Eliminating ½ Mass Corrections for REE^{2+} Interferences in Methods 200.8 and 6020

Using Multi-Quad ICP-MS

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For the Better

Rare-Earth Elements – Not So Rare After-all…

- Increasingly used in modern society
- Enter environment via disposal of obsolete devices
  - Electronics are obsolete after only 1-2 years…

Source: https://www.usgs.gov/media/images/earth-mri-common-uses-rare-earth-elements

Element	Crustal Abund. (PPM)
Au	0.004
Ag	0.075
Pb	14
Cu	60

Element	Symbol	Atomic number	Crustal abundance
	Light REEs		PPM
Lanthanum	La	57	39
Cerium	Ce	58	66.5
Praseodymium	Pr	59	9.2
Neodymium	Nd	60	41.5
Samarium	Sm	62	7.05
Europium	Eu	63	2.0
Gadolinium	Gd	64	6.2
	Heavy REEs		PPM
Terbium	Tb	65	1.2
Dysprosium	Dy	66	5.2
Holmium	Ho	67	1.3
Erbium	Er	68	3.5
Thulium	Tm	69	0.52
Ytterbium	Yb	70	3.2
Lutetium	Lu	71	0.8
Yttrium	Y	39	33

Source: https://pubs.usgs.gov/fs/2014/3078/pdf/fs2014-3078.pdf

REEs are less rare than the precious metals of Au and Ag…

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Review of the Analytical Problem

- REE^{2+} species cause false positives for key elements
  - Recent focus on As and Se
    - EPA Region 4 (2015) by Walton and White
    - Smith, et. al., J. Anal. At. Spectrom., 2019, 34, 2094
- *However, As are Se are NOT the only elements affected by M^{2+} interferences*
  - Zn impacted by Ba^{2+}
  - Ge and Kr impacted by REE^{2+}
    - ^{72}Ge common Internal Standard

Element	Isotopes	M2+ Masses of Interest	Elements Affected	Crustal Abund. (PPM)	1st IP* (kJ/mol)	2nd IP* (kJ/mol)
Nd	**142,143,144**,145,**146**,148,150	71, 72, 73, 75, 79	**Ga, Ge, As, Br**	41.5	533	1040
Sm	144, **147, 148, 149**, 150, **152, 154**	72, 74, 75, 76, 77	**Ge, As, Se**	7.05	544	1070
Er	162, 164, **166, 167, 168, 170**	81, 82, 83, 84, 85	**Br, Kr, Se, Sr,**	3.5	589	1150
Dy	156, 158, 160, **161, 162, 163, 164**	78, 79, 80, 81, 82	**Kr, Se, Br**	5.2	573	1130
Gd	152, 154, **155, 156, 157, 158, 160**	76, 77, 78, 79, 80	**Ge, Se, Kr, Br**	6.2	593	1170
Ce	136, 138, **140, 142**	68, 69, 70, 71	**Zn, Ga, Ge**	66.5	534	1050
La	138, **139**	66	**Zn**	39	538	1067
Ba	130, 132, 134, 135, 136, **137, 138**	65, 66, 67, 68, 69	**Cu, Zn, Ga**	340	503	965
Ar	36, 38, 40	18, 19, 20	O, Ne	1.5	1520	2666

** Source: https://en.wikipedia.org/wiki/Molar_ionization_energies_of_the_elements*

Isotopes in **BOLD** text > 10% abundance

Why Haven't We Worried About This Before?

- We did actually
- Optimization criteria for most ICP-MS systems keep particular M^{2+}/M^{+} ratios below a given threshold
  - 1990's: $Ba^{2+}/Ba^{+} \leq 3\%$
    - Some customers with Zn contamination in system/tune solution couldn't meet this specification
  - 2000's: $Ce^{2+}/Ce^{+} \leq 3\%$
    - Presence of ^{70}Ge less likely to affect Ce^{2+}/Ce^{+}
- Premise was that the error due to M^{2+} interferences limited to less than 3%.
- However, these specifications are in Standard or No Gas Mode

NexION® 2000 ICP-MS

Oxide and Doubly-charged Species

Measured under identical operating conditions used to achieve sensitivity and detection-limit specifications.

CeO+/Ce+	< 0.025
Ce++/Ce+	< 0.03

Specification (units)	Element/Ratio	7900 ICP-MS
Sensitivity (Mcps/ppm)	Li (7) Y (89) Tl (205)	55 320 250
Background (cps)	No gas (9 u)	1
Oxide ratio (%)	CeO/Ce CeO/Ce (HMI-25)	1.5 0.5
Doubly-charged ratio (%)	Ce^{2+}/Ce	3

Specification	iCAP Q ICP-MS Series		
STD Mode	iCAP Qa	iCAP Qc	iCAP Qs
Oxides (%)			
CeO/Ce[b]	<2	<2	<2
Double Charged (%)			
Ba^{++}/Ba^{+}[b]	<3	<3	<3

