Separation Methods Utilizing Oxalate-HCl on Anion Exchange Resins

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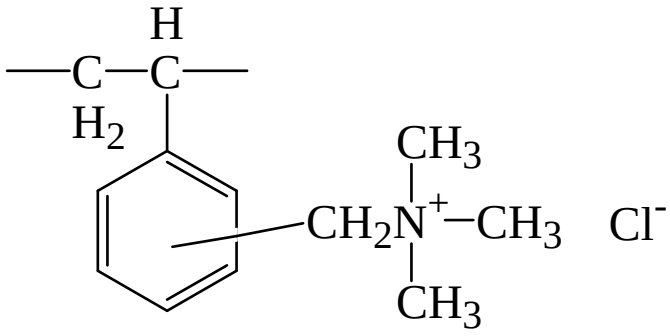
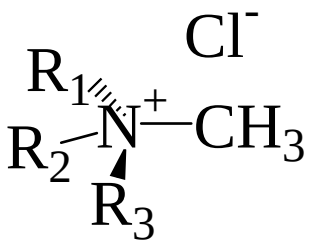
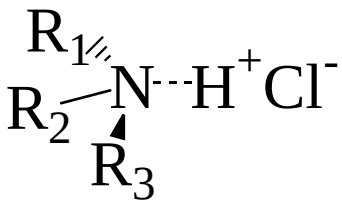
Anion Exchangers



Strong Base
Anion Exchange
Resin (1x8)
1.2 meq/mL



TEVA
(Quaternary Amine)
0.65 meq/mL



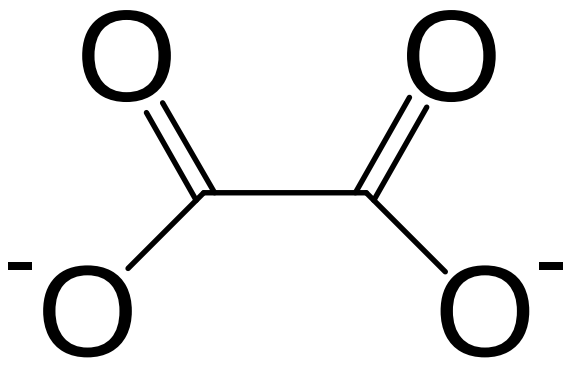
Weak Base
(Tertiary Amine)
0.65 meq/mL

Anion Exchange

AG 1-X8 resin	
OH^-	1.0
F^-	1.6
Propionate	2.6
Acetate	3.2
Formate	4.6
HPO_4^-	5.0
IO_3^-	5.5
HCO_3^-	6.0
Cl^-	22
NO_2^-	24
BrO_3^-	27
HSO_3^-	27
CN^-	28
Br^-	50
NO_3^-	65
ClO_3^-	74
HSO_4^-	85
Phenate	110
I^-	175
Citrate	220
Salicylate	450
Benzene-sulfonate	500

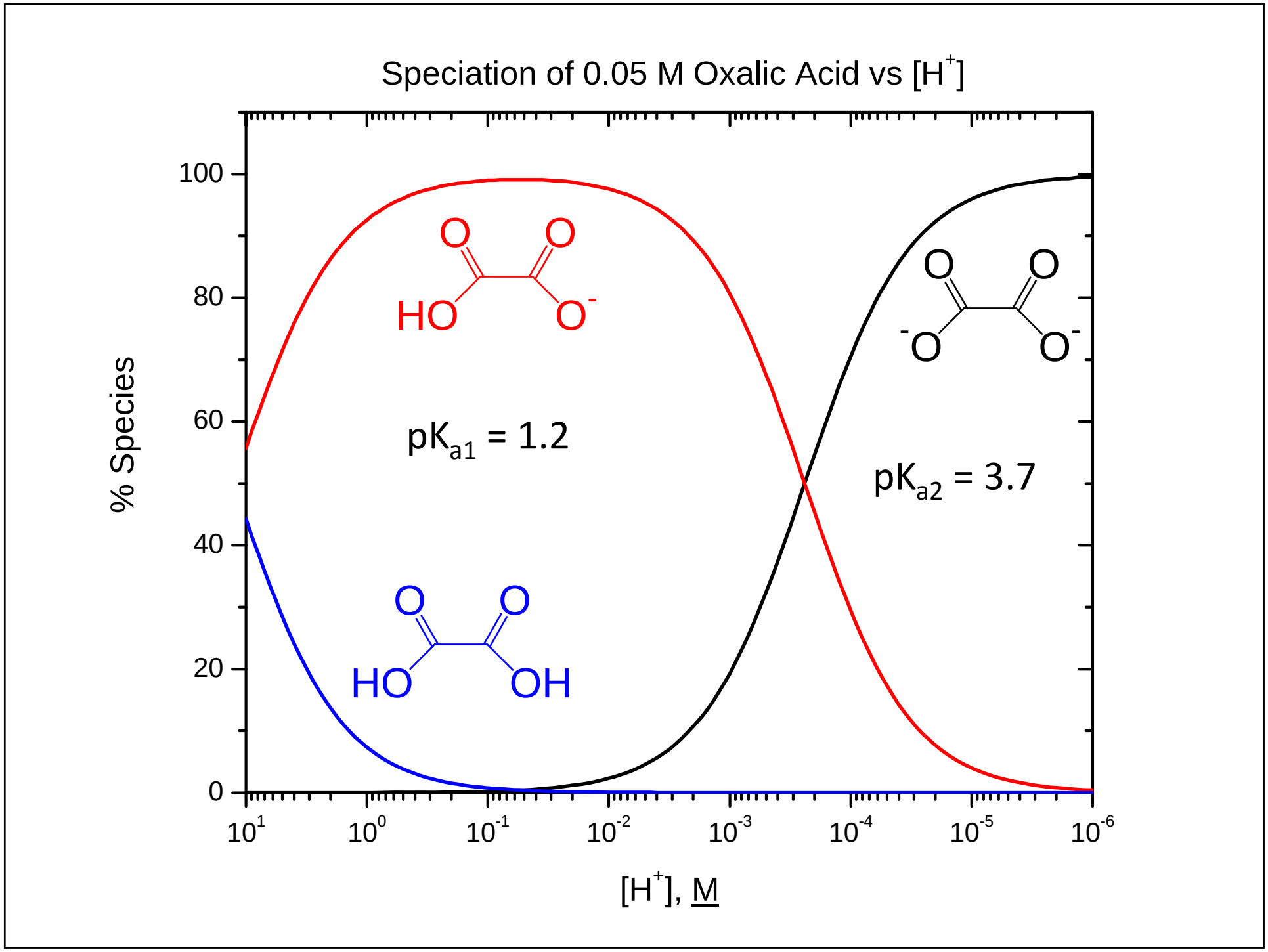
TcO_4^-, ReO_4^-, MoO_4^{2-}, WO_4^{2-}

$Th(NO_3)_5^-$, $UO_2Cl_4^{2-}$, $FeCl_4^-$

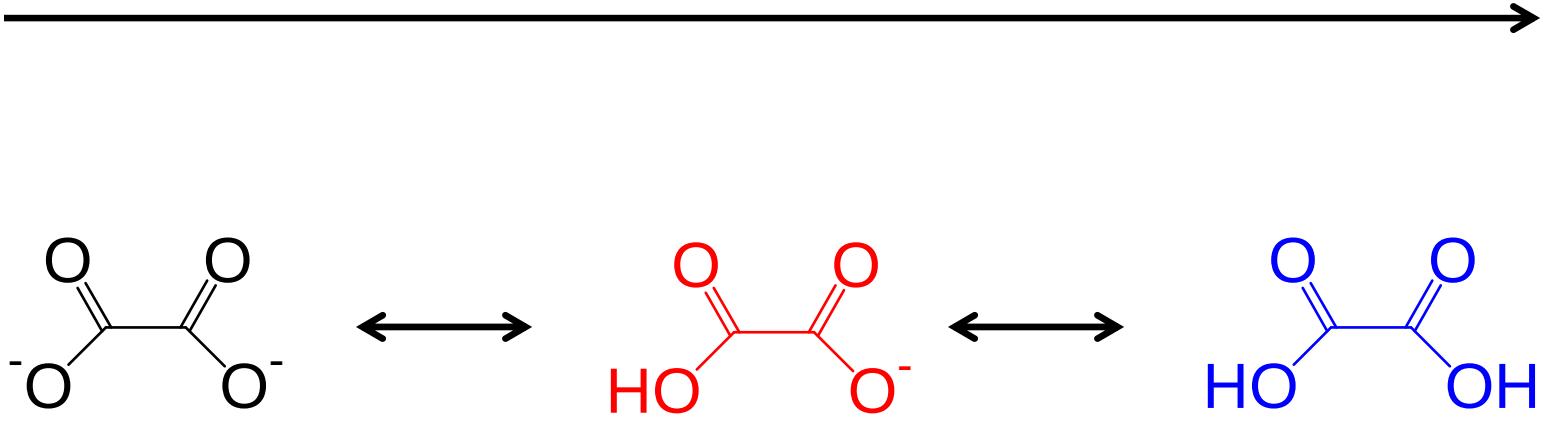


+ HCl

Strelow, et al., Analytical Chemistry, 44(14), pp 2352-2356, 1972.


Speciation of 0.05 M Oxalic Acid vs [H+]
% Species
100
80
60
40
20
0
10^1
10^0
10^-1
10^-2
10^-3
10^-4
10^-5
10^-6
[H+], M
pKa1 = 1.2
pKa2 = 3.7
HO
O
O-
OH

