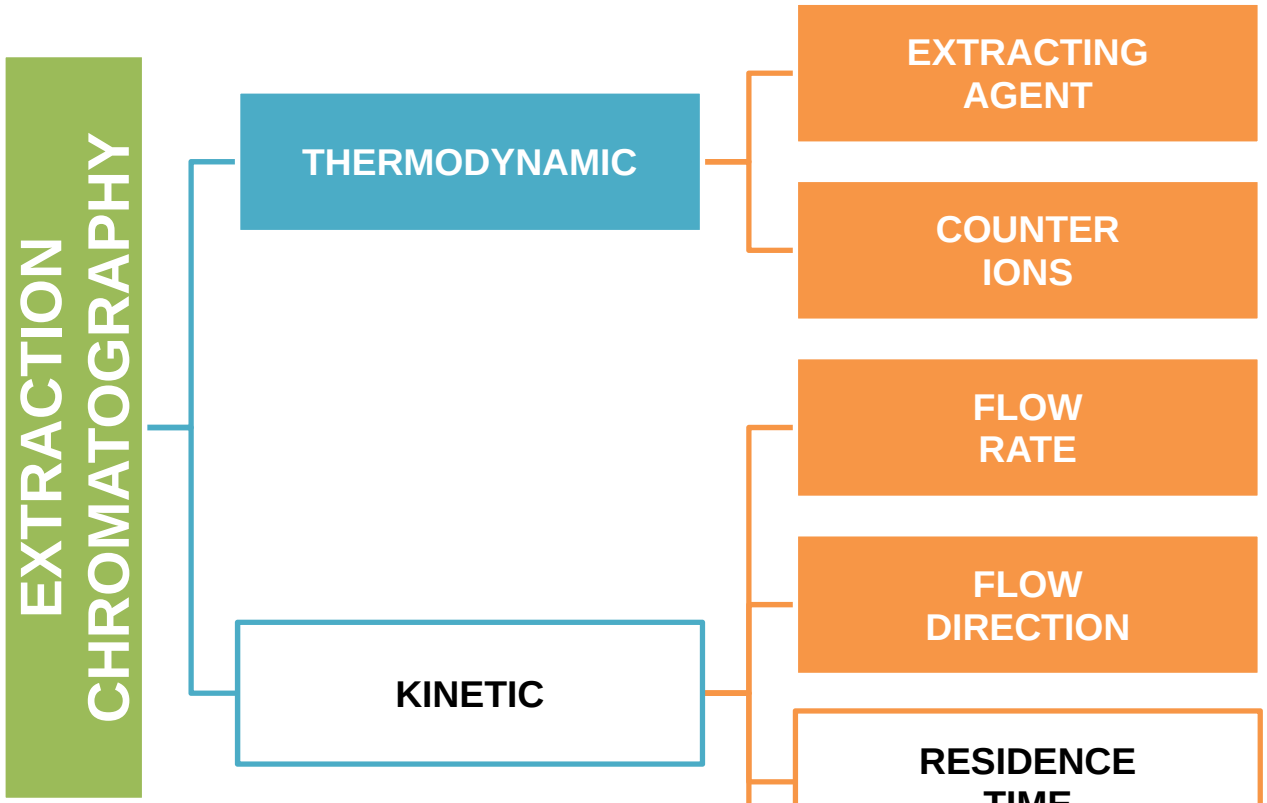


REVERSED-FLOW CHROMATOGRAPHY

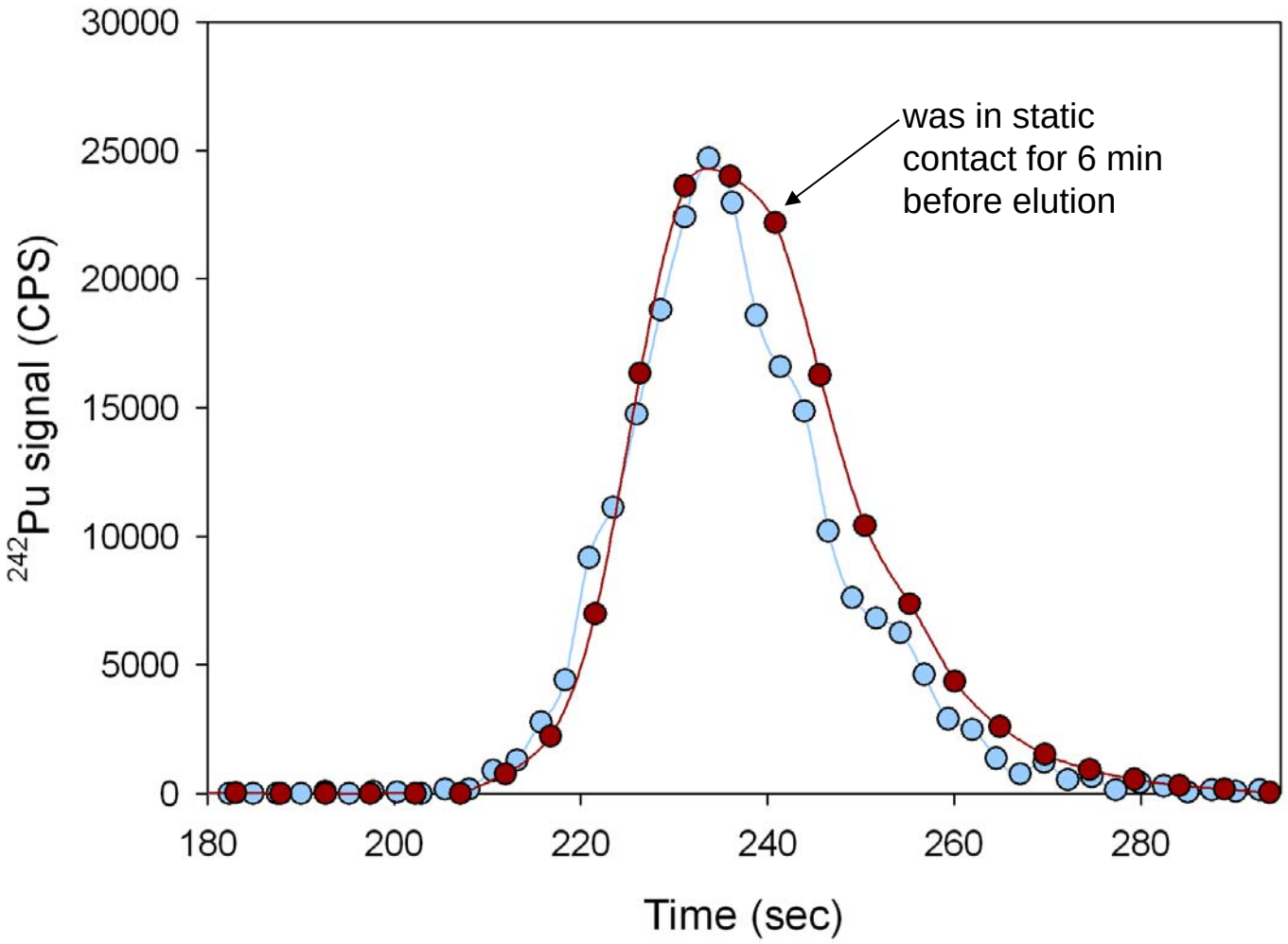


Parameters (*n* = 3)	Direct-Flow	Reversed-Flow	$\%\Delta_{R-D}$
Area	999 048 ±14 995	1 044 063 ±37 273	4.5
FWHM	25 ±0.98	23 ±0.98	– 8.0
Peak Max.	94 379 ±4 385	98 234±2 626	4.1