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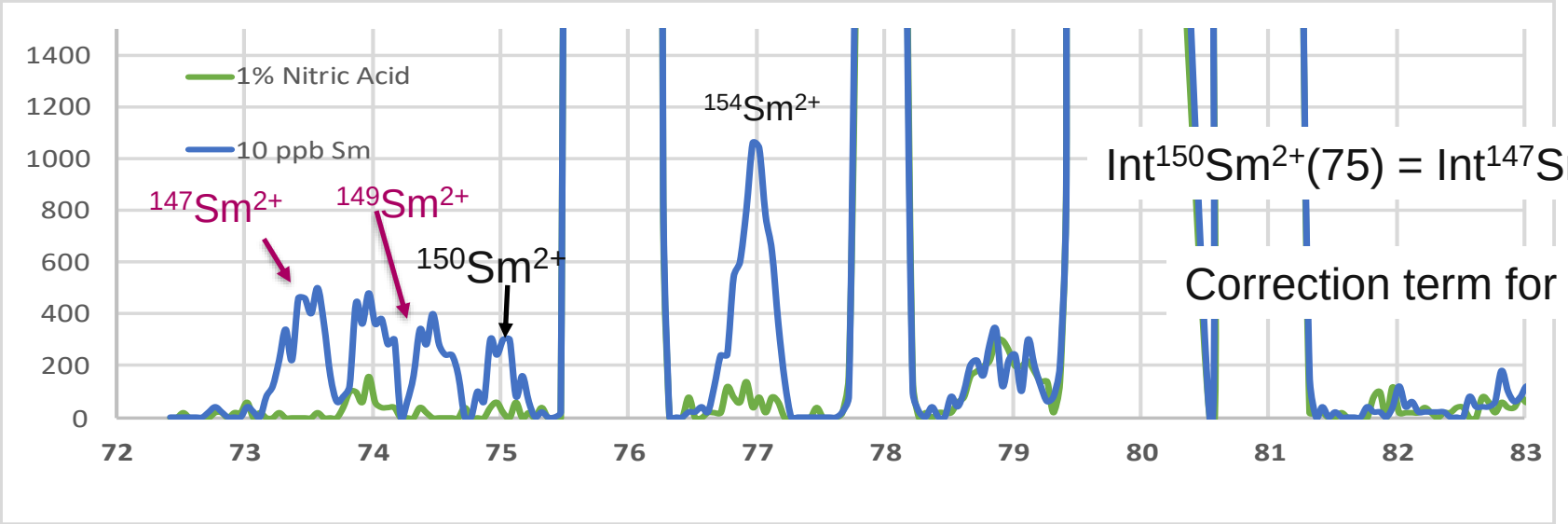
Should Method 200.8 Update Include ½ Mass Corrections for REE^{2+} ?

- Requires increased resolution to ≤0.5 amu so can see ½ mass peaks resolved
- NexIONs allow custom resolution for a specific mass range (e.g. 70-82)
  - Sensitivity at other masses not impacted
- Overlay of 10 ppb Sm with 1% nitric acid
  - Can see Sm^{2+} peaks at 73.5, 74, 74.5, 75

	Analyte	Mass (amu)	Measured Mass (amu)	Mass Calibration DAC Value	Resolution DAC Value	Measured Peak Width (amu)	Custom Resolution
2	Mg	23.985	23.975	4625	2059	0.689761	■
3	Ge72	71.922	71.925	14223	2085	0.435699	☑
4	Ge73	72.923	72.925	14423	2084	0.455552	☑
5	Ge74	73.922	73.925	14623	2084	0.459955	☑
6	As	74.922	74.925	14824	2084	0.454591	☑
7	Se77	76.92	76.925	15226	2084	0.445832	☑
8	Se78	77.917	77.925	15434	2085	0.437878	☑
9	Ar2H	80.933	80.925	16024	2085	0.444775	☑
10	Se82	81.917	81.925	16228	2084	0.504999	☑
11	In	114.904	114.875	22804	2065	0.712246	■



$Int^{150}Sm^{2+}(75) = Int^{147}Sm^{2+}(73.5) * Abund\ ^{150}Sm/^{147}Sm$

Correction term for ^{75}As: - mass 73.5 * 0.4933

Should have verification protocol for mass calibration and equations…

What is the Extent of the Analytical Problem?

- NexION 2000 – Single Quad
  - Standard Mode: Ce^{++}/Ce = 2.14%
  - He Collision Mode: Ce^{++}/Ce = 2.67%
- Single element and REE mix
  - Single source
  - Could be contamination present
- More significant as As/Se < 10 ppb
  - 3% error 10 ppb As or Se signal = 0.3 ppb
  - **3% error 1 ppb As or Se signal = 0.03 ppb**

Standard Mode (0.45 amu)	Apparent As (ppb)	Apparent ^{78}Se (ppb)	Apparent ^{82}Se (ppb)
10 ppb Nd	**0.059**	**0.048**	0.018
10 ppb Sm	**0.038**	**0.057**	**0.047**
10 ppb Gd	---	**0.230**	**0.043**
10 ppb Dy	---	---	**0.60**

He Collision (0.45 amu)	Apparent As (ppb)	Apparent ^{78}Se (ppb)	Apparent ^{82}Se (ppb)
10 ppb Nd	**0.24**	---	---
10 ppb Sm	**0.147**	---	---
10 ppb Gd	---	**2.15**	0.013
10 ppb Dy	---	---	**6.4**