Increasing HCl Concentration

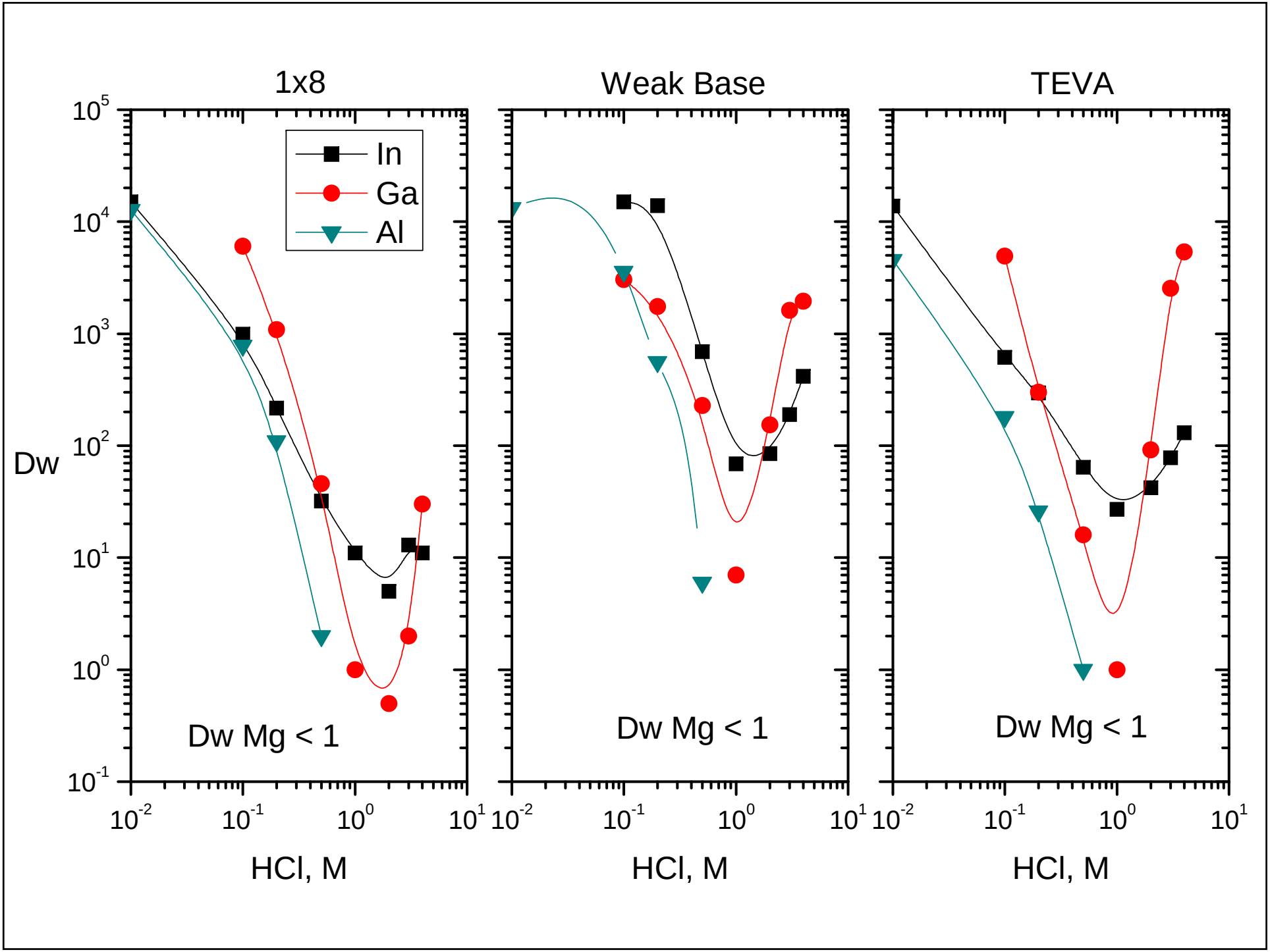


M^{n+} → MCl → MCl_x^-

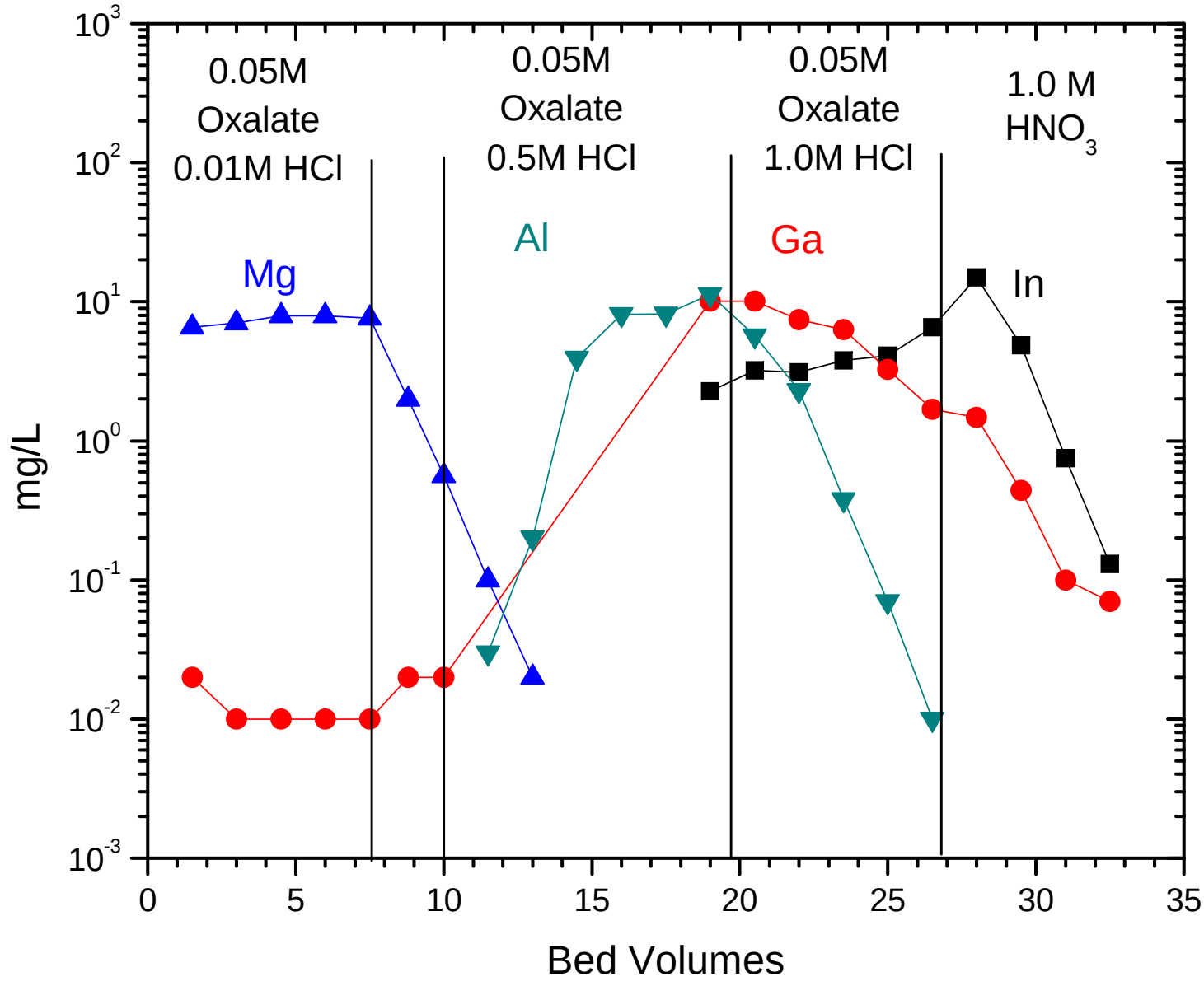
Chloride competition for extraction

Example #1

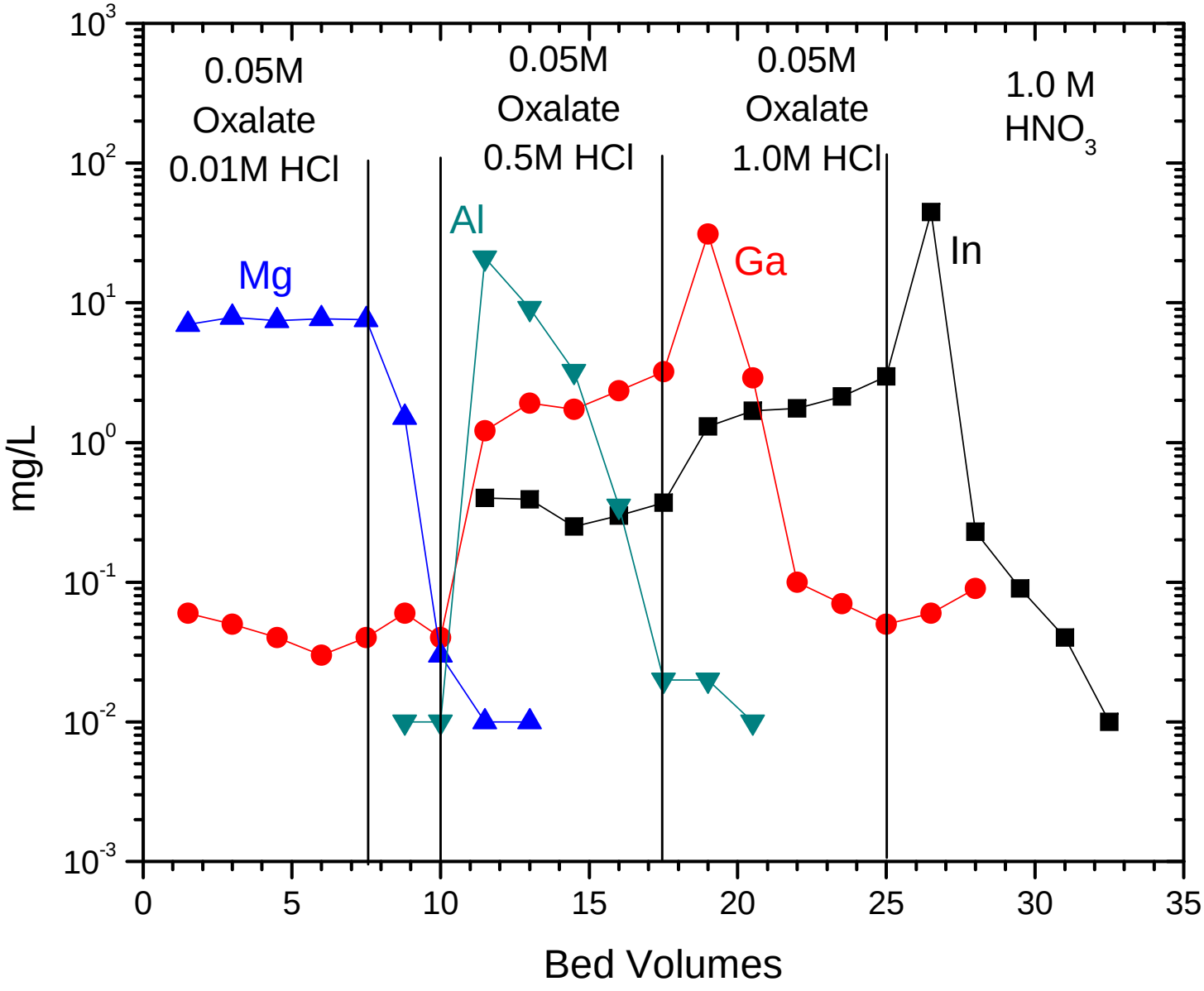
Metal	Ion Charge	Oxalate logK 1	Oxalate logK 2	Oxalate logK 3	Chloride logK 1	Chloride logK 2	Chloride logK 3
Mg	2+	2.76			0.2		
Al	3+	6.2	11.4	15.8	-1.0		
Ga	3+	6.4	12.3	17.8	0.01	3.6	4.0
In	3+	6	11.4	14.5	2.3	11.4	14.5


1x8
Weak Base
TEVA
In
Ga
Al
Dw
Dw Mg < 1
Dw Mg < 1
Dw Mg < 1
HCl, M
HCl, M
HCl, M
10^{5}
10^{4}
10^{3}
10^{2}
10^{1}
10^{0}
10^{-1}
10^{-2}
10^{-1}
10^{0}
10^{1}

