Extraction Chromatographic Studies of Db homologs with Eichrom's DGA Resin

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Separation Requirements

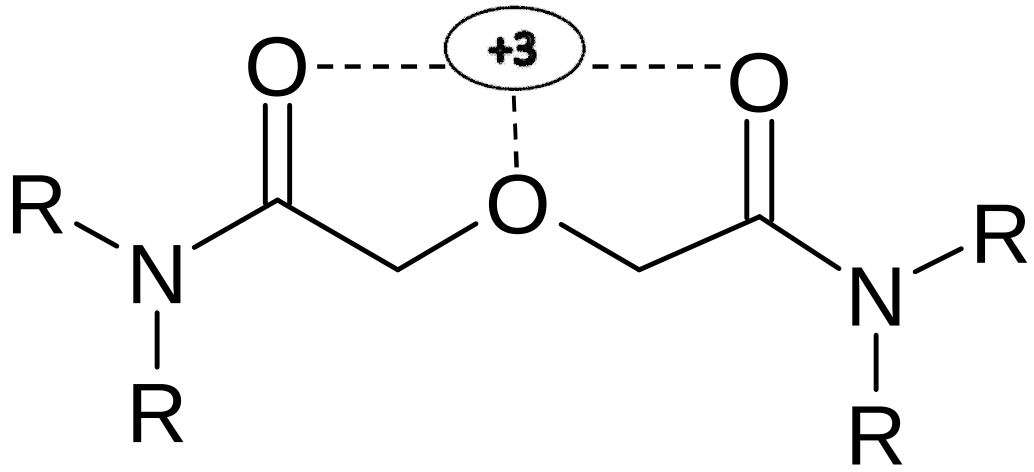
- Rapid
- Large number of exchange steps
- Highly Selective
- Preferably a continuous process
- Samples easily prepared for α spec

Extraction Chromatography fulfills all of these

Background

- Aliphatic amines have been shown to extract Rf and Db homologs[1-3]
- DGA is selective for +3, +4 and +5 ions[4]
- Complex formation is dependent on solution conditions
  - HNO_3/HF versus a pure system

1 Schädel, M. et. al. Radiochim. Acta 1992, 57,(2-3), 85
2 Paulus, W. et. al. Journal of Alloys and Compounds, 1998, 271-273, 292-295
3 Kasamatsu, Y. et. al. Journal of Radioanalytical Nuclear Chemistry, 2009, 279, (2), 271
4 http://www.eichrom.com/products/info/DGA_resin.cfm