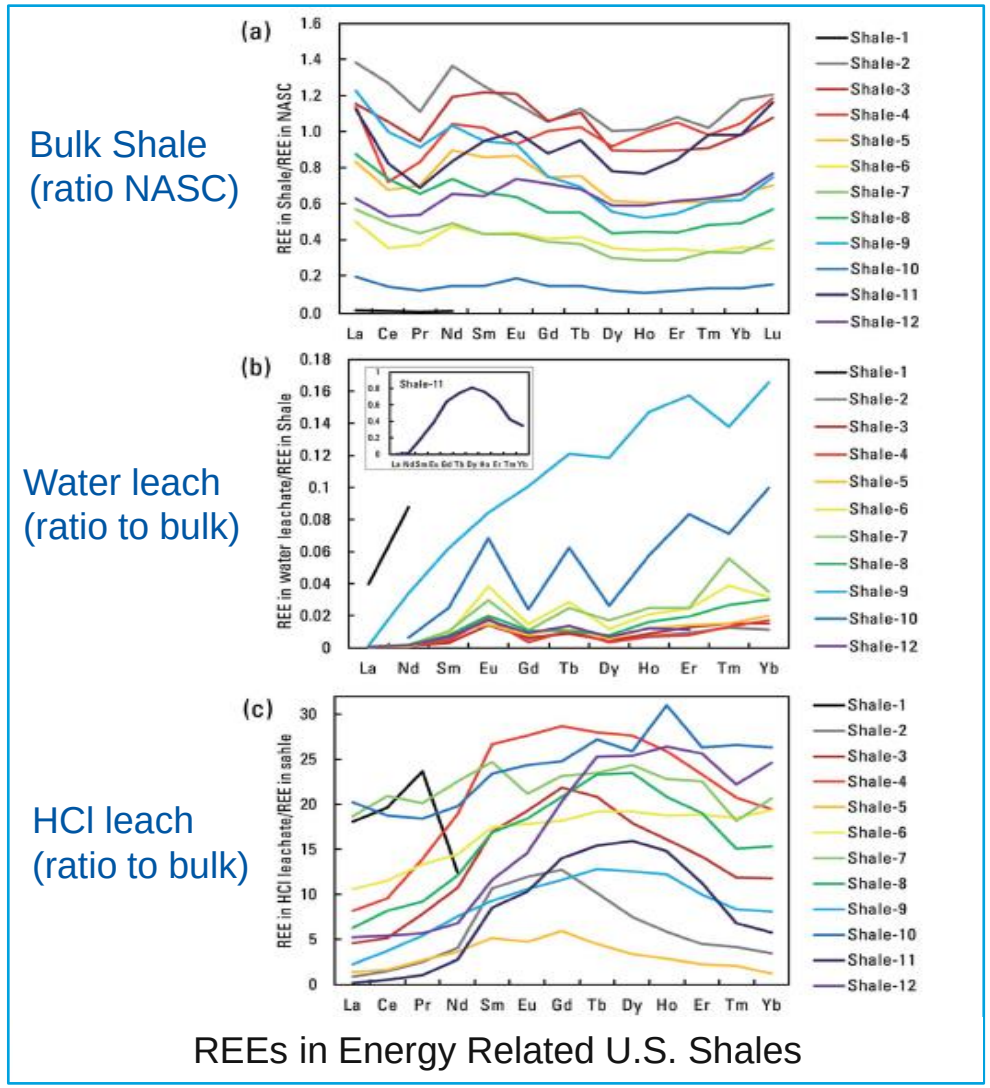
NexION 2000 – Single Quad Data

More significant if As and/or Se << REE concentration…

Understanding the Extent of the Interference

- Recent studies compare apparent concentrations As and Se
  - Smith, et. al, J. Anal. At. Spectrom., 2019, 34, 2094
    - Only used Nd, Sm, Gd
  - Walton and White, EPA Region 4 (2015)
    - Looked at Nd, Sm, Gd, Dy, Eu, Er
    - Used empirical IEC type corrections (as in ICP-OES)

- *In reality, single REE generally not present, nor will all REEs be at same concentration*
  - Concentrations and REEs source dependent
  - Geologic/Environmental
    - Groundwater sources expected to follow REE present in underlying bedrock/geology
      - Dependent upon leaching conditions
  - Industrial waste
    - Source material dependent
    - Sample preparation method dependent



REEs in Energy Related U.S. Shales

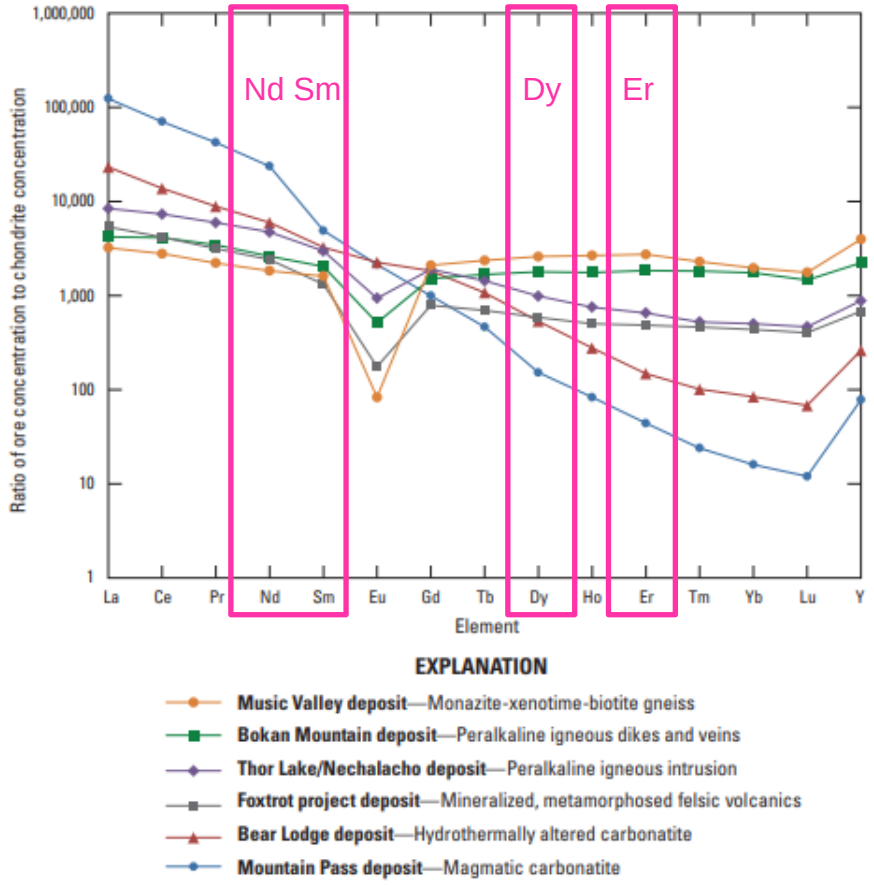
Figure from: Bern, et.al, Environ. Sci.: Processes Impacts, 2021, 23, 1198

Ground and Surface Waters Impacted by Underlying Geology

Figure 04. World map showing locations of active or recently active rare-earth-element (REE) mines and ongoing advanced exploration projects. The exploration projects are at the assessment stage, meaning that they are being evaluated to determine if they are economic to develop. REE resource estimates, which are usually based on extensive drilling programs, have been conducted on all the projects. Tables 03 and 04 contain additional information about the deposits shown on this map. Mountain Pass Mine in California (United States) was placed on care-and-maintenace status in 2015.