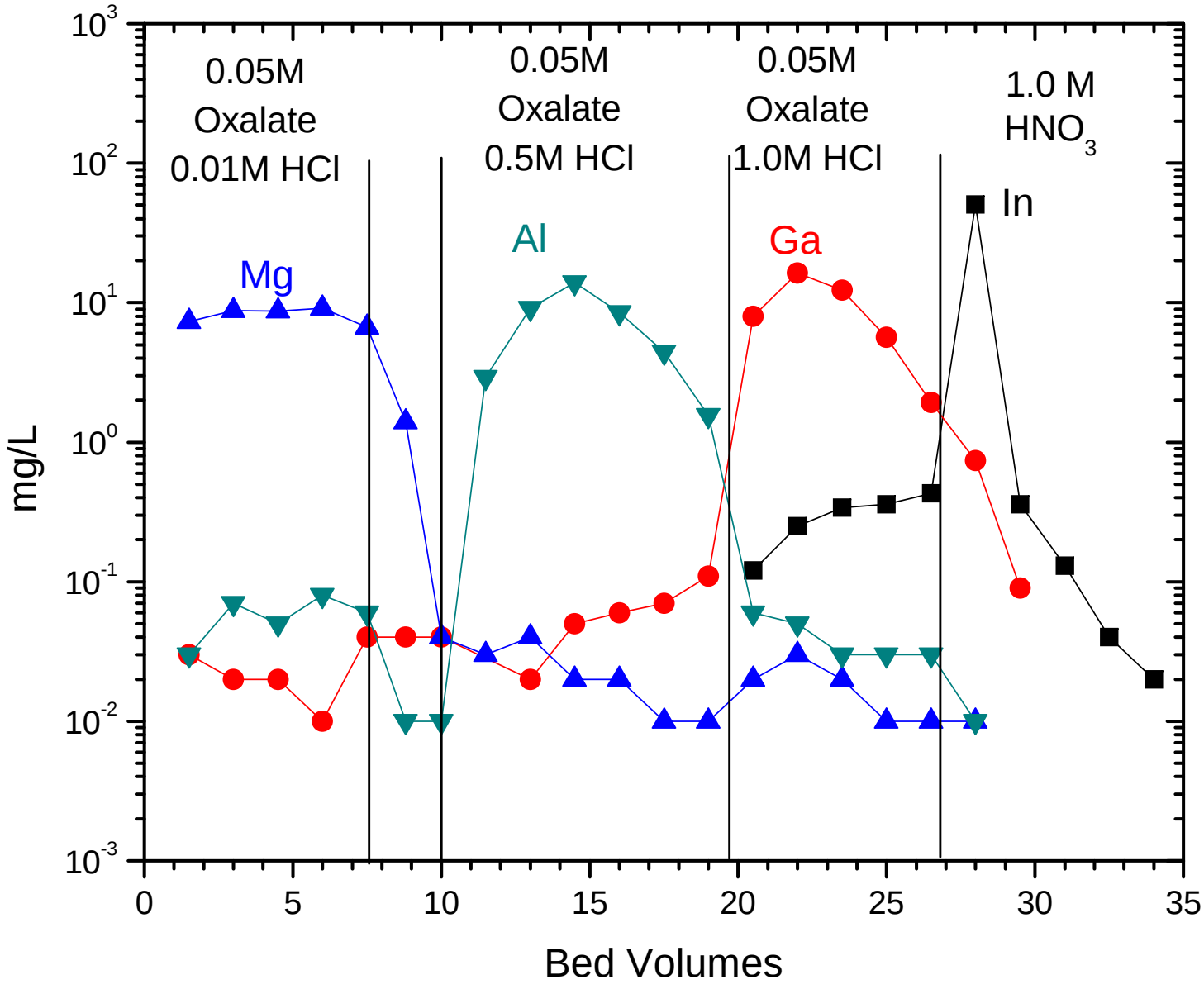
Elution on 2mL Cartridge of 1x8 Resin (50-100 μm), 21(1)°C, 2mL/min



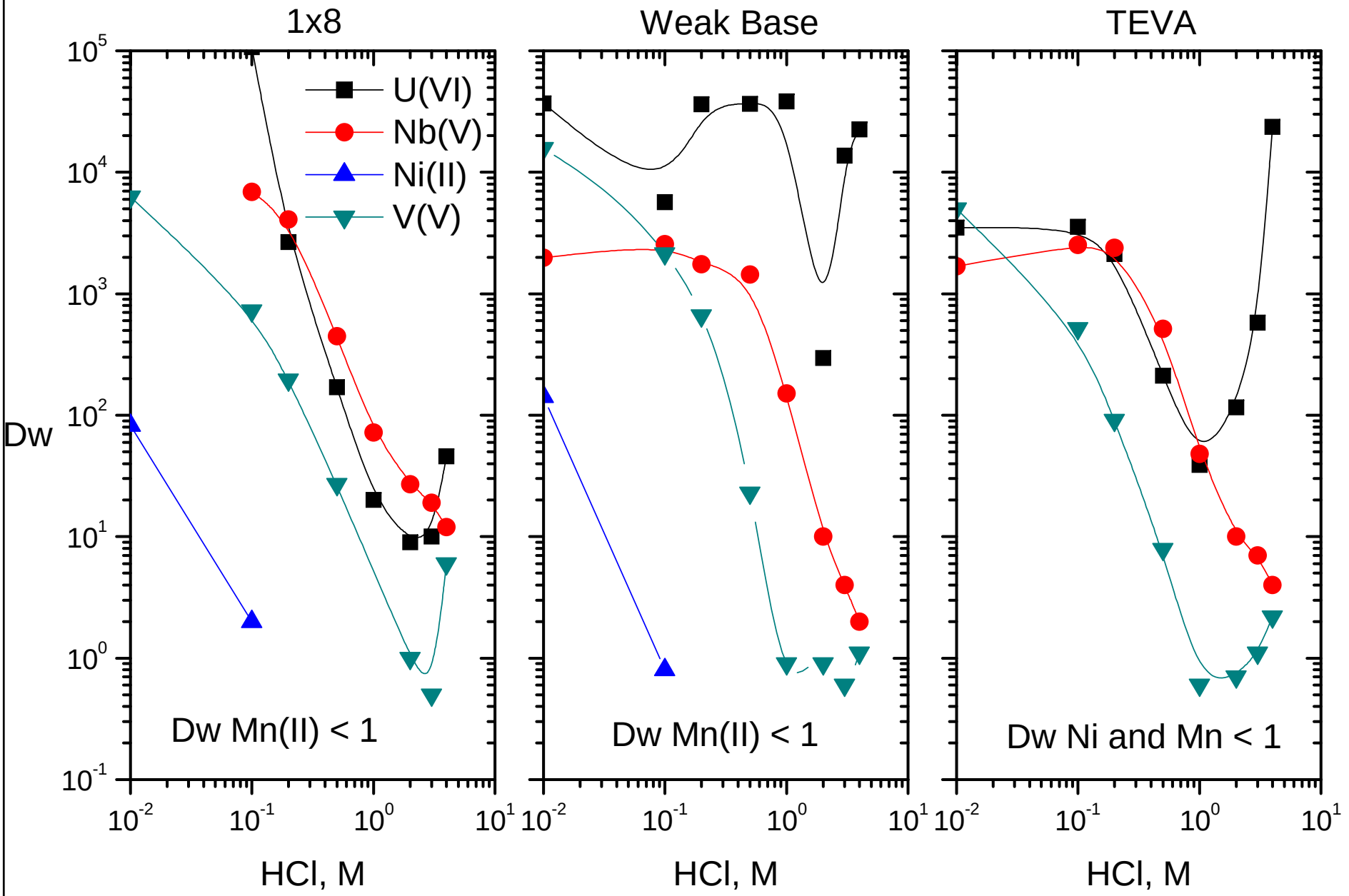
Elution on 2mL Cartridge of TEVA Resin (50-100 μm), 21(1)°C, 2mL/min



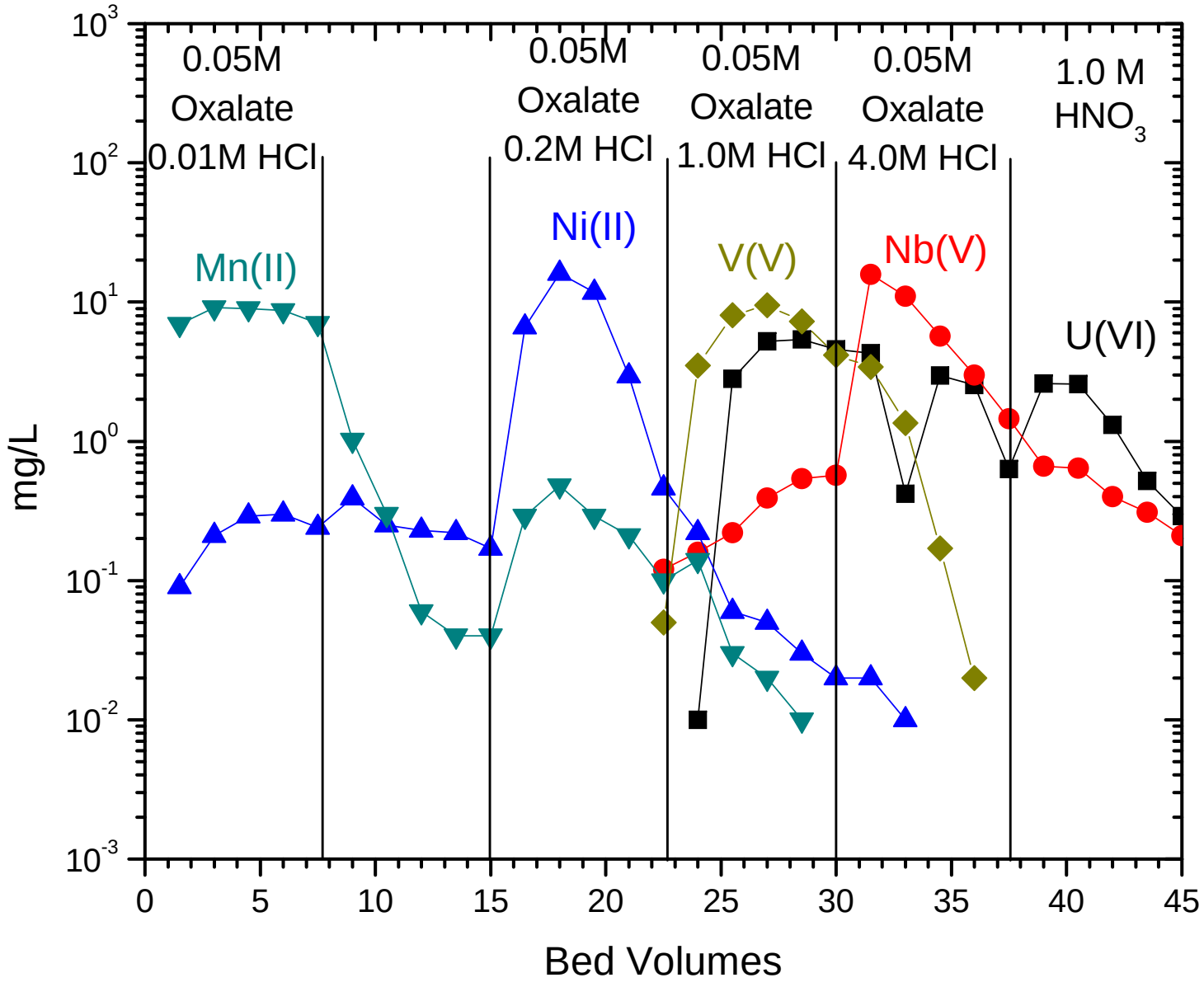
Elution on 2mL Cartridge of Weak Base Resin (50-100 μm), 21(1)°C, 2mL/min