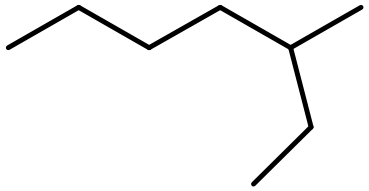
DGA

Un-branched

R =

Branched

R =

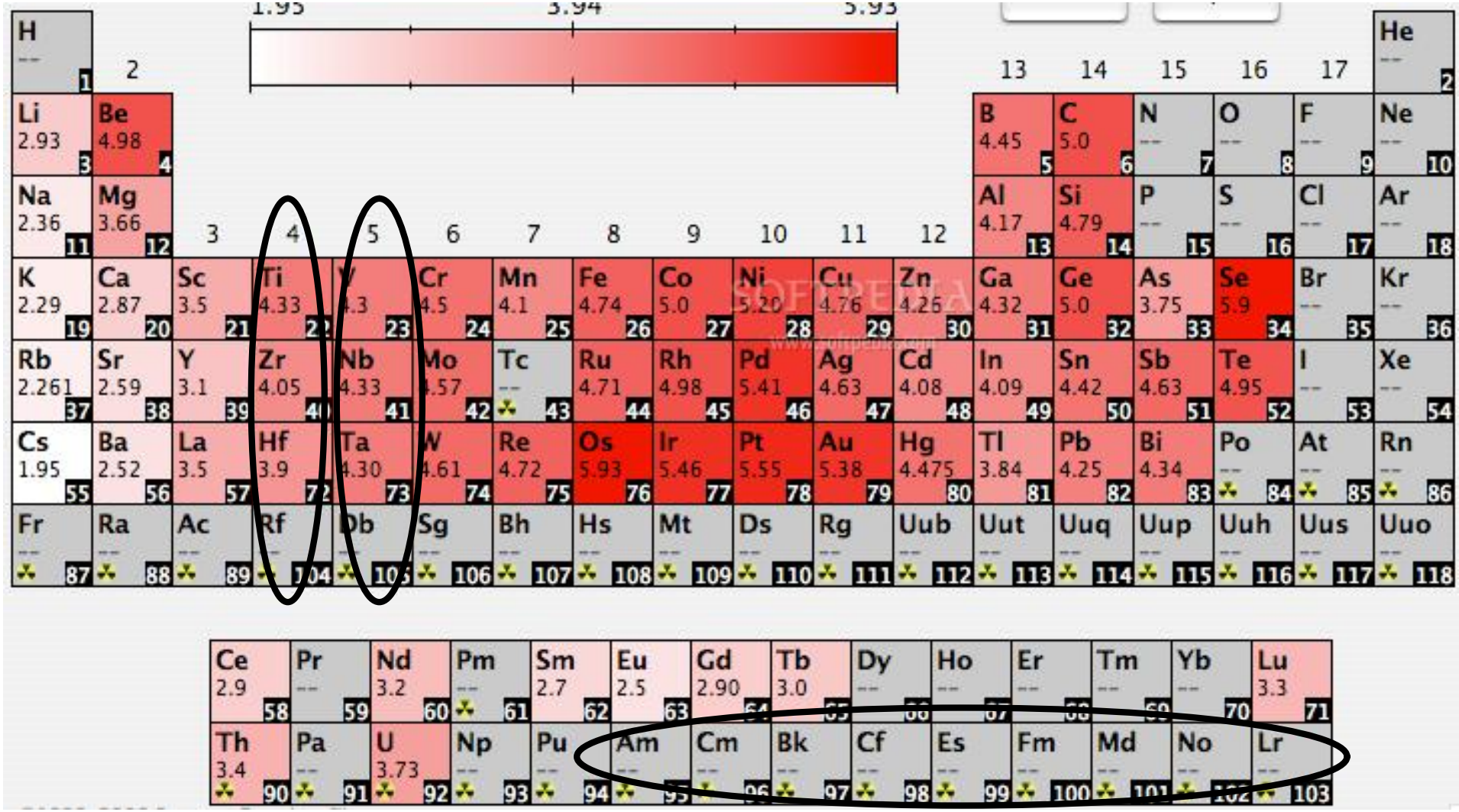


Column Studies

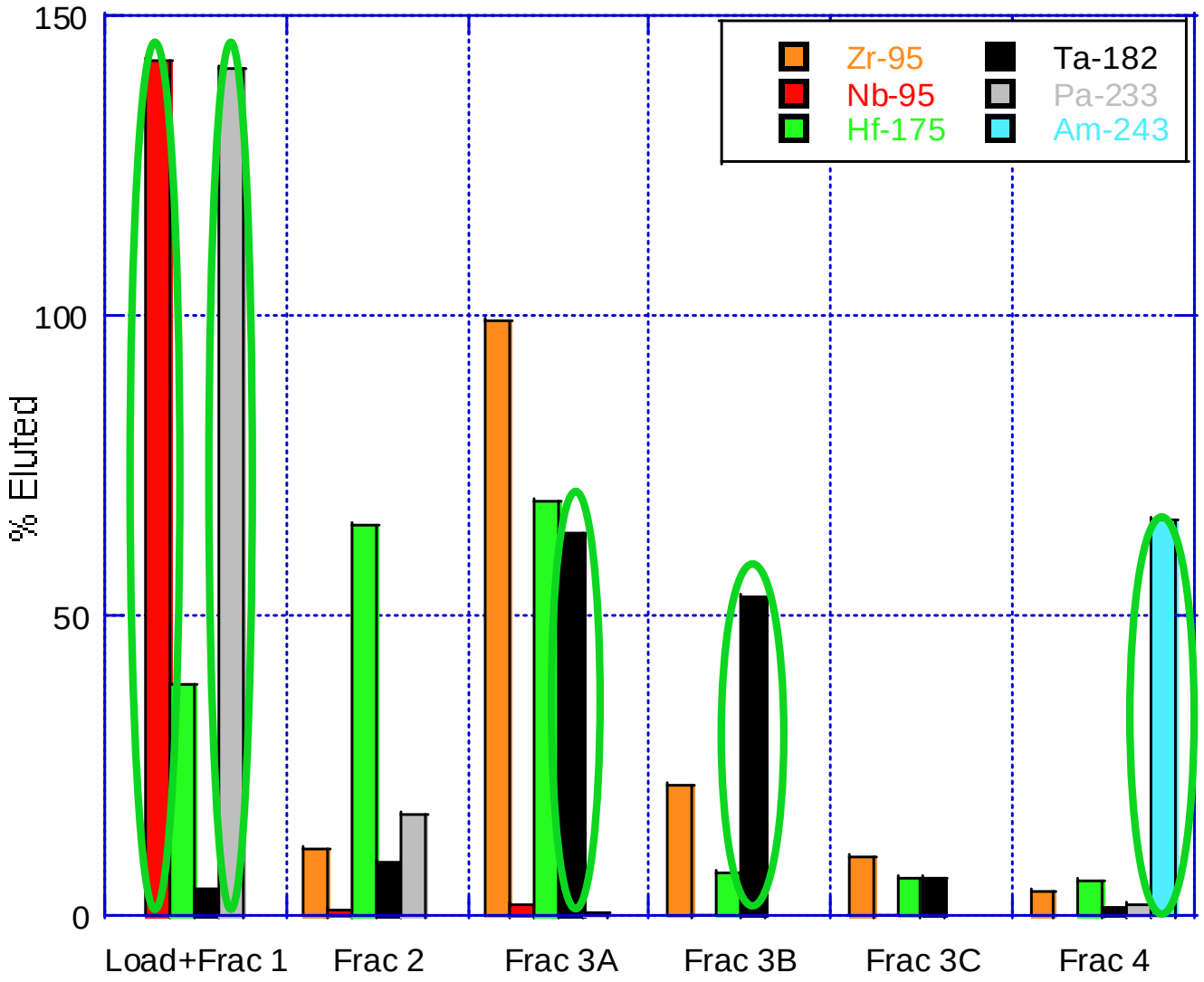
- $^{95}Zr/^{95}$ Nb, ^{182}Ta, ^{175}Hf, ^{233}Pa, ^{243}Am all added to a 15mL PPE centrifuge tube
- Evaporation and Reconstitution
- Counted for 30 minutes
- Loaded and eluted from DGA pre-packed column
- Evaporated to dryness, reconstituted with 4M HNO_3
- Counted for 30 minutes

Evaporation and Reconstitution

- Activity added to sample and evaporated to dryness
- Reconstitution in 6M HCl/8M HF
- Evaporation to dryness
- Reconstitution in con. HNO_3
- Evaporation to dryness
- Reconstitution in 1mL of load solution