Source: https://pubs.usgs.gov/pp/1802/o/pp1802o.pdf

- Ratios of REEs vary with geologic deposits
  - Carbonatites also have very high Ba levels



Caution: If Er present, Standard ^{83}Kr Corrections for Se Inaccurate

- ^{83}Kr normally used to correct for isobaric overlap of Kr on ^{78}Se and ^{82}Se
  - Only isotope of Kr without isobaric overlap

Krypton (Kr) Isotopes	Abundance	Isobaric Overlap
78	0.35	78Se
80	2.25	80Se, 80Ar
82	11.6	82Se
83	11.5	
84	57	85Sr
86	17.3	86Sr

- ^{166}Er a major isotope of Er (33.6%)
- Formation of $^{166}Er^{++}$ (mass 83) will result in overcorrection for Kr
  - Incorrect ^{78}Se and ^{82}Se results

Erbium (Er) Isotopes	Abundance	Er++	Interference For
162	0.014	81	81Br
164	1.61	82	82Se, 82Kr
166	33.6	83	83Kr
167	22.95	83.5	
168	26.8	84	84Kr
170	14.9	85	85Rb

- IUPAC isotope abundances generally best measurement on single/selected sample type(s)
- REE's undergo isotopic fractionation during environmental/geochemical processes
  - 2018 study on Mississippi River showed ^{147}Sm/^{144}Nd ratio varies from 0.11-0.35
  - Impact stoichiometric corrections such as ½ mass corrections

This could be an issue for inexperienced/untrained operators…

Caution: If Er Present, Standard ^{83}Kr Corrections for Se Inaccurate

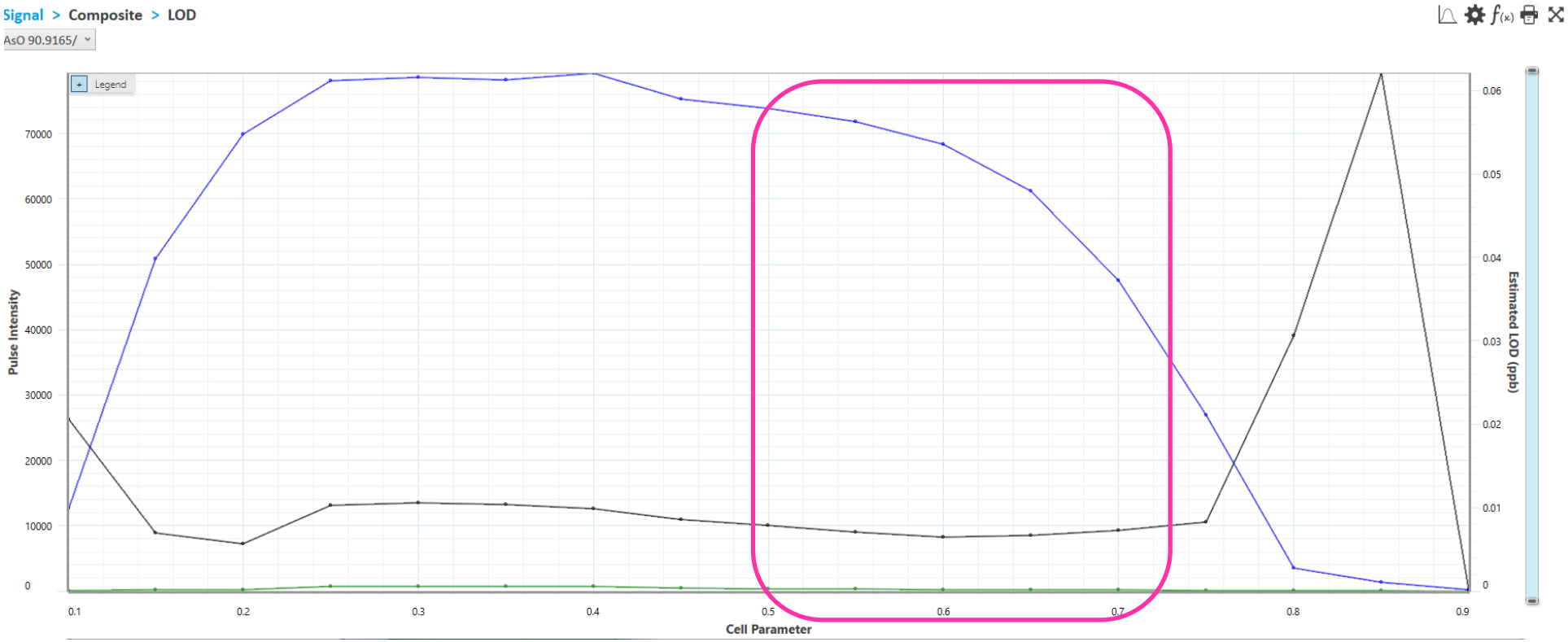
- ^{83}Kr normally used to correct for isobaric overlap of Kr on ^{78}Se and ^{82}Se
  - Only isotope of Kr without isobaric overlap
- ^{166}Er a major isotope of Er (33.6%)
- Formation of $^{166}Er^{++}$ (mass 83) results in overcorrection for Kr at ^{78}Se and ^{82}Se

STD Mode: With Kr isobaric, no REE^{2+}			
Sample Id	**As (75) (ppb)**	**Se (78) (ppb)**	**Se (82) (ppb)**
10 ppb As+Se	9.817	9.640	9.863
10 ppb Er	-0.001	-0.733	-2.297
1 ppb As+Se	0.873	1.042	0.950
1 ppb As+Se 10 ppb REE	0.955	1.301	-0.607
10 ppb As+Se 50 ppb REE	9.259	9.908	2.213

STD Mode: No Kr or REE^{2+} corrections			
Sample Id	**As (75) (ppb)**	**Se (78) (ppb)**	**Se (82) (ppb)**
10 ppb As+Se	9.817	9.640	9.867
10 ppb Er	-0.001	-0.710	0.010
1 ppb As+Se	0.873	1.043	0.919
1 ppb As+Se 10 ppb REE	0.955	1.322	1.405
10 ppb As+Se 50 ppb REE	9.259	10.012	12.452