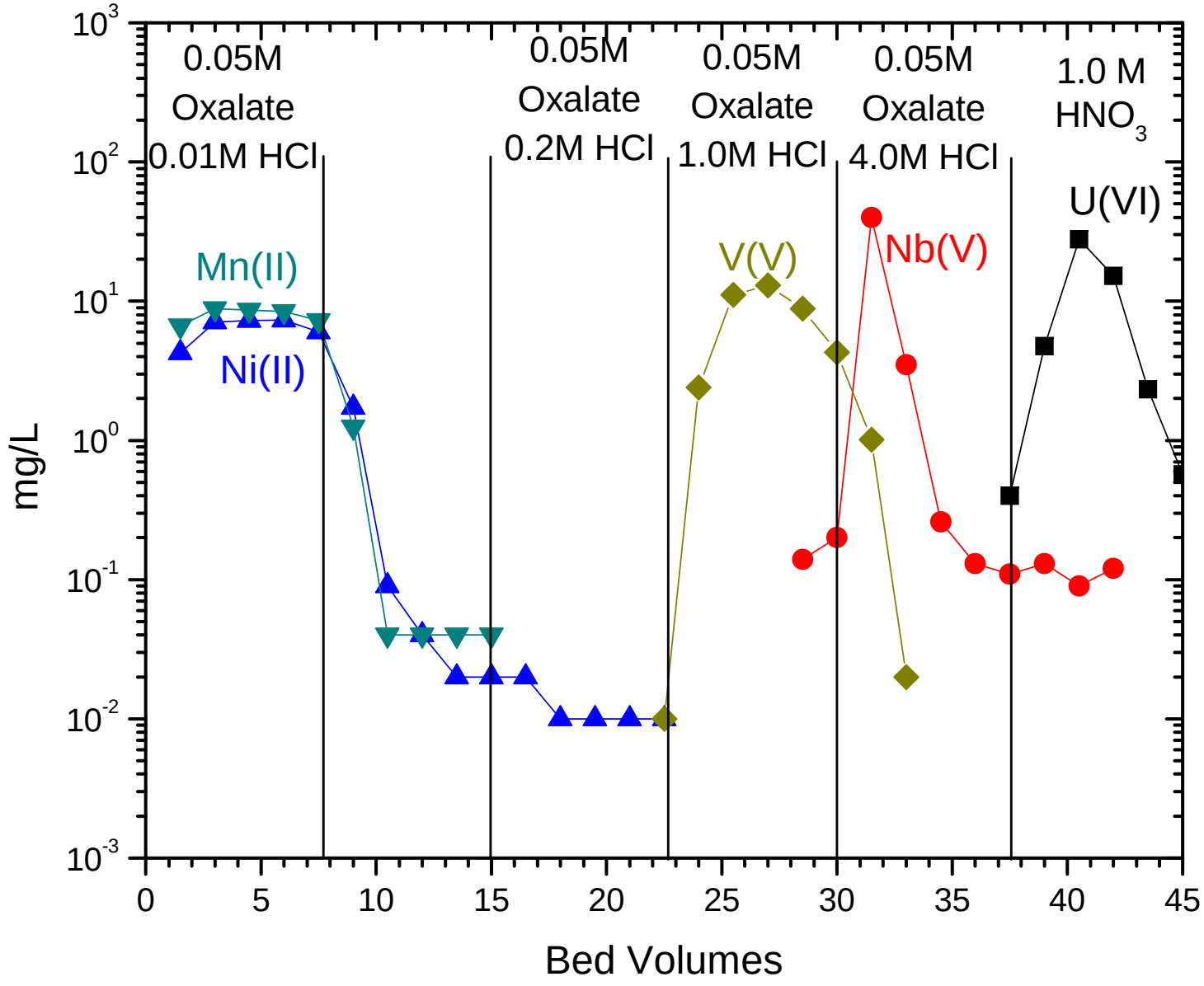
Example #2


1x8
Weak Base
TEVA
U(VI)
Nb(V)
Ni(II)
V(V)
Dw
Dw Mn(II) < 1
Dw Mn(II) < 1
Dw Ni and Mn < 1
HCl, M
HCl, M
HCl, M

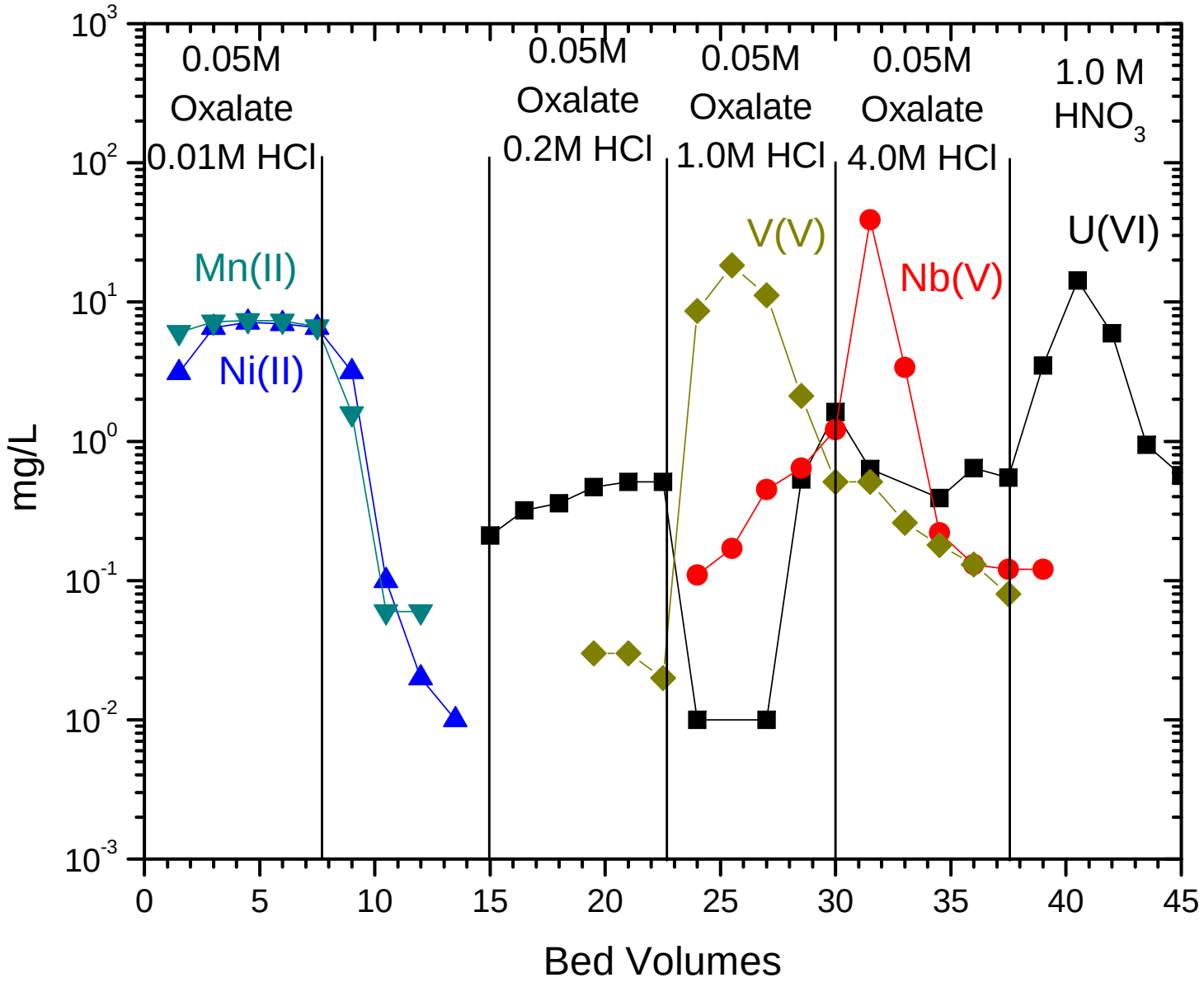
Elution on 2mL Cartridge of 1x8 Resin (50-100 μm), 21(1)°C, 2mL/min



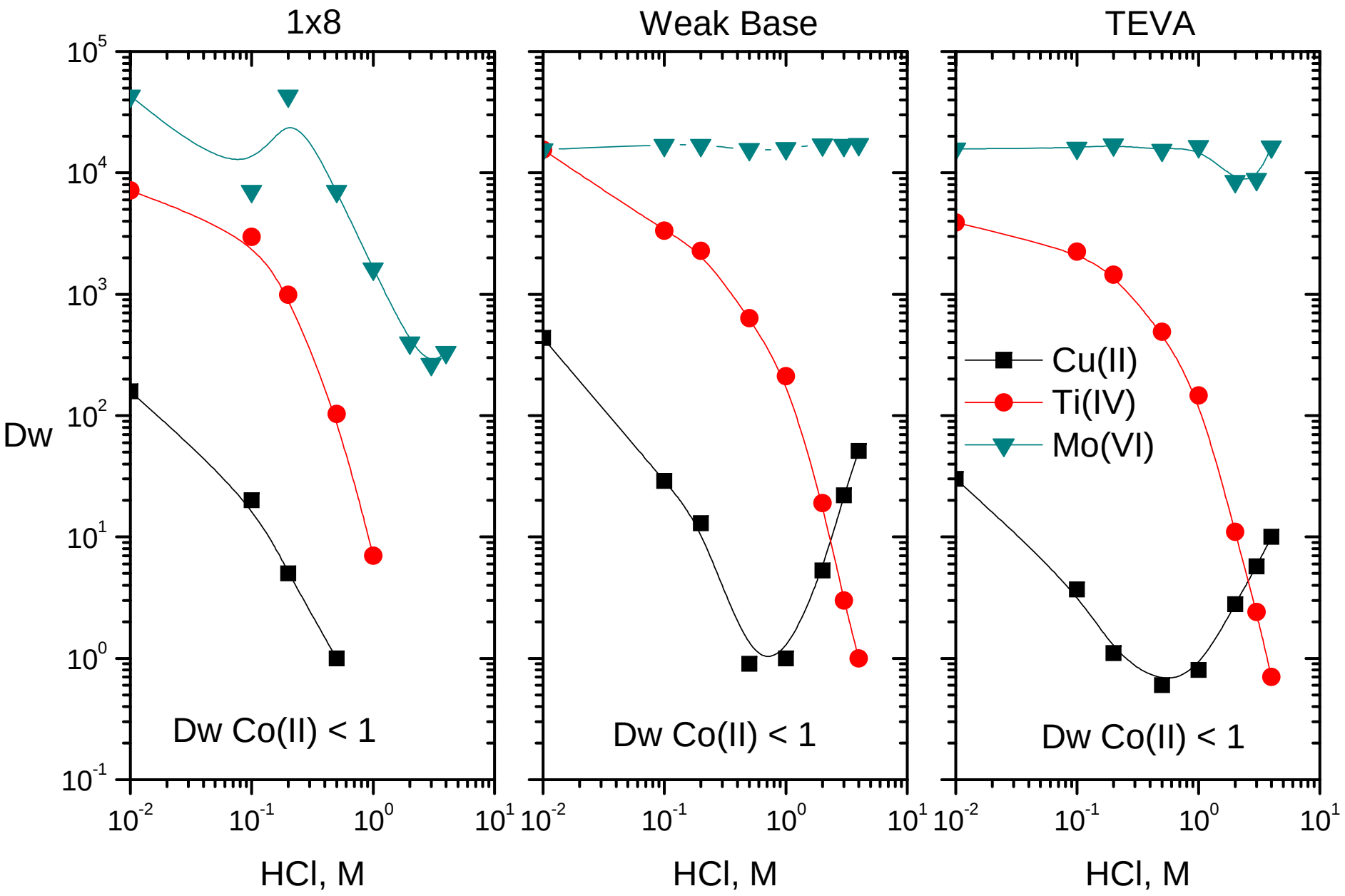
Elution on 2mL Cartridge of Weak Base Resin (50-100 μm), 21(1)°C, 2mL/min