1.95
3.94
5.93
H -- 1
He -- 2
2
13
14
15
16
17
Li 2.93 3
Be 4.98 4
B 4.45 5
C 5.0 6
N -- 7
O -- 8
F -- 9
Ne -- 10
Na 2.36 11
Mg 3.66 12
3
4
5
6
7
8
9
10
11
12
Al 4.17 13
Si 4.79 14
P -- 15
S -- 16
Cl -- 17
Ar -- 18
K 2.29 19
Ca 2.87 20
Sc 3.5 21
Ti 4.33 22
V 4.3 23
Cr 4.5 24
Mn 4.1 25
Fe 4.74 26
Co 5.0 27
Ni 5.20 28
Cu 4.76 29
Zn 4.26 30
Ga 4.32 31
Ge 5.0 32
As 3.75 33
Se 5.9 34
Br -- 35
Kr -- 36
Rb 2.261 37
Sr 2.59 38
Y 3.1 39
Zr 4.05 40
Nb 4.33 41
Mo 4.57 42
Tc -- 43
Ru 4.71 44
Rh 4.98 45
Pd 5.41 46
Ag 4.63 47
Cd 4.08 48
In 4.09 49
Sn 4.42 50
Sb 4.63 51
Te 4.95 52
I -- 53
Xe -- 54
Cs 1.95 55
Ba 2.52 56
La 3.5 57
Hf 3.9 72
Ta 4.30 73
W 4.61 74
Re 4.72 75
Os 5.93 76
Ir 5.46 77
Pt 5.55 78
Au 5.38 79
Hg 4.475 80
Tl 3.84 81
Pb 4.25 82
Bi 4.34 83
Po -- 84
At -- 85
Rn -- 86
Fr -- 87
Ra -- 88
Ac -- 89
Rf -- 104
Db -- 105
Sg -- 106
Bh -- 107
Hs -- 108
Mt -- 109
Ds -- 110
Rg -- 111
Uub -- 112
Uut -- 113
Uuq -- 114
Uup -- 115
Uuh -- 116
Uus -- 117
Uuo -- 118
Ce 2.9 58
Pr -- 59
Nd 3.2 60
Pm -- 61
Sm 2.7 62
Eu 2.5 63
Gd 2.90 64
Tb 3.0 65
Dy -- 66
Ho -- 67
Er -- 68
Tm -- 69
Yb -- 70
Lu 3.3 71
Th 3.4 90
Pa -- 91
U 3.73 92
Np -- 93
Pu -- 94
Am -- 95
Cm -- 96
Bk -- 97
Cf -- 98
Es -- 99
Fm -- 100
Md -- 101
No -- 102
Lr -- 103