Other Possible Solutions – Mass Shift As Using Oxygen to Mass 91

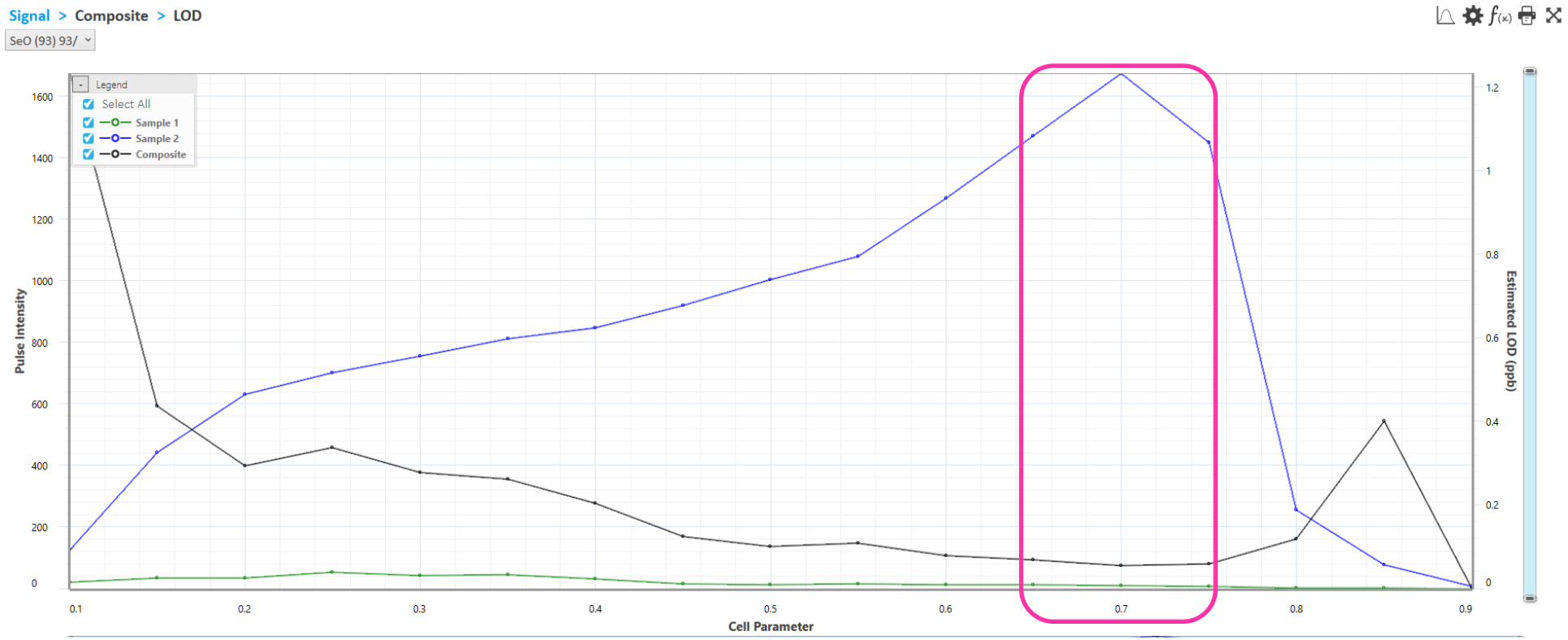
- NexION 2000 (Single Quad)
- AsO (91) RPq Optimization at Cell Gas = 0.9
  - RPq setting on Quadrupole inside Reaction Cell adjusts mass bandpass inside cell controls reactions
    - RPq Range 0.5 to 0.65 (based on LOD)



Can be used to confirm results obtained in Standard and He Collision Modes

Possible Solution – Mass Shift Se Using Oxygen to Mass 93, 94, or 98

- NexION 2000 Single Quad
- $^{77}Se^{16}O$ (93) RPq Optimization at O2 = 0.9
- RPq setting on Quadrupole inside Reaction Cell adjusts mass bandpass inside cell controls reactions
  - RPq Optimum = 0.7



Note: Cell Gas and RPq similar for $^{78}Se^{16}O$ (94) $^{82}Se^{16}O$ (98)

NexION 2000 Mixed Mode Method for Standard, He Collision, and Mass Shift

- AsSe Custom resolution tuning file for 0.5 amu
- Did NOT use internal standards
  - Short run
- Put ½ mass corrections for STD and KED
  - As 75 (Nd, Sm)
  - Se 78 (Gd, Dy)
  - Se 82 (Dy)
  - No ½ mass corrections for Er++ on Se(82)
- Initially left in Kr correction for ^{78}Se and ^{82}Se

Method Parameters

Sweeps/Reading: 20
MassCal File: Default_AsSe custom.tun
Readings/Replicate: 1
Conditions File: default.dac
Replicates: 3

Method Timing

For each reading	33.496s
For each replicate	33.496s
Pressurization delays	+60s
Exhaust delays	+60s
Channel delays	+60s
Settling delays	+0s
Flow switching	+0s