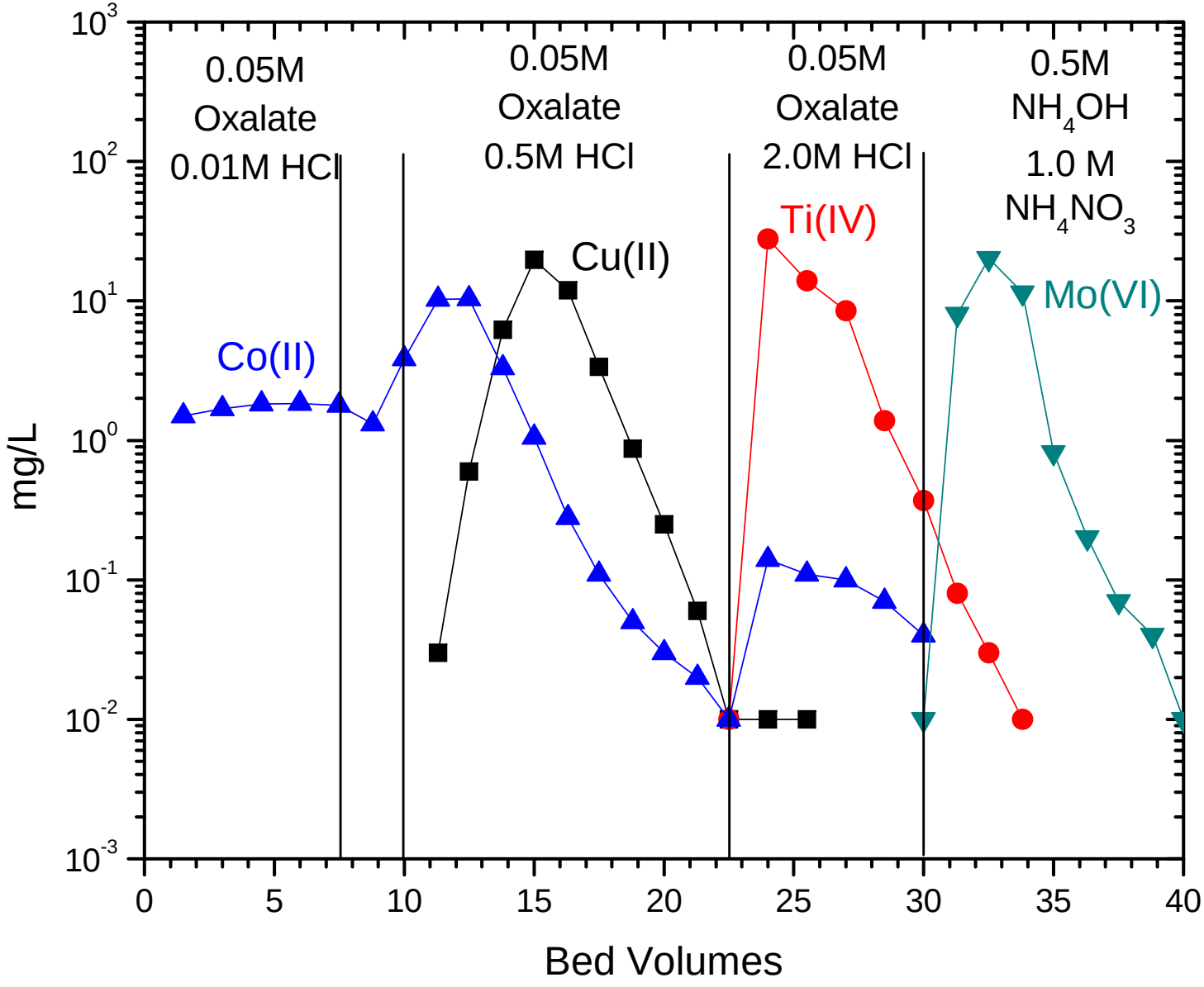
Elution on 2mL Cartridge of TEVA Resin (50-100 μm), 21(1)°C, 2mL/min



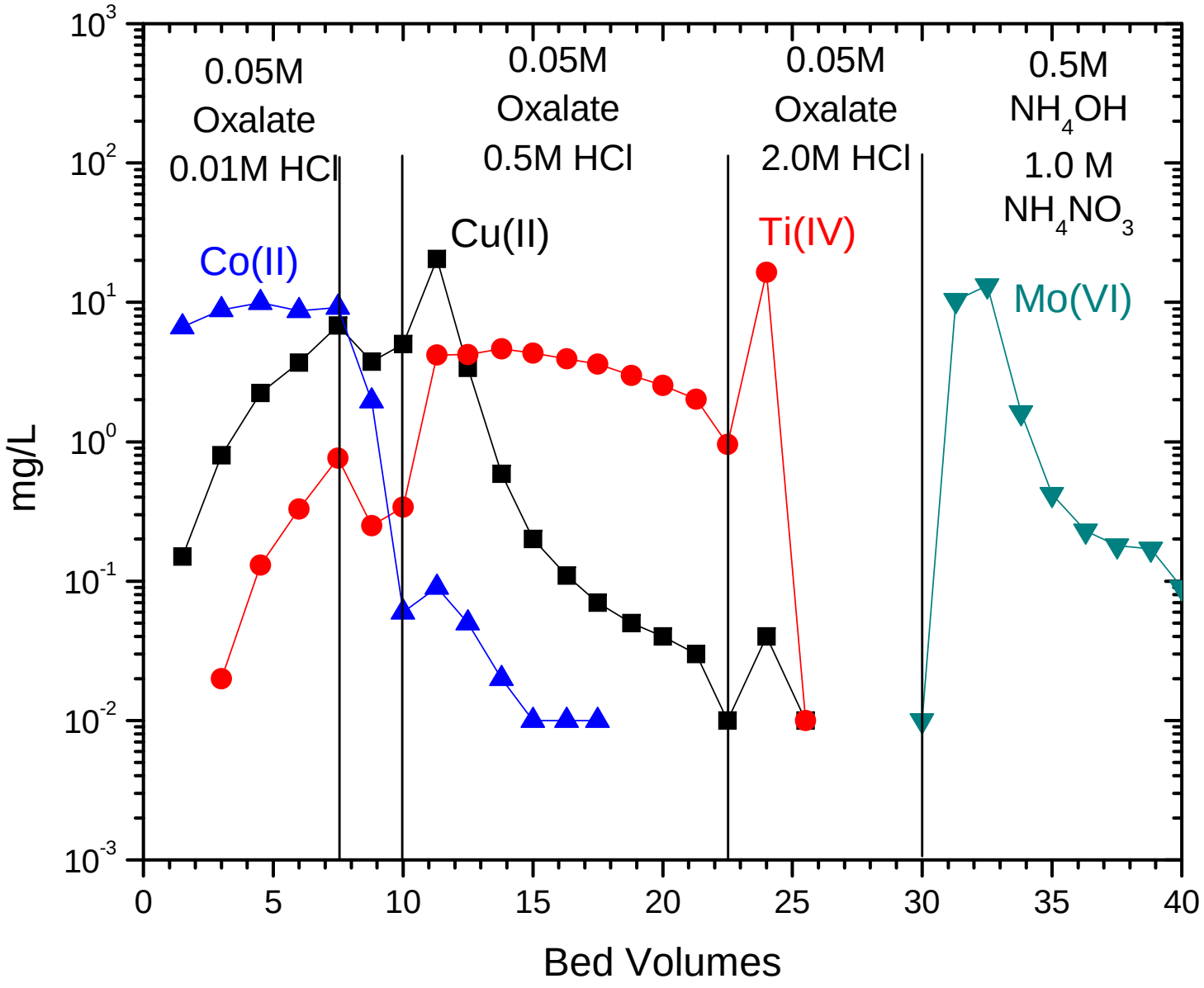
Example #3


1x8
Weak Base
TEVA
Dw
HCl, M
HCl, M
HCl, M
Dw Co(II) < 1
Dw Co(II) < 1
Dw Co(II) < 1
Cu(II)
Ti(IV)
Mo(VI)

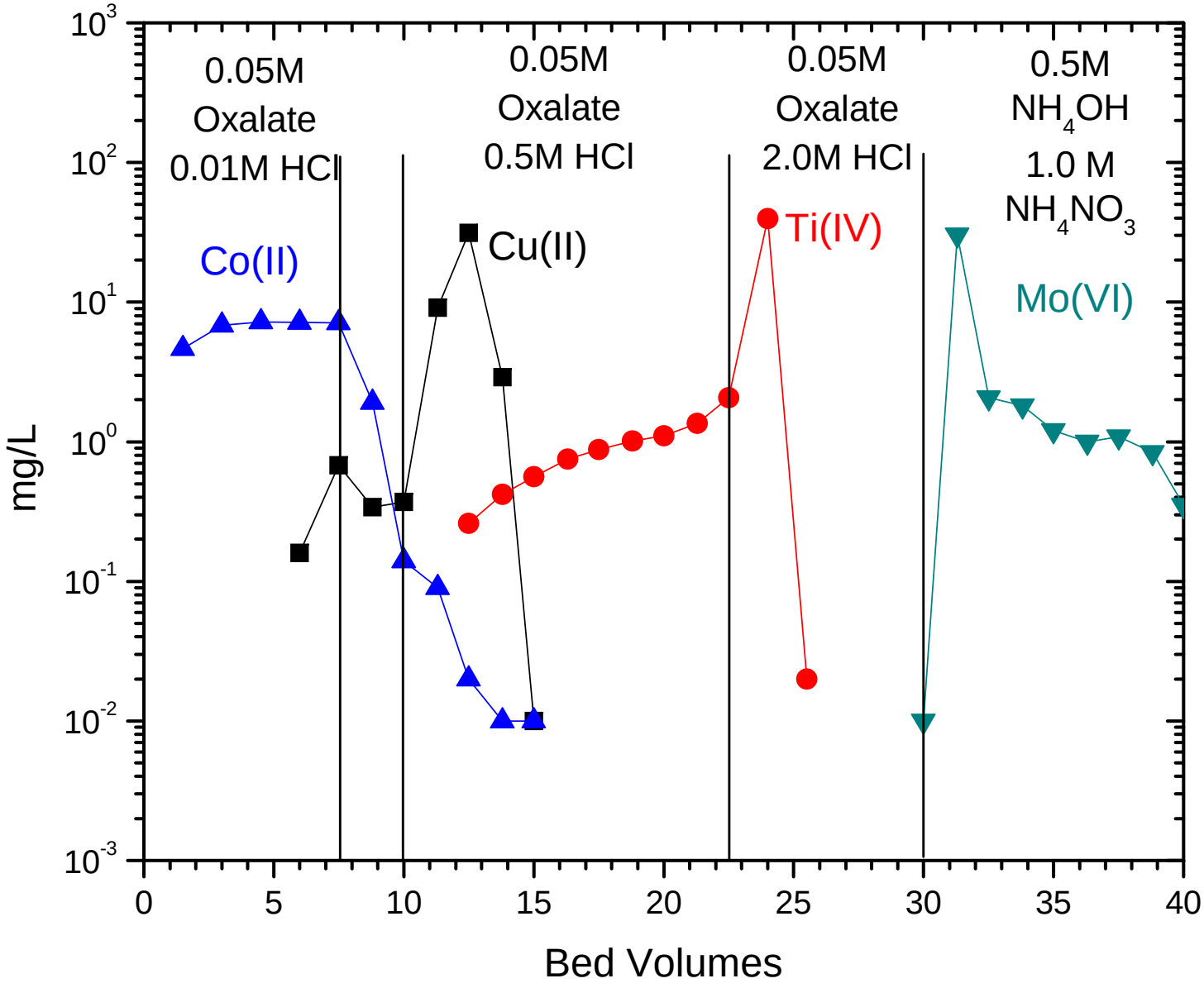
Elution on 2mL Cartridge of 1x8 Resin (50-100 μm), 21(1)°C, 2mL/min