6M HCl/0.1M HF Load Solution



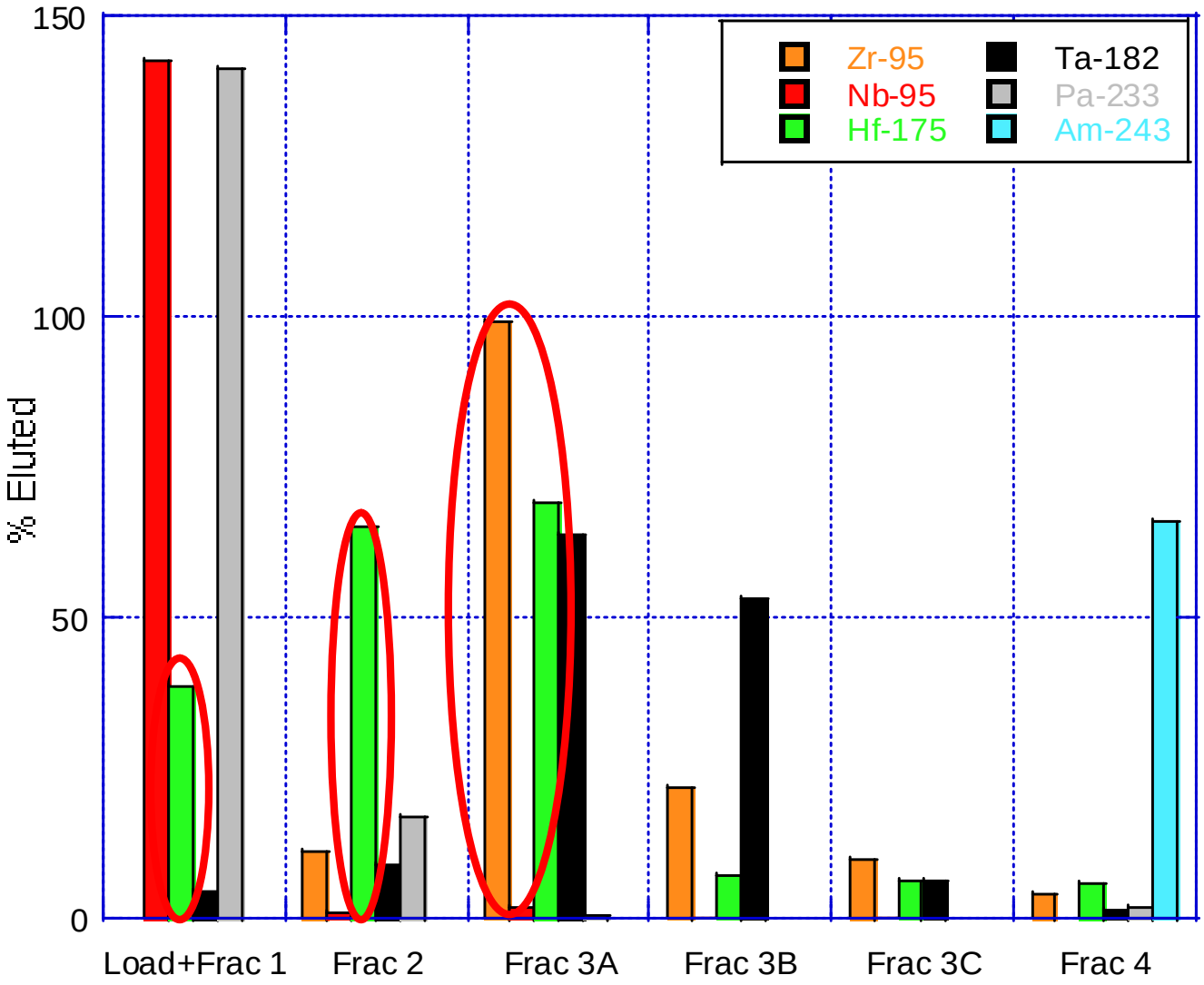
Frac1 =
4M HNO_3/0.001M HF

Frac 2 =
0.4M HNO_3/0.02M HF

Frac 3 =
8M HNO_3/1M HF

Frac 4 = 0.1M
Ammonium Bioxalate

6M HCl/0.1M HF Load Solution



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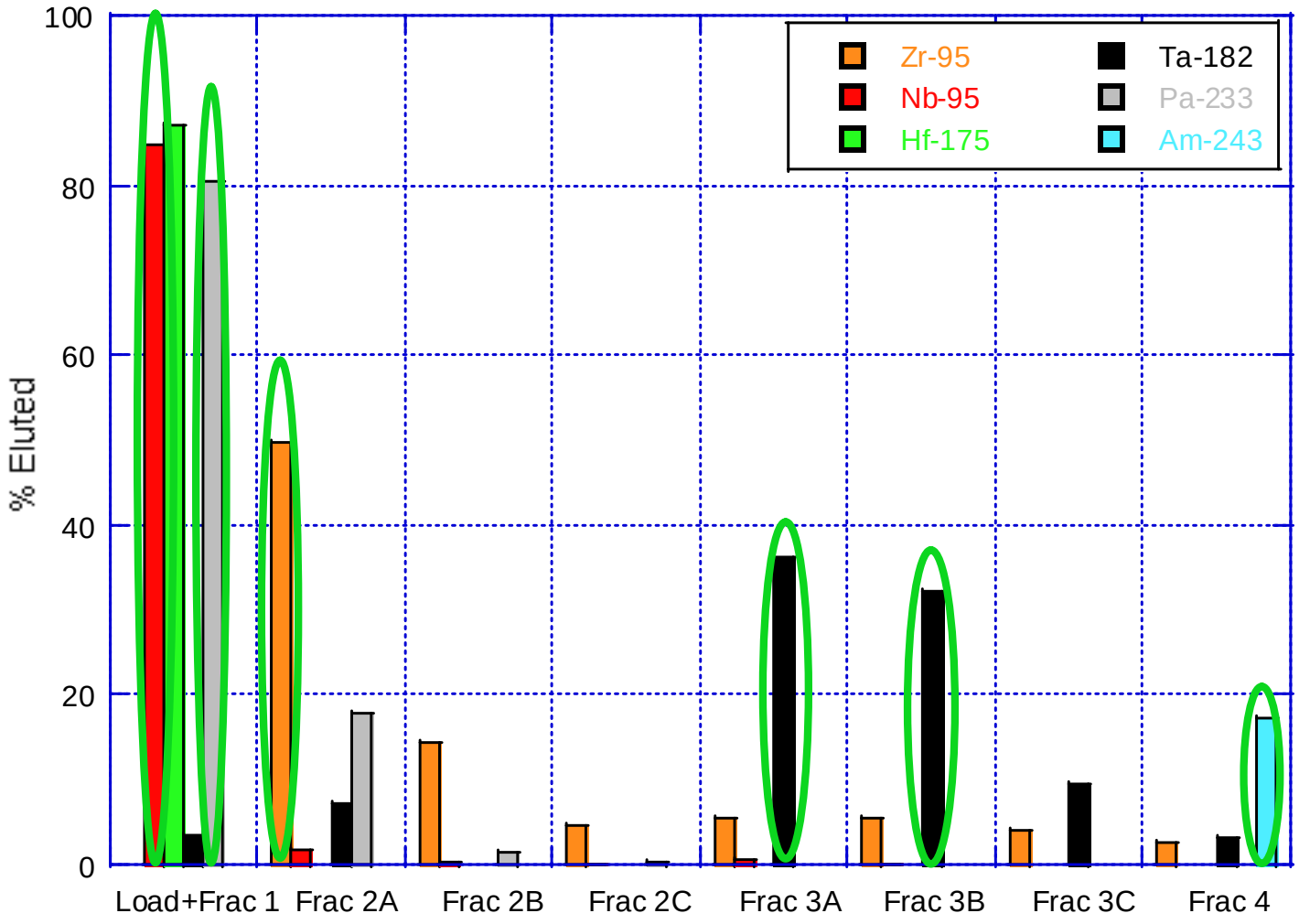
Frac 4 = 0.1M
Ammonium Bioxalate