STRATEGIES STUDIED



MODIFYING THE RESIDENCE TIME



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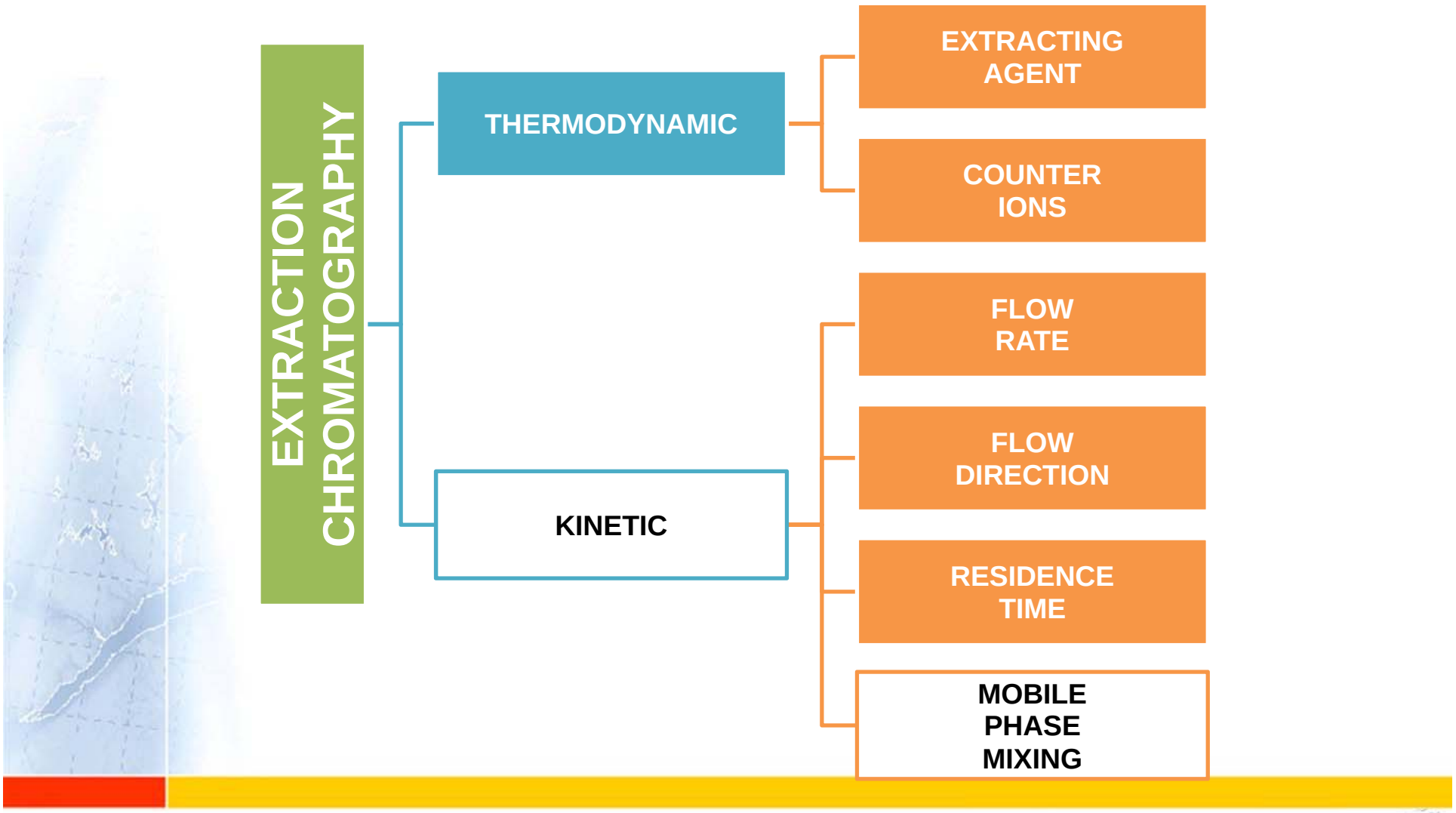