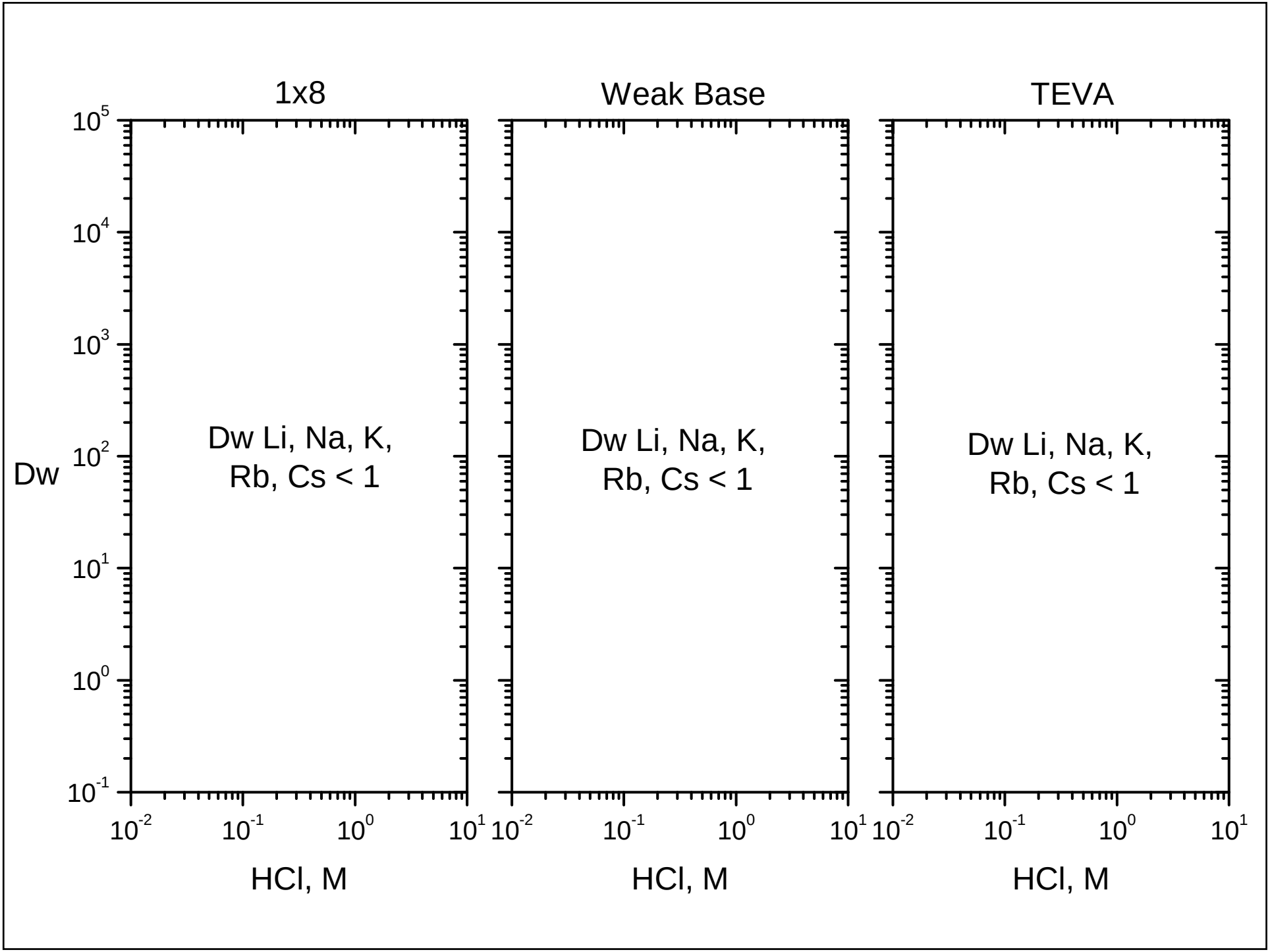


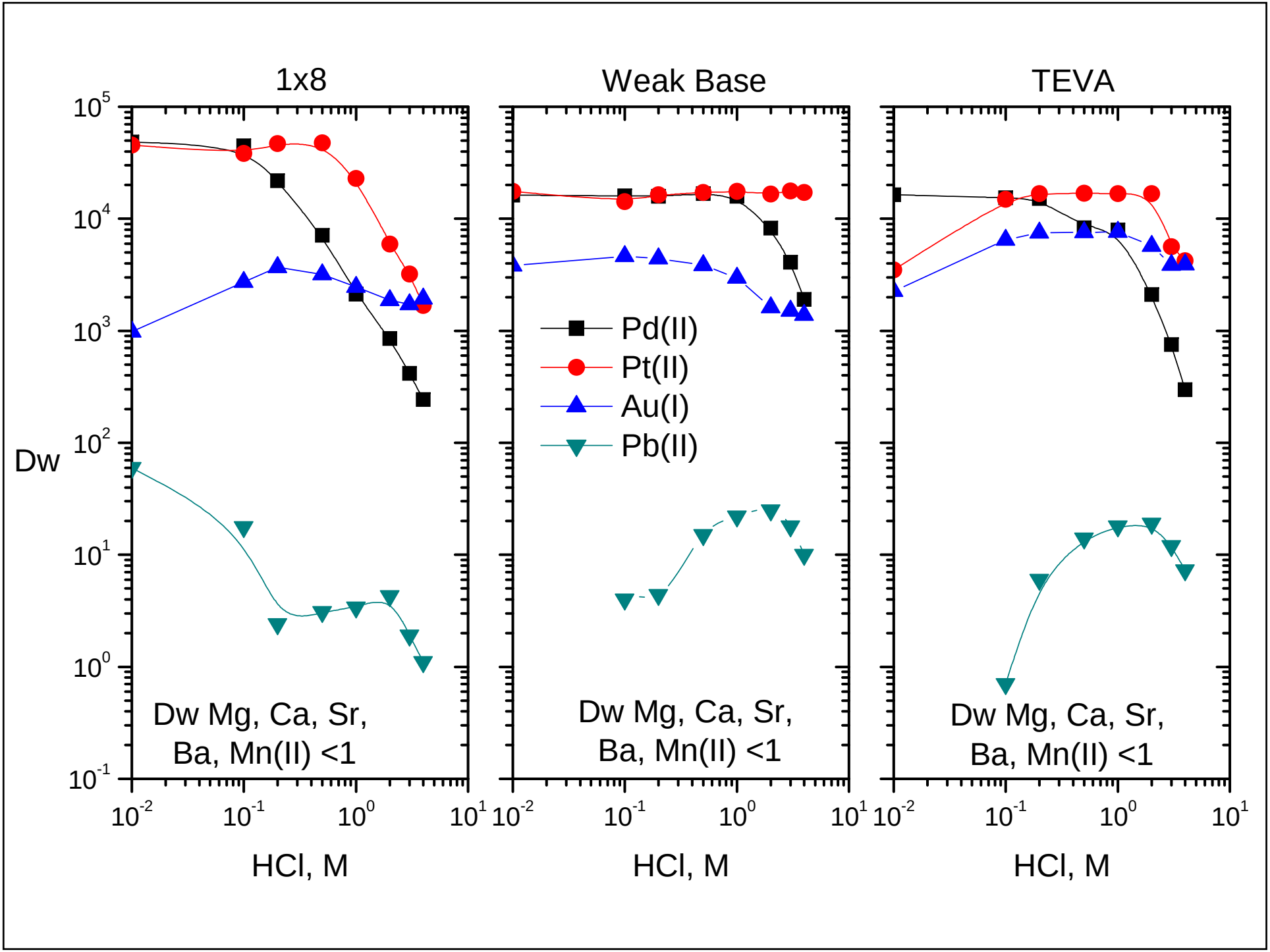
Elution on 2mL Cartridge of Weak Base Resin (50-100 μm), 21(1)°C, 2mL/min