Total estimated sample time: 0hrs 4min 40sec

Notes

Analytes

Int Std	Scan Mode	Analyte	Mass	MCA Channels	IGM	Dwell Time Per AMU	Integration Time	Corrections	Profile	Helium	RPa	RPq	Ammonia	Oxygen
1	Peak Hopping	As	74.9216	1	KED QID	50	1000	-mass72.5*0.6795-mass73.5*0.4933	Helium KED-...	3.7	0	0.25	0	0
2	Peak Hopping	Se (78)	77.9173	1	KED QID	50	1000	- 0.030886*Kr 83 -mass77.5*1.383-mass81.5*0.00241	Helium KED-...	3.7	0	0.25	0	0
3	Peak Hopping	Se (82)	81.9167	1	KED QID	50	1000	- 1.008122 * Kr 83 - mass81.5*1.132	Helium KED-...	3.7	0	0.25	0	0
4	Peak Hopping	Ba (137)	136.905	1	KED QID	50	1000		Helium KED-...	3.7	0	0.25	0	0
5	Peak Hopping	Nd (146)	145.913	1	KED QID	50	1000		Helium KED-...	3.7	0	0.25	0	0
6	Peak Hopping	Sm (147)	146.915	1	KED QID	50	1000		Helium KED-...	3.7	0	0.25	0	0
7	Peak Hopping	Gd (157)	156.934	1	KED QID	50	1000		Helium KED-...	3.7	0	0.25	0	0
8	Peak Hopping	Dy (163)	162.925	1	KED QID	50	1000		Helium KED-...	3.7	0	0.25	0	0
9	Peak Hopping	Er (167)	166.932	1	KED QID	50	1000		Helium KED-...	3.7	0	0.25	0	0
10	Peak Hopping	As (75) STD	74.9216	1	STD/DRC...	50	1000	-mass72.5*0.6795-mass73.5*0.4933	Standard	0	0	0.25	0	0
11	Peak Hopping	Se (78) STD	77.9173	1	STD/DRC...	50	1000	- 0.030886*Kr 83 -mass77.5*1.383-mass81.5*0.00241	Standard	0	0	0.25	0	0
12	Peak Hopping	Se (82) STD	81.9167	1	STD/DRC...	50	1000	- 1.008122 * Kr 83- mass81.5*1.132	Standard	0	0	0.25	0	0
13	Peak Hopping	Ba (137) -1	136.905	1	STD/DRC...	50	1000		Standard	0	0	0.25	0	0
14	Peak Hopping	Nd (146) -1	145.913	1	STD/DRC...	50	1000		Standard	0	0	0.25	0	0
15	Peak Hopping	Sm (147) -1	146.915	1	STD/DRC...	50	1000		Standard	0	0	0.25	0	0
16	Peak Hopping	Gd (157) -1	156.934	1	STD/DRC...	50	1000		Standard	0	0	0.25	0	0
17	Peak Hopping	Dy (163) -1	162.925	1	STD/DRC...	50	1000		Standard	0	0	0.25	0	0
18	Peak Hopping	Er (167) -1	166.932	1	STD/DRC...	50	1000		Standard	0	0	0.25	0	0
19	Peak Hopping	AsO (91)	90.9165	1	STD/DRC...	50	1000		Oxygen DRC	0	0	0.55	0	0.9
20	Peak Hopping	SeO (93)	93	1	STD/DRC...	50	1000		Oxygen DRC	0	0	0.7	0	0.9
21	Peak Hopping	SeO (94)	94	1	STD/DRC...	50	1000		Oxygen DRC	0	0	0.7	0	0.9
22	Peak Hopping	SeO (98)	98	1	STD/DRC...	50	1000		Oxygen DRC	0	0	0.7	0	0.9

Allows Standard, He Collision and O_2 Mass Shift during same acquisition

Comparison Using Proposed REE ½ Mass Corrections: He Collision Mode

- Obvious False positives for Se with REE present at 10 ppb and 50 ppb levels
  - Mixed REE spike with Nd, Sm, Gd, Dy, Er, Ba
- With REE ½ Mass Corrections
  - Over/under correction for As and Se results

He Collision Mode: No Kr or REE^{2+} corrections

Sample Id	As 75 (ppb)	Se 78 (ppb)	Se 82 (ppb)
10 ppb As+Se	9.758	10.026	9.351
10 ppb Nd	0.257	0.045	0.073
10 ppb Sm	0.178	0.015	0.094
10 ppb Gd	-0.004	2.284	0.073
10 ppb Dy	-0.004	0.049	6.203
10 ppb Ba	-0.003	0.023	0.021
10 ppb Er	-0.003	0.041	0.377
1 ppb As+Se	0.851	1.078	1.151
1 ppb As+Se 10 ppb REE	1.192	2.757	6.893
10 ppb As+Se 50 ppb REE	10.581	20.339	36.403

He Collision With REE^{2+} corrections for Nd, Sm, Gd, Dy

Sample Id	As 75 (ppb)	Se 78 (ppb)	Se 82 (ppb)
10 ppb As+Se	9.758	10.011	9.258
10 ppb Nd	-0.193	0.055	0.026
10 ppb Sm	-0.120	0.020	0.094
10 ppb Gd	-0.004	-0.900	0.049
10 ppb Dy	-0.006	0.045	-4.922
10 ppb Ba	-0.004	0.033	-0.038
10 ppb Er	-0.005	0.036	0.376
1 ppb As+Se	0.850	1.061	1.137
1 ppb As+Se 10 ppb REE	0.570	-0.009	-2.695
10 ppb As+Se 50 ppb REE	7.467	6.726	-10.335

Note: Data above shown WITHOUT Kr equations – no Er^{2+} correction (didn't collect data at 83.5 amu)

Other Options: ½ Mass REE Corrections vs. O2 Mass Shift (Single Quad)

- REE ½ Mass Corrections
  - Over correction for As and Se results when tested with mixed REE spikes
    - Nd, Sm, Gd, Dy, Er, Ba
- Using O2 Mass shift results in more accurate results for all isotopes of As and Se
  - However, some caution is warranted as real samples contain have many more elements present

He Collision With REE^{2+} corrections for Nd, Sm, Gd, Dy

Sample Id	As 75 (ppb)	Se 78 (ppb)	Se 82 (ppb)
10 ppb As+Se	9.758	10.011	9.258
10 ppb Nd	-0.193	0.055	0.026
10 ppb Sm	-0.120	0.020	0.094
10 ppb Gd	-0.004	-0.900	0.049
10 ppb Dy	-0.006	0.045	-4.922
10 ppb Ba	-0.004	0.033	-0.038
10 ppb Er	-0.005	0.036	0.376
1 ppb As+Se	0.850	1.061	1.137
1 ppb As+Se 10 ppb REE	0.570	-0.009	-2.695
10 ppb As+Se 50 ppb REE	7.467	6.726	-10.335

NexION 2000 (SQ) Using O2 Mass Shift

Sample Id	AsO 91 (ppb)	SeO 93 (ppb)	SeO 94 (ppb)	SeO 98 (ppb)
10 ppb As+Se	9.841	9.804	9.965	9.940
10 ppb Nd	0.005	0.022	0.047	0.139
10 ppb Sm	0.001	0.008	0.019	0.024
10 ppb Gd	-0.001	0.011	-0.005	-0.046
10 ppb Dy	-0.001	0.005	-0.001	0.042
10 ppb Ba	-0.002	0.000	-0.008	0.009
10 ppb Er	-0.002	-0.003	-0.003	0.040
1 ppb As+Se	0.869	0.900	0.938	0.908
1ppb As+Se 10ppb REE	0.874	0.906	1.030	0.890
10ppb As+Se 50ppb REE	8.964	10.122	10.139	9.362