Changing Elution Conditions



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Frac 3 =
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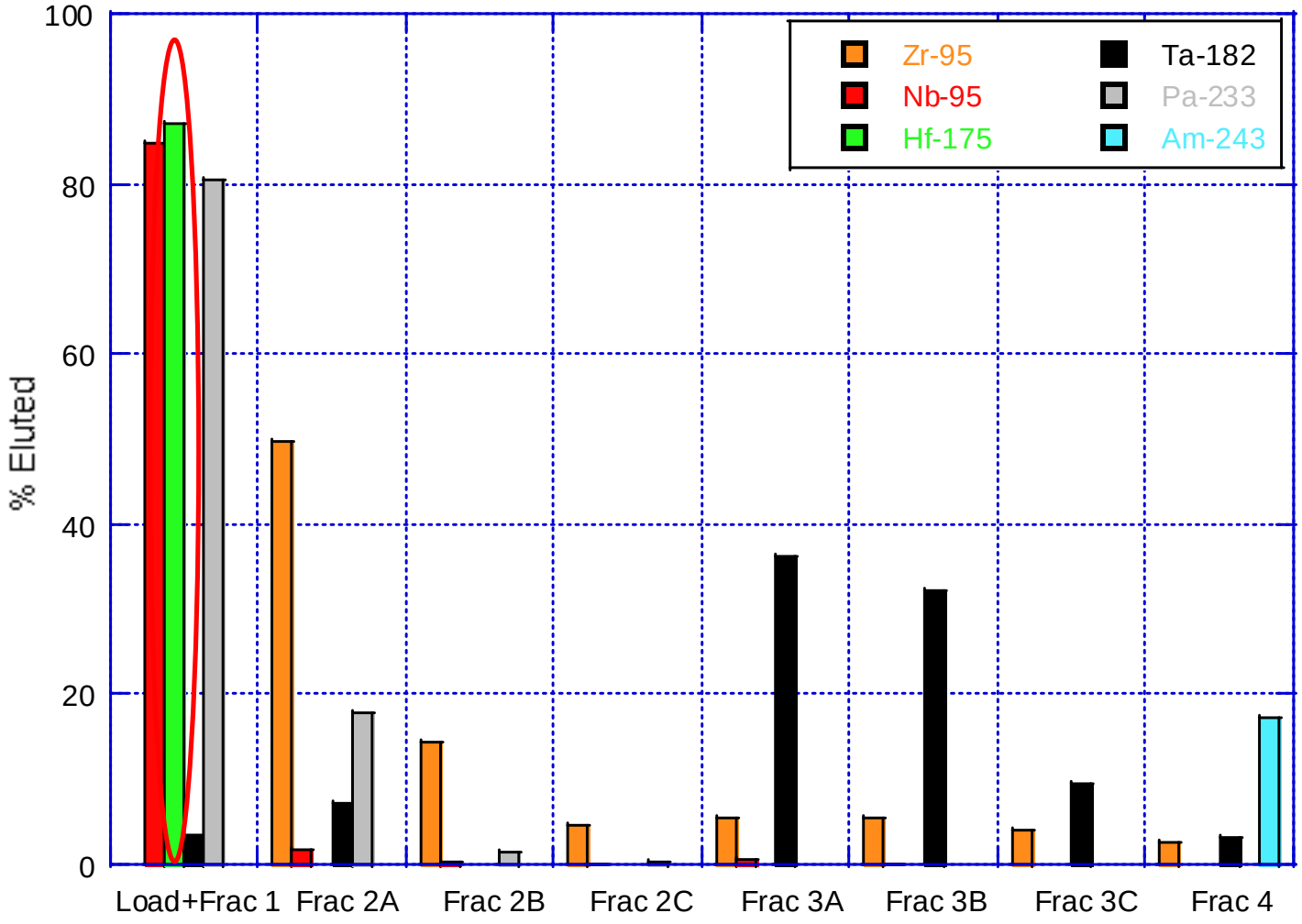
Frac 4 = 0.1M
Ammonium Bioxalate

Changing Elution Conditions



Frac1 =
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Frac 2 =
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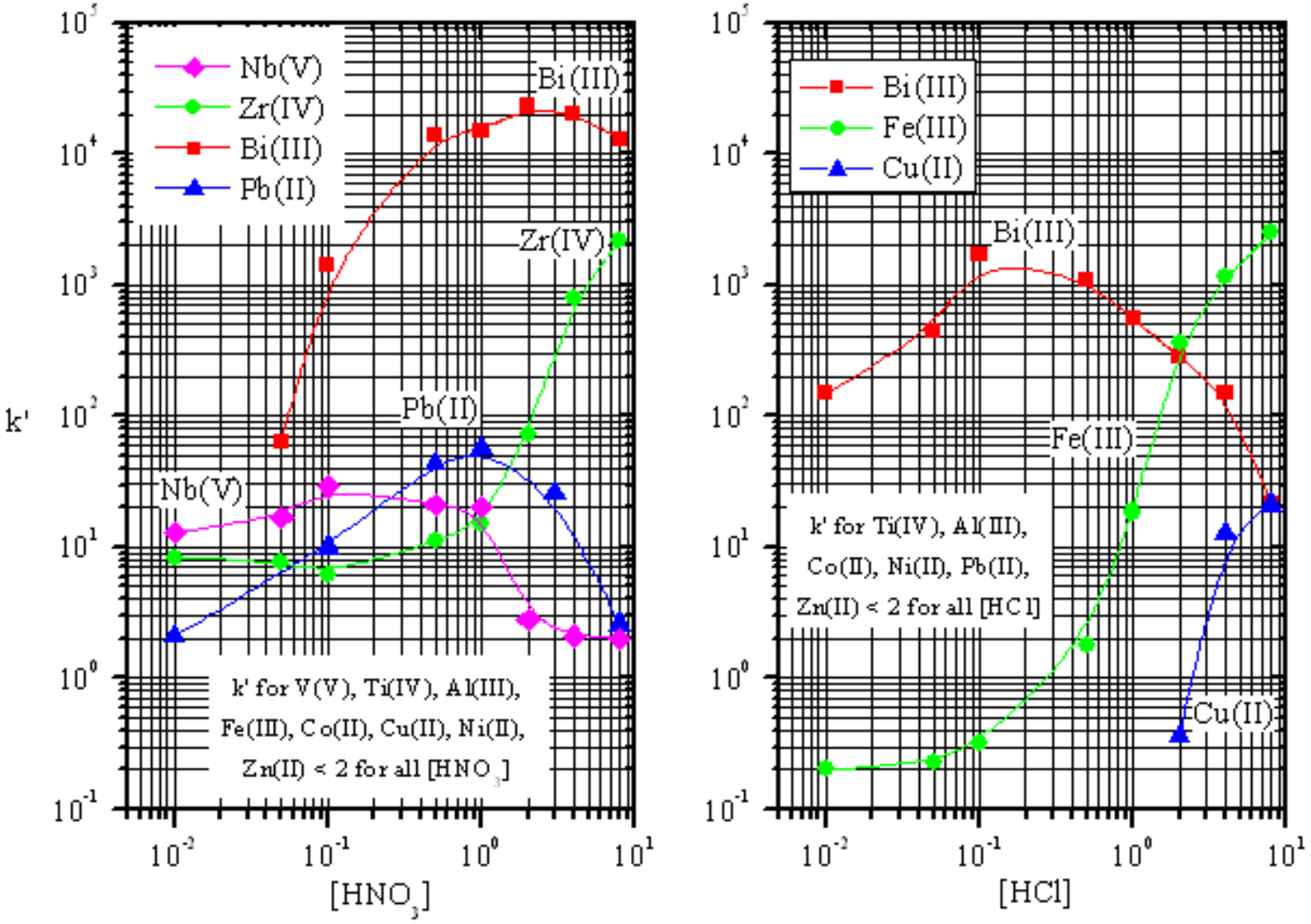
Frac 3 =
8M HNO_3/1M HF