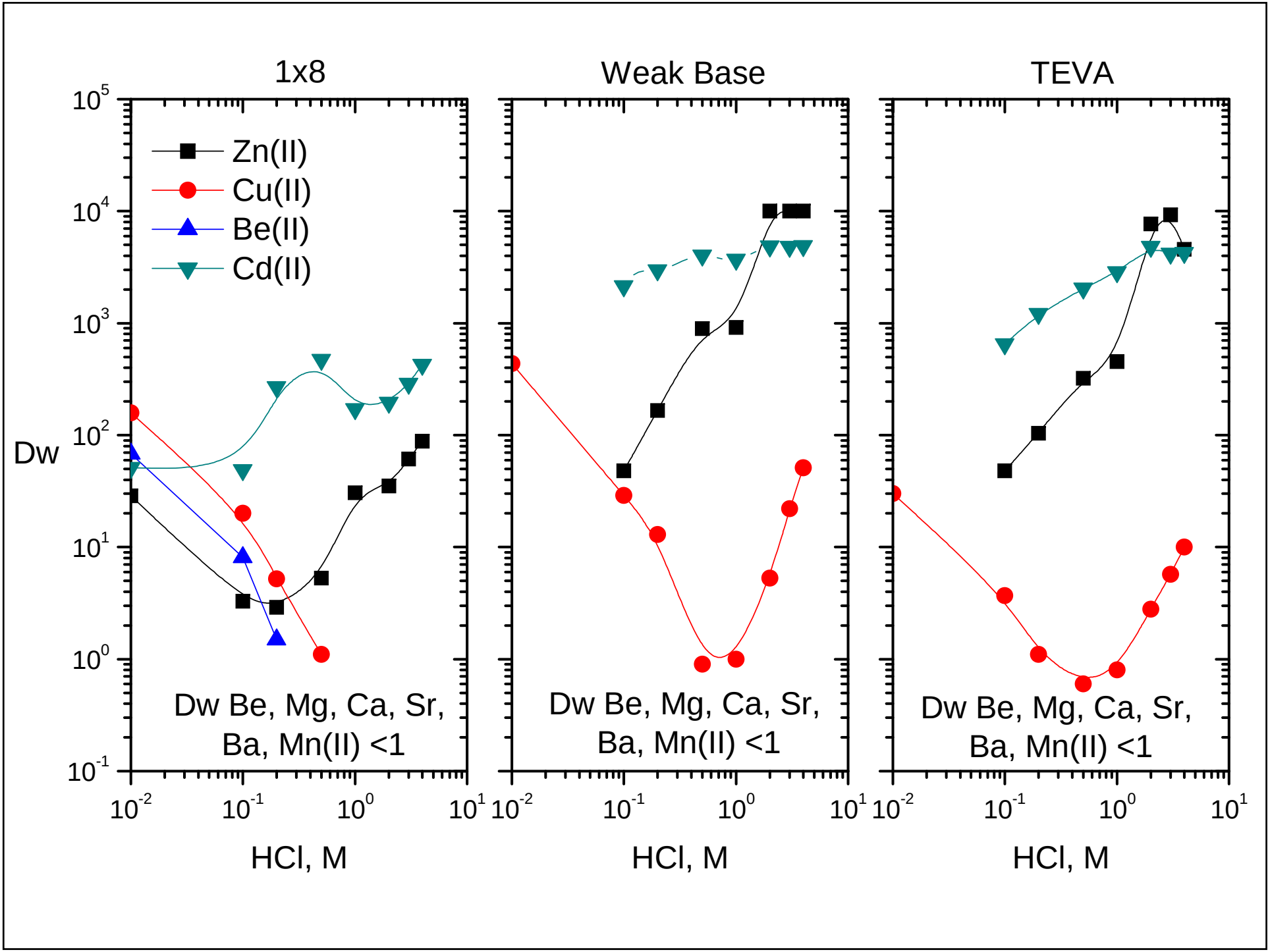


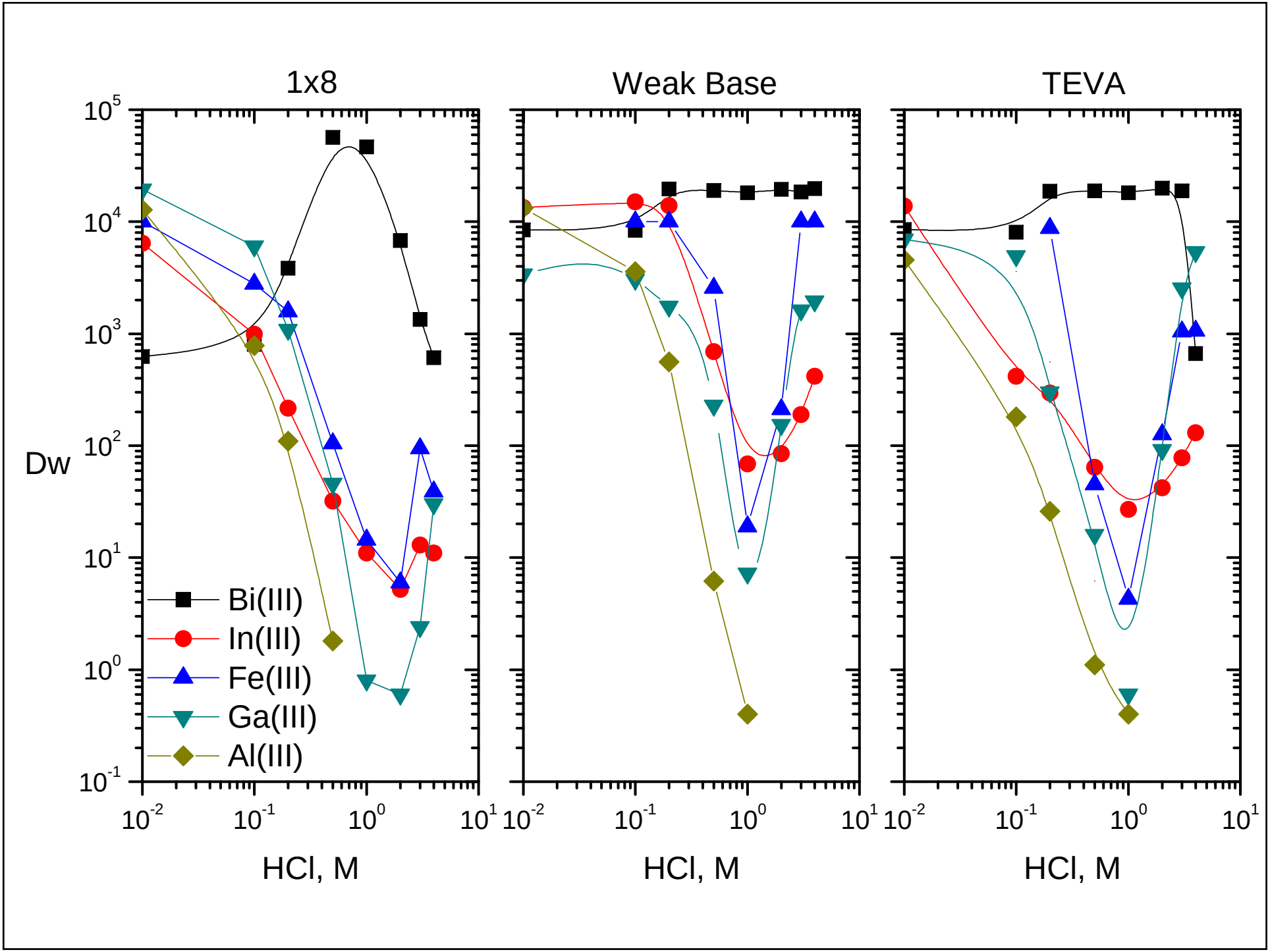
Elution on 2mL Cartridge of TEVA Resin (50-100 μm), 21(1)°C, 2mL/min