Note: Data above shown WITHOUT Kr equations – Used single conditions for As/Se mass shift

USGS Reference Sample Comparison – Arsenic Recovery

- Some USGS Reference Water Samples have REE data - MPV determined by round robin study
  - At higher As concentrations the effect of REEs on recoveries is negligible
  - At lower concentrations the ½ mass REE corrections (for Nd and Sm) affect results – possible overcorrection
- Most results are similar
  - NOTE: Single point calibration at 1 ppb for As and Se
  - Perhaps more accurate results when O_2 Mass Shift is used to move As to AsO at mass 91

Arsenic (ppb)	MPV (error F-σ)	STD Mode No 1/2 Mass	STD Mode with 1/2 Mass	He Collision No 1/2 Mass	He Collision With 1/2 Mass	Mass Shift AsO (91)
T-221	17.1 (1.04)	15.4	15.4	15.5	**15.4**	**15.7**
T-227	0.315 (0.04)	0.261	**0.255**	0.244	**0.218**	**0.265**
T-231	3.16 (0.393)	2.56	2.56	2.45	**2.44**	**2.49**

Elements (ppb)	Ba	Ce	Nd	Sm	Dy	Gd	Dy	Er	Mo	Zr*	Nb*
T-221	29	0.837	0.581	0.101	0.053	0.091	0.053	0.028	0.522	**0.024**	**0.024**
T-227	27.4	0.686	0.52	0.114	0.085	0.117	0.085	0.041	0.25	**0.011**	**0.010**
T-231	0.408	0.408	0.305	0.048	0.021	0.039	0.021	0.01	0.74	**0.014**	**0.007**

**Note: Zr and Nb determined using SurveyScan data*

Note: USGS SRS Samples are natural waters – More information at: https://bqs.usgs.gov/srs/FactSheet.htm

USGS Reference Sample Comparison – Selenium Recovery

- At lower Se concentrations the ½ mass REE (for Dy and Gd only) corrections more significant
- Could argue O_2 Mass Shift results for $^{77}Se^{16}O$ at mass 93 closer to MPV value
  - NOTE: Single point calibration at 1 ppb for As and Se

Selenium (78) ppb	MPV (error F-σ)	STD Mode No 1/2 Mass	STD Mode with 1/2 Mass	He Collision No 1/2 Mass	He Collision With 1/2 Mass	Mass Shift SeO (94)	Mass Shift SeO (93)
T-221	3.80 (0.297)	2.128	2.125	3.377	3.259	**4.578**	**3.941**
T-227	**0.172 (0.122)**	**-1.274**	**-1.281**	**0.139**	**0.087**	**0.580**	**0.163**
T-231	**1.11 (1.01)**	**-1.310**	**-1.314**	0.316	0.310	**1.896**	**0.473**

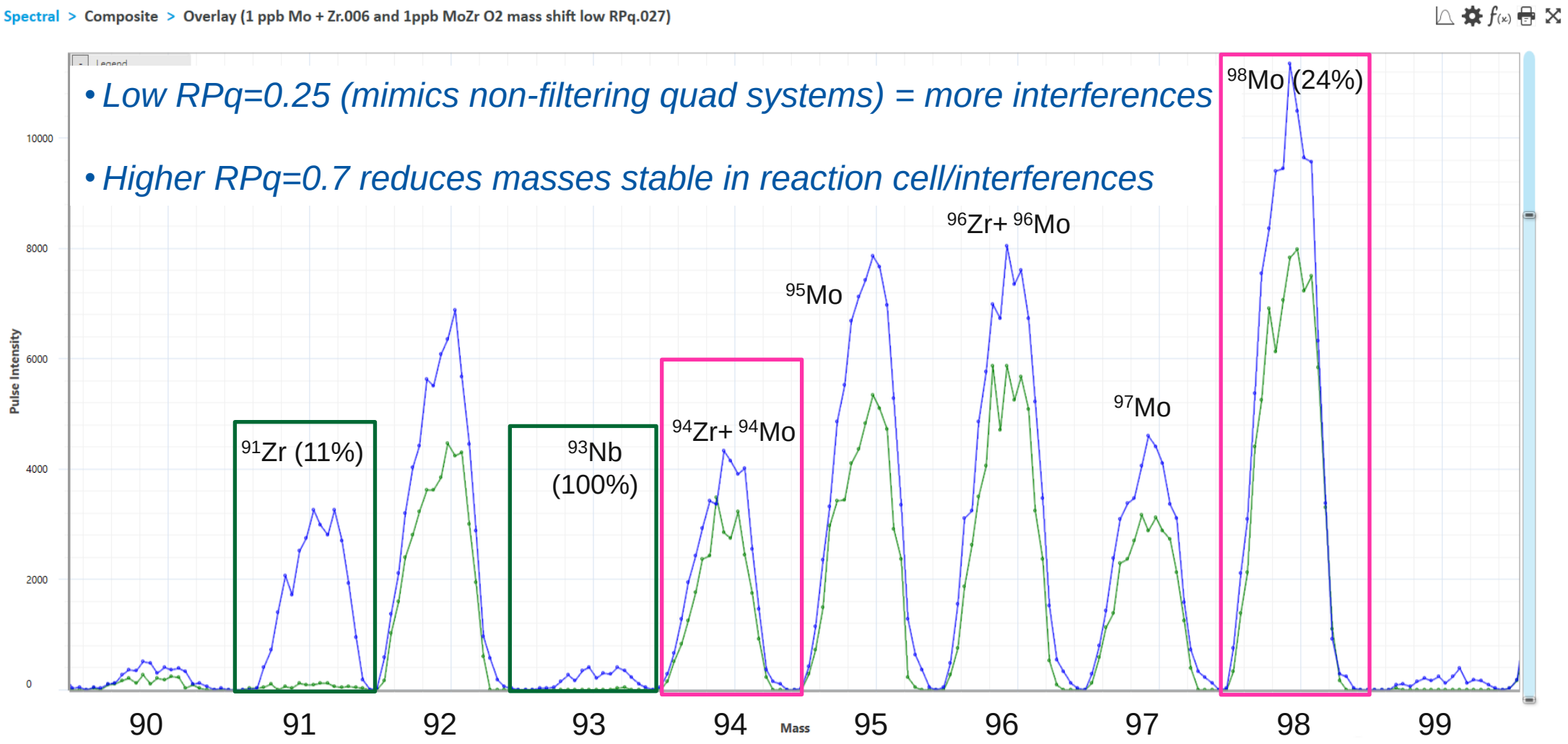
Selenium (82) ppb	MPV (error F-σ)	STD Mode No 1/2 Mass	STD Mode with 1/2 Mass	He Collision No 1/2 Mass	He Collision With 1/2 Mass	Mass Shift SeO (98)	Mass Shift SeO (93)
T-221	3.80 (0.297)	3.307	3.294	3.264	3.047	**10.742**	**3.941**
T-227	**0.172 (0.122)**	0.097	0.080	**0.251**	**0.121**	**3.479**	**0.163**
T-231	**1.11 (1.01)**	0.547	0.540	0.408	0.337	**10.075**	**0.473**