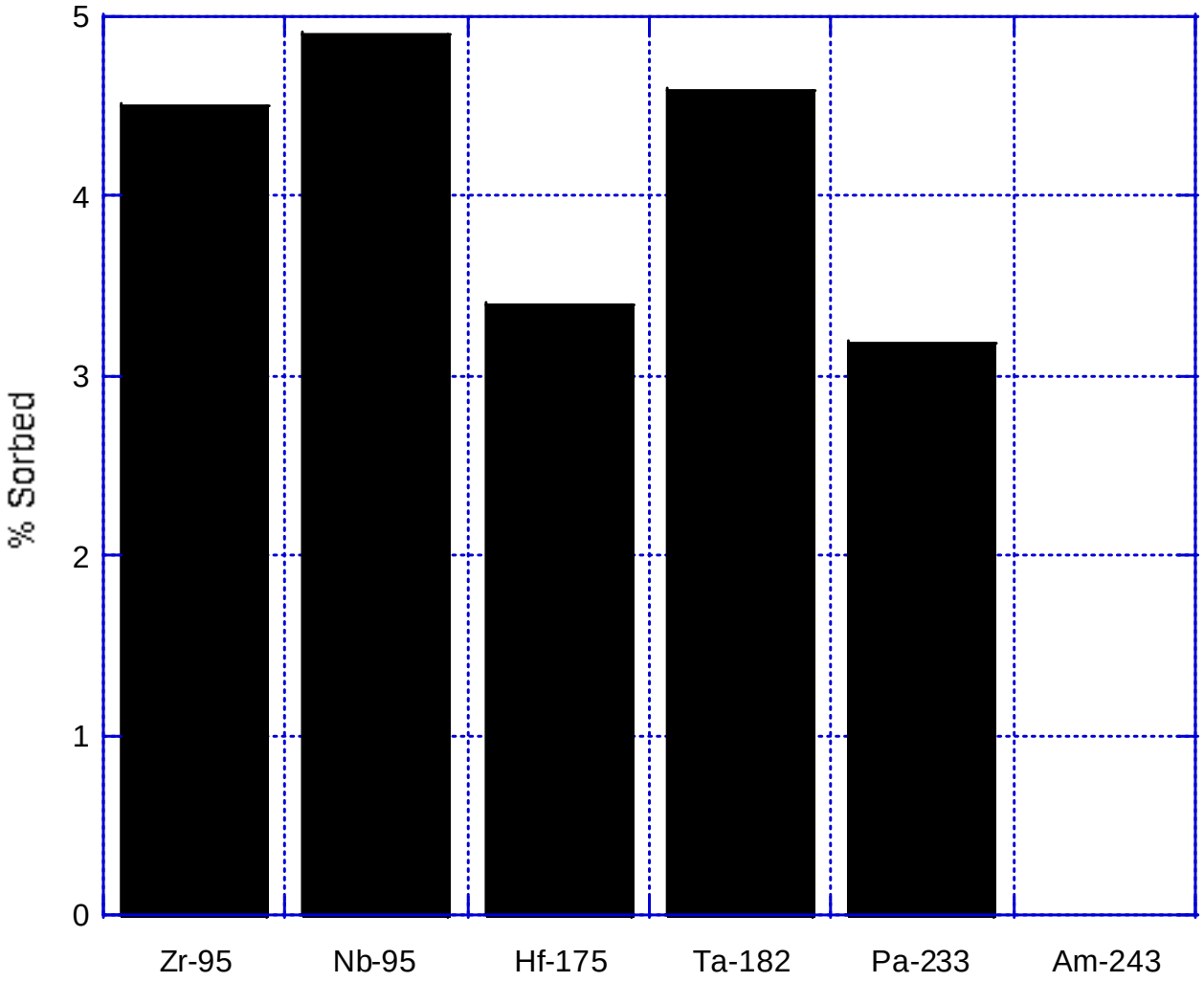
Frac 4 = 0.1M
Ammonium Bioxalate

Separating Group IV and V[4]