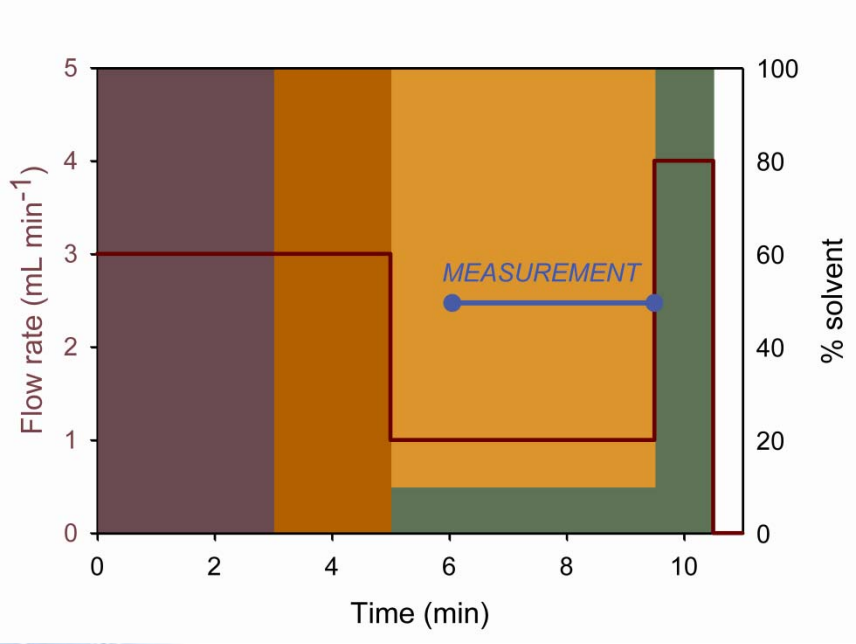
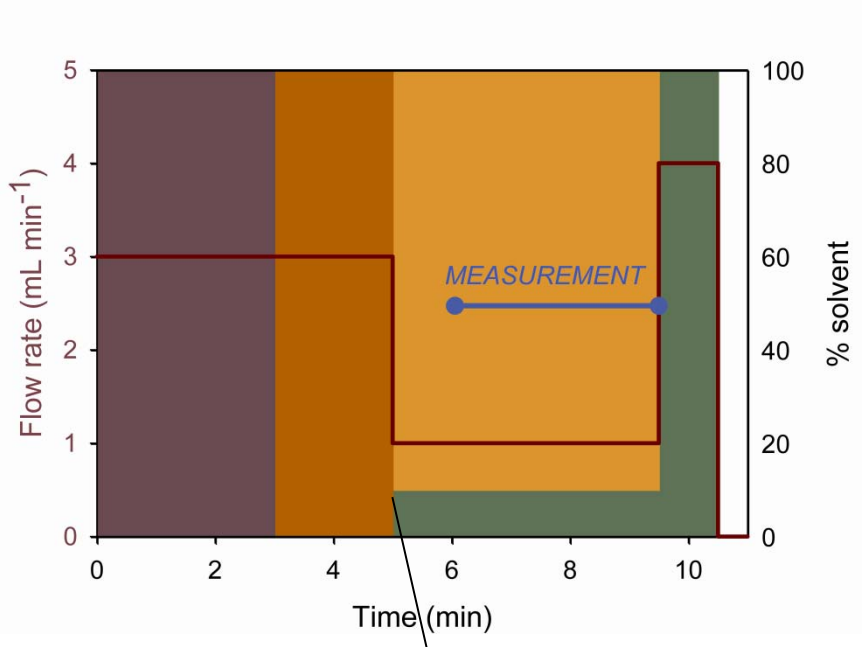
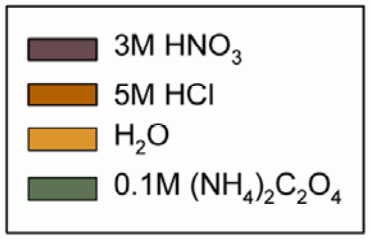