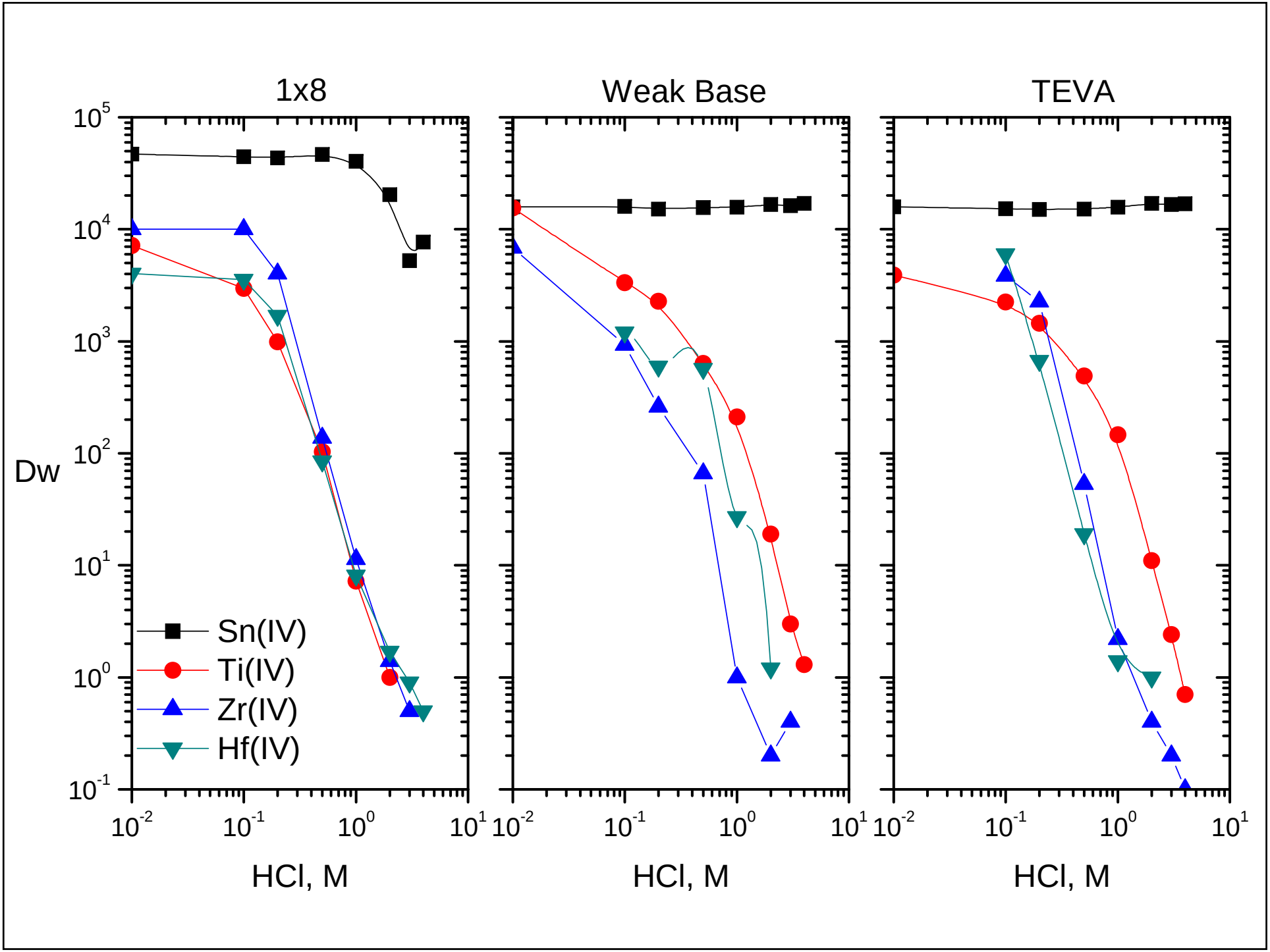


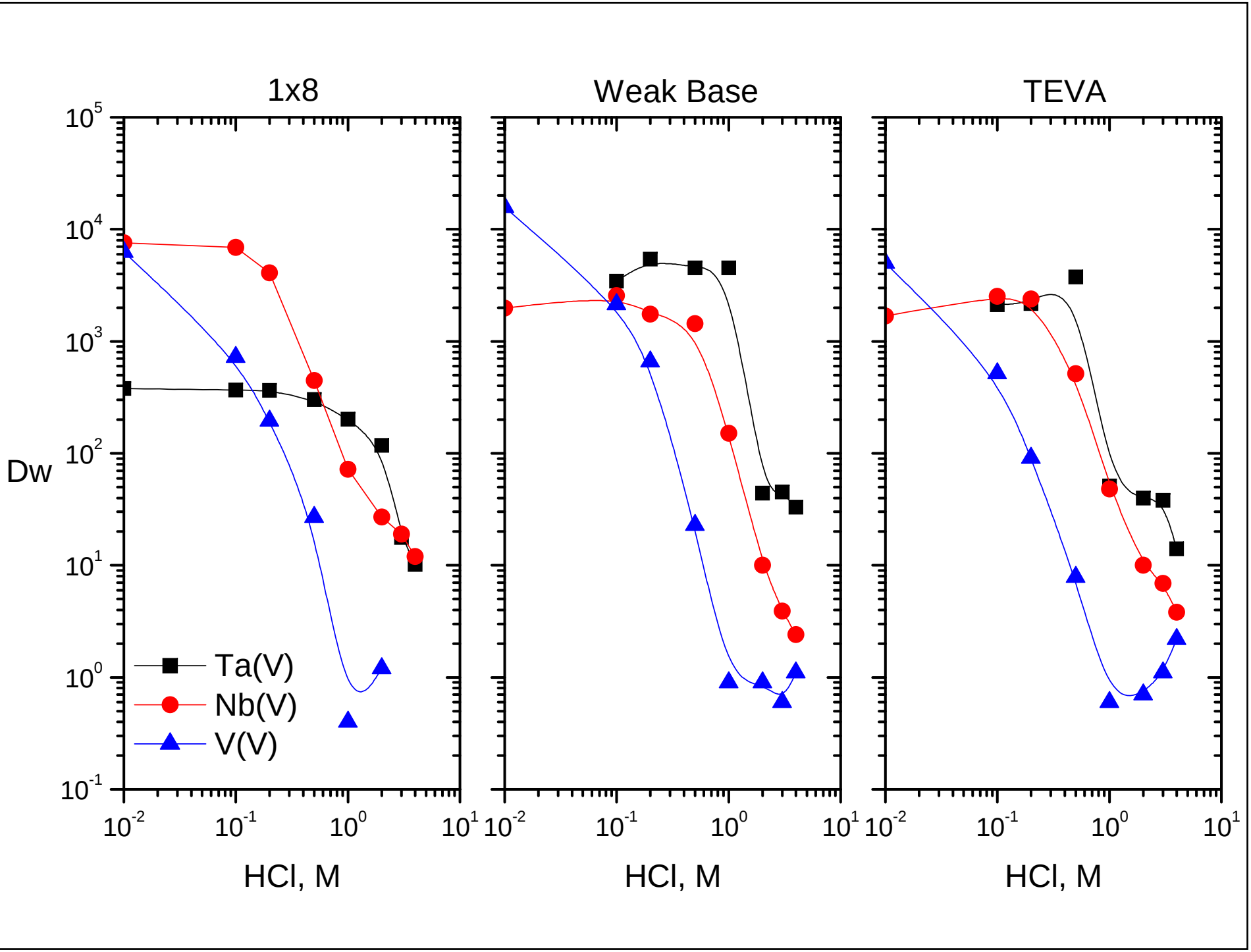

1x8
Weak Base
TEVA
Dw
10^5
10^4
10^3
10^2
10^1
10^0
10^{-1}
Dw Li, Na, K,
Rb, Cs < 1
10^{-2}
10^{-1}
10^0
10^1
HCl, M

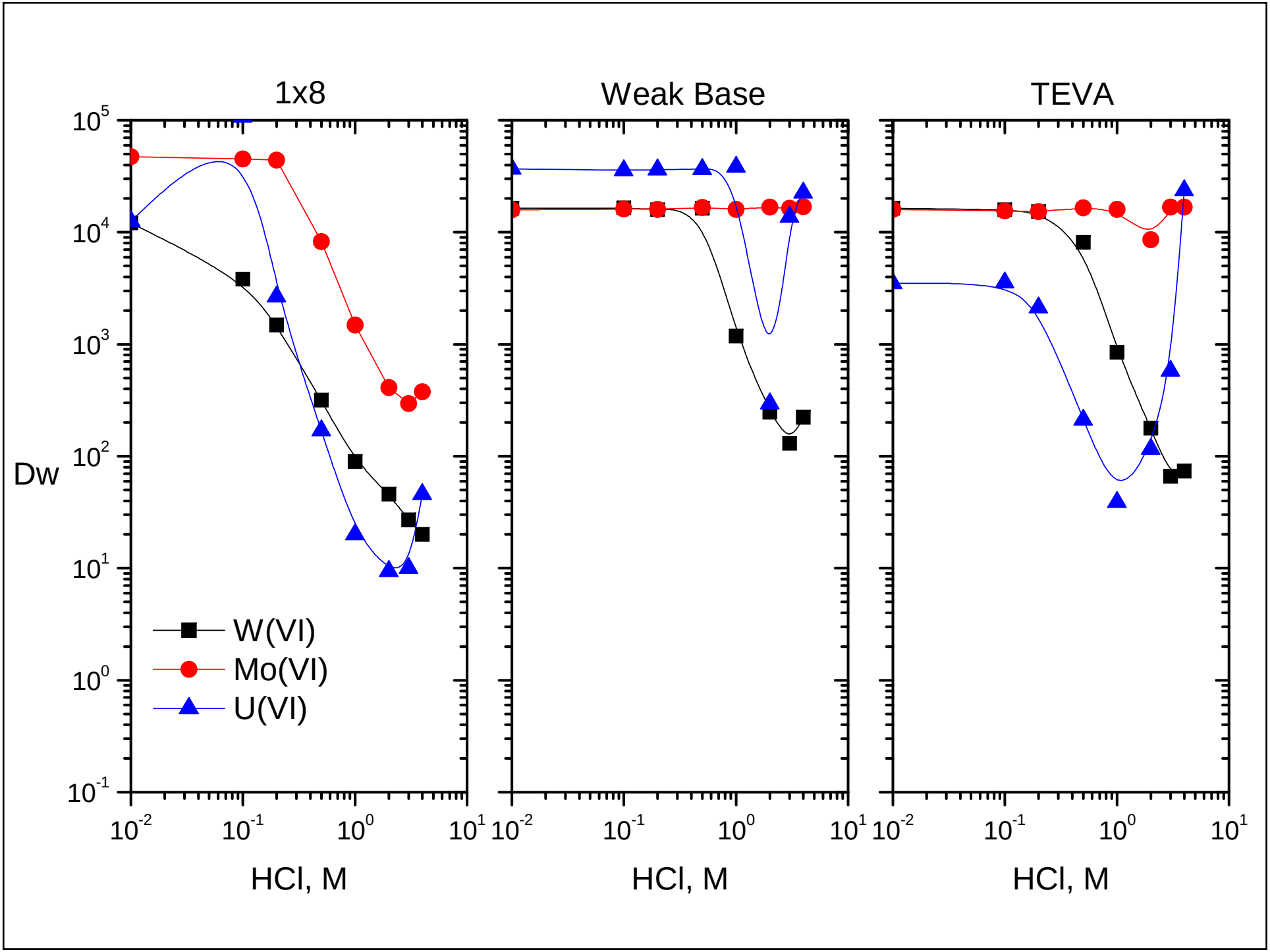

1x8
Weak Base
TEVA
Dw
10^5
10^4
10^3
10^2
10^1
10^0
10^{-1}
10^{-2}
10^{-1}
10^0
10^1
HCl, M
Pd(II)
Pt(II)
Au(I)
Pb(II)
Dw Mg, Ca, Sr,
Ba, Mn(II) <1


1x8
Weak Base
TEVA
Zn(II)
Cu(II)
Be(II)
Cd(II)
Dw
Dw Be, Mg, Ca, Sr, Ba, Mn(II) <1
HCl, M


1x8
Weak Base
TEVA
Dw
HCl, M
HCl, M
HCl, M
Bi(III)
In(III)
Fe(III)
Ga(III)
Al(III)


1x8
Weak Base
TEVA
Dw
HCl, M
HCl, M
HCl, M
Sn(IV)
Ti(IV)
Zr(IV)
Hf(IV)


1x8
Weak Base
TEVA
Dw
HCl, M
HCl, M
HCl, M
Ta(V)
Nb(V)
V(V)


1x8
Weak Base
TEVA
Dw
10^5
10^4
10^3
10^2
10^1
10^0
10^{-1}
10^{-2}
10^{-1}
10^0
10^1
HCl, M
W(VI)
Mo(VI)
U(VI)

k' on Weak Base Resin

	Oxidation		M, HCl (0.05M Oxalic acid)							
Element	**State**	**Group**	**0.01**	**0.10**	**0.20**	**0.50**	**1.0**	**2.0**	**3.0**	**4.0**
Sn	IV	14	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$
W	VI	6	9800	9900	9600	9800	710	150	78	130
Pd	II	10	$>10^4$	$>10^4$	$>10^4$	$>10^4$	9500	5000	2500	1100
Mo	VI	6	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$
Bi	III	15	5000	5000	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$
Pt	II	10	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$
Ta	V	5	N/A	3400	5400	4500	4500	44	45	33
Cd	II	12	N/A	2100	3000	4000	3700	4900	4800	4900
In	III	13	8100	9000	8300	420	41	51	110	250
Nb	V	5	1200	1500	1000	870	91	5.8	2.3	1.4
U	VI	An	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$	180	8200	$>10^4$
Zn	II	12	N/A	50	170	9000	920	$>10^4$	$>10^4$	$>10^4$
Ti	IV	4	9300	2000	1400	380	130	12	1.8	0.8
Fe	III	8	N/A	$>10^4$	$>10^4$	2600	19	200	$>10^4$	$>10^4$
Zr	IV	4	N/A	6900	930	260	66	1.0	0.2	0.4
Hf	IV	4	N/A	1200	600	570	27	1.2	<0.5	<0.5
Ga	III	13	2000	1800	1100	140	4.3	92	970	1200
Pb	II	14	N/A	4.0	4.4	15	22	25	18	10
V	V	5	9486	1300	400	14	0.5	0.5	0.4	0.7
Al	III	13	7983	200	340	3.7	< 0.5	< 0.5	< 0.5	< 0.5
Cu	II	11	263	17	8.0	0.5	0.6	3.2	13	31
Ni	II	10	85	0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Th	IV	An	ppt	ppt	ppt	ppt	ppt	3.2	< 0.5	< 0.5
Re	VII	7	N/A	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Cr	III	6	N/A	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
Au	I	11	2300	2800	2700	2300	1800	970	900	830
k' Co, Mn, Be, Mg, Ca, Sr, Ba, Li, Na, K, Rb, Cs <0.5 for all HCl concentrations										

k' on TEVA Resin

	Oxidation		M, HCl (0.05M Oxalic acid)							
Element	**State**	**Group**	**0.01**	**0.10**	**0.20**	**0.50**	**1.0**	**2.0**	**3.0**	**4.0**
Sn	IV	14	N/A	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$
W	VI	6	9800	9600	9200	4900	510	110	40	45
Pd	II	10	9800	9200	9100	5000	4800	1300	450	180
Mo	VI	6	9600	9300	9200	9900	9600	5100	$>10^4$	$>10^4$
Bi	III	15	5100	4800	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$	400
Pt	II	10	N/A	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$
Ta	V	5	N/A	2100	2200	3800	51	40	38	14
Cd	II	12	N/A	650	1200	2000	2900	4800	4100	4300
In	III	13	8300	250	180	38	16	25	47	78
Nb	V	5	1000	1500	1400	310	29	6.1	4.1	2.3
U	VI	An	2100	2100	1300	130	23	70	350	$>10^4$
Zn	II	12	N/A	48	100	320	450	7700	9300	4600
Ti	IV	4	2300	1400	870	300	90	6.7	1.5	0.4
Fe	III	8	N/A	6500	8800	45	4.3	130	1100	1100
Zr	IV	4	N/A	3800	2300	53	2.2	0.4	0.2	0.1
Hf	IV	4	N/A	6000	670	19	1.4	1.0	<0.5	<0.5
Ga	III	13	4200	3000	180	9.7	0.4	55	1500	3200
Pb	II	14	N/A	0.7	6.0	14	18	19	12	7.3
V	V	5	3000	310	55	4.7	0.4	0.4	0.6	1.3
Al	III	13	2700	110	16	0.7	< 0.5	< 0.5	< 0.5	< 0.5
Cu	II	11	18	2.2	0.7	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
Th	IV	An	ppt	ppt	ppt	ppt	ppt	40	36	<0.5
Re	VII	7	N/A	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$	$>10^3$
Cr	III	6	N/A	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
Au	I	11	1400	3900	4500	4600	4600	3400	2300	2300
k' Co, Mn, Be, Mg, Ca, Sr, Ba, Li, Na, K, Rb, Cs <0.5 for all HCl concentrations										