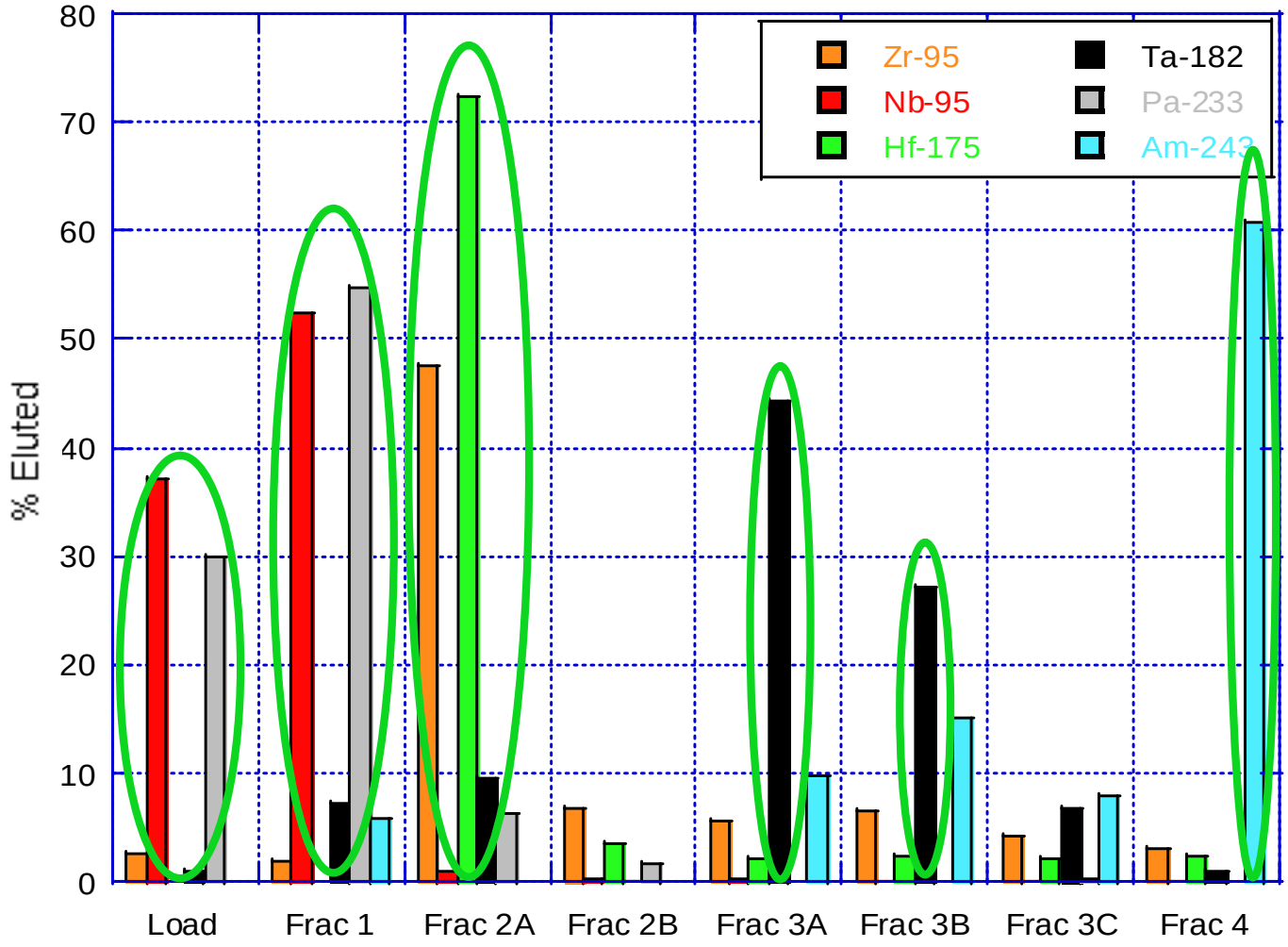


4 http://www.eichrom.com/products/info/DGA_resin.cfm

Loading Behavior from 10M HNO_3/0.1M HF



Elution Behavior from 10M HNO_3/ 0.1M HF



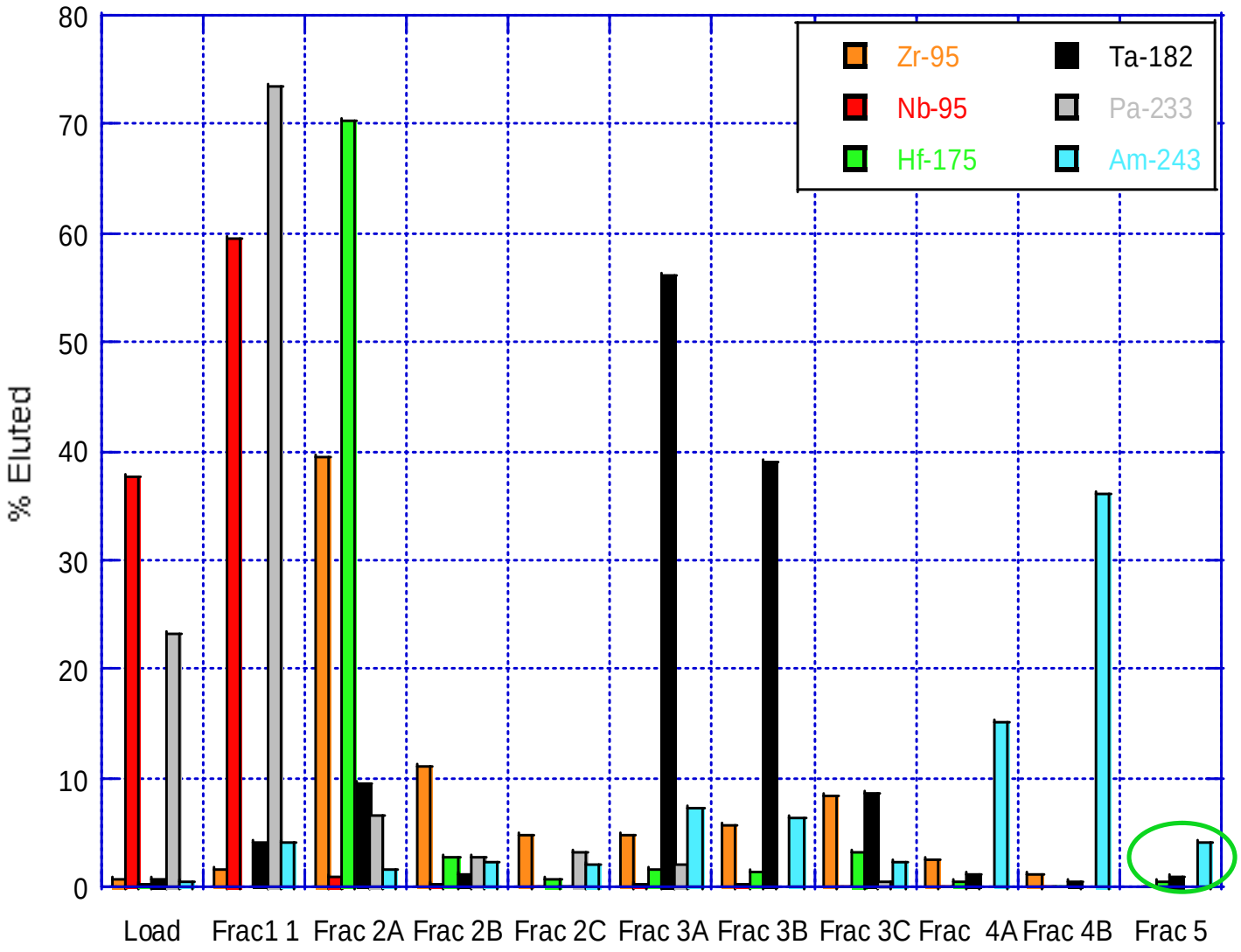
Frac1 =
4M HNO_3/0.001M HF

Frac 2 =
0.4M HNO_3/0.02M HF

Frac 3 =
8M HNO_3/1M HF

Frac 4 = 0.1M
Ammonium Bioxalate

Am Concentration/DGA Regeneration



Frac1 = 4M HNO_3/0.001M HF

Frac 2 = 0.4M HNO_3/0.02M HF

Frac 3 = 8M HNO_3/1M HF

Frac 4 = 0.1M HCl

Frac 5 = 0.1M Ammonium Bioxalate

Conclusions

- Elution conditions for DGA have been optimized
  - Load solution of 10M HNO_3/0.1M HF
  - Nb and Pa elute with 2mL of 4M HNO_3/0.001M HF
  - Zr and Hf elute with 2x5mL of 0.4M HNO_3/0.02M HF
  - Ta elutes with 3x5mL 8M HNO_3/1M HF
  - Am elutes with 2x5mL of 0.1M HCl