Elements (ppb)	Ba	Ce	Nd	Sm	Dy	Gd	Dy	Er	Mo	Zr*	Nb*
T-221	29	0.837	0.581	0.101	0.053	0.091	0.053	0.028	0.522	**0.024**	**0.024**
T-227	27.4	0.686	0.52	0.114	0.085	0.117	0.085	0.041	0.25	**0.011**	**0.010**
T-231	0.408	0.408	0.305	0.048	0.021	0.039	0.021	0.01	0.74	**0.014**	**0.007**

**Note: Zr and Nb determined using SurveyScan data*

Note: Results at 94 and 98 affected by Mo and Zr (94) present, no Kr or Er corrections

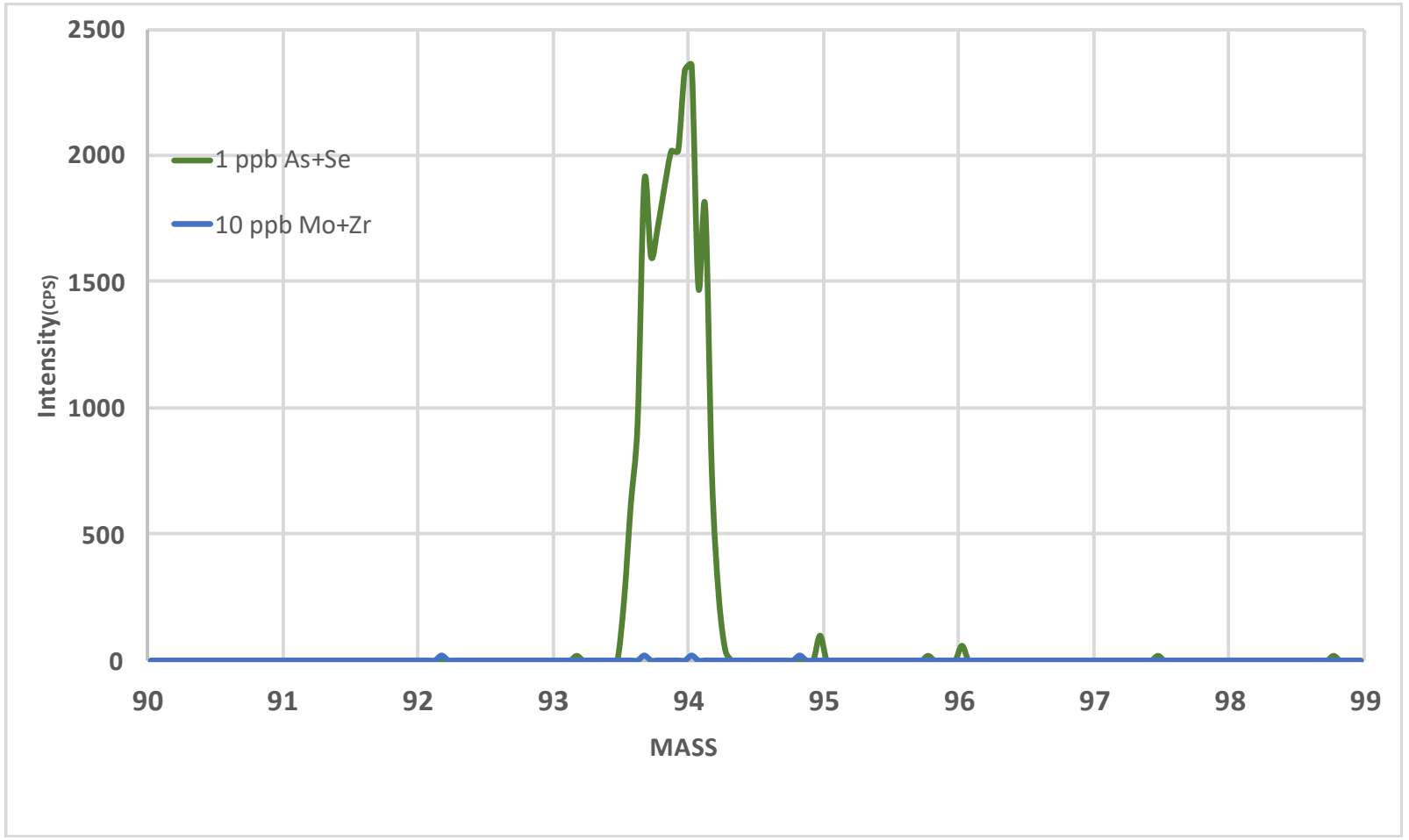
Advantage of Tunable RPq in Reaction Cell Quadrupole: O_2 Mass Shift for Se



1 ppb Mo and Zr - O_2 Mass shift with RPq=0.7 (Green) and RPq=0.25 (Blue)

NexION 5000: The Case for Multi-quadrupole ICP-MS for O_2 Mass Shifts

- Q1 = 78
- Q3=90-100
- Oxygen Mass Shift: O_2=1.2, RPq=0.80
- 1 ppb As+Se (Green)
- 10 ppb Mo+Zr (Blue)
- No signal at mass 94 except from $^{78}Se^{16}O$
  - Q1 setting of 78 excludes all Mo and Zr isotopes from entering cell



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