ELIMINATING THE ELUENT MIXING

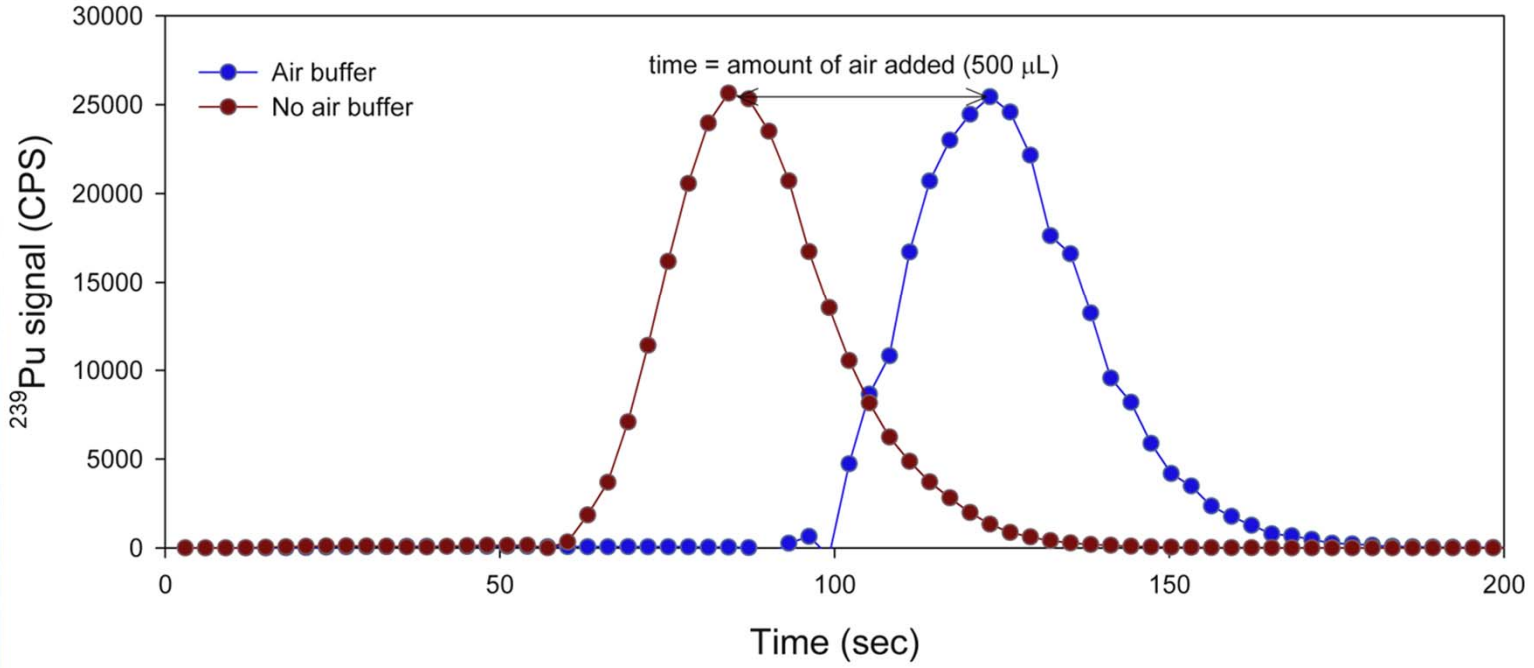






Air was introduced before 0.01M $(NH_4)_2C_2O_4$

ELIMINATING THE ELUENT MIXING



Parameters (*n* = 3)	Air Buffer	No Air Buffer	%Δ
Area	268 141 ±12 491	253 301 ±14 392	5.5
FWHM	27.04 ±0.76	24.04 ±0.76	11.1
Peak Max.	24 587 ±1 334	25 643 ±1 109	4.1

CONCLUSIONS

- Choice of extractant and eluent:
  - *Guided by the type of extraction (separation or pre-concentration) and analysis (on-line, off-line, radiometric, mass spectrometric) performed.*
- Flow rate:
  - *Slower the better for pre-concentration (while difference might not be significantly measurable), faster for separation.*

CONCLUSIONS

- Flow direction:
  - *If column size minimized already, little improvement*
  - *If column size >required, could lead to some improvement (?)*
- Residence time:
  - *Longer = more tailing and wider peak*
- Solvent mixing:
  - *Did not seem to improve overall detectability in our specific case, but did not make it worse.*

ACKNOWLEDGEMENTS

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CFI (equipment)
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