- DGA can be reused

Future Work

- Elution curves for Nb and Pa were the same for previous load solutions but need to be re-examined under optimized conditions
- Automation trials with DGA
- DGA column viability and kinetics studies
- Optimization of DGA system for Rf chemistry

Acknowledgements

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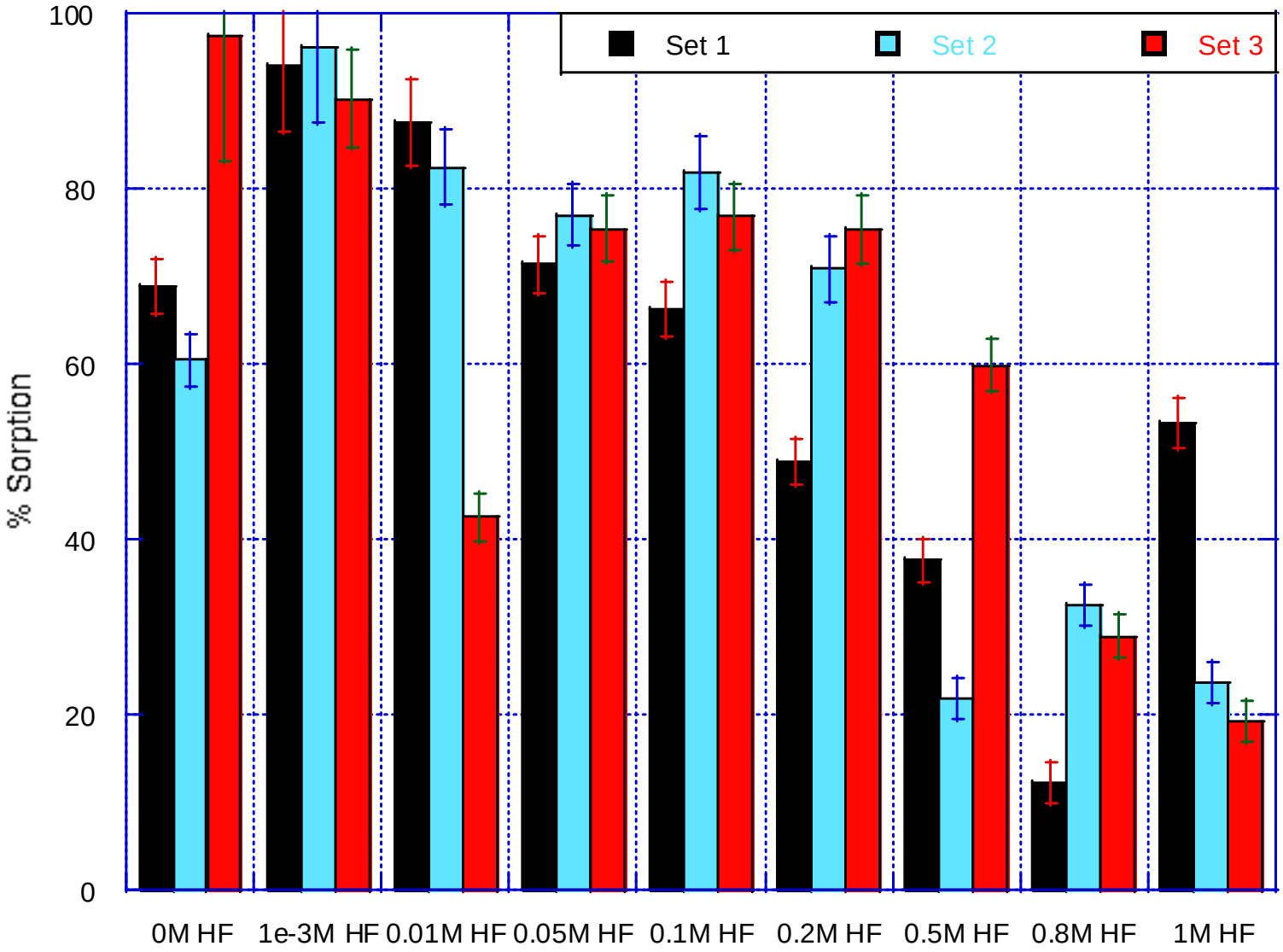
Batch Method[5]

- 1 mL of ^{182}Ta placed in a PPE 15 mL centrifuge tube
- Samples counted for 30 minutes
- Samples evaporated to dryness, reconstituted with HNO_3/HF or HCl/HF solution
- Samples transferred to a clean tube
- Samples counted for 30 minutes

5 Horwitz et. al. Solvent Extraction and Ion Chromatography 23, 3, (2005)

Ta Sorption From 4MHNO$_3$/HF



Ta Sorption from 6M HCl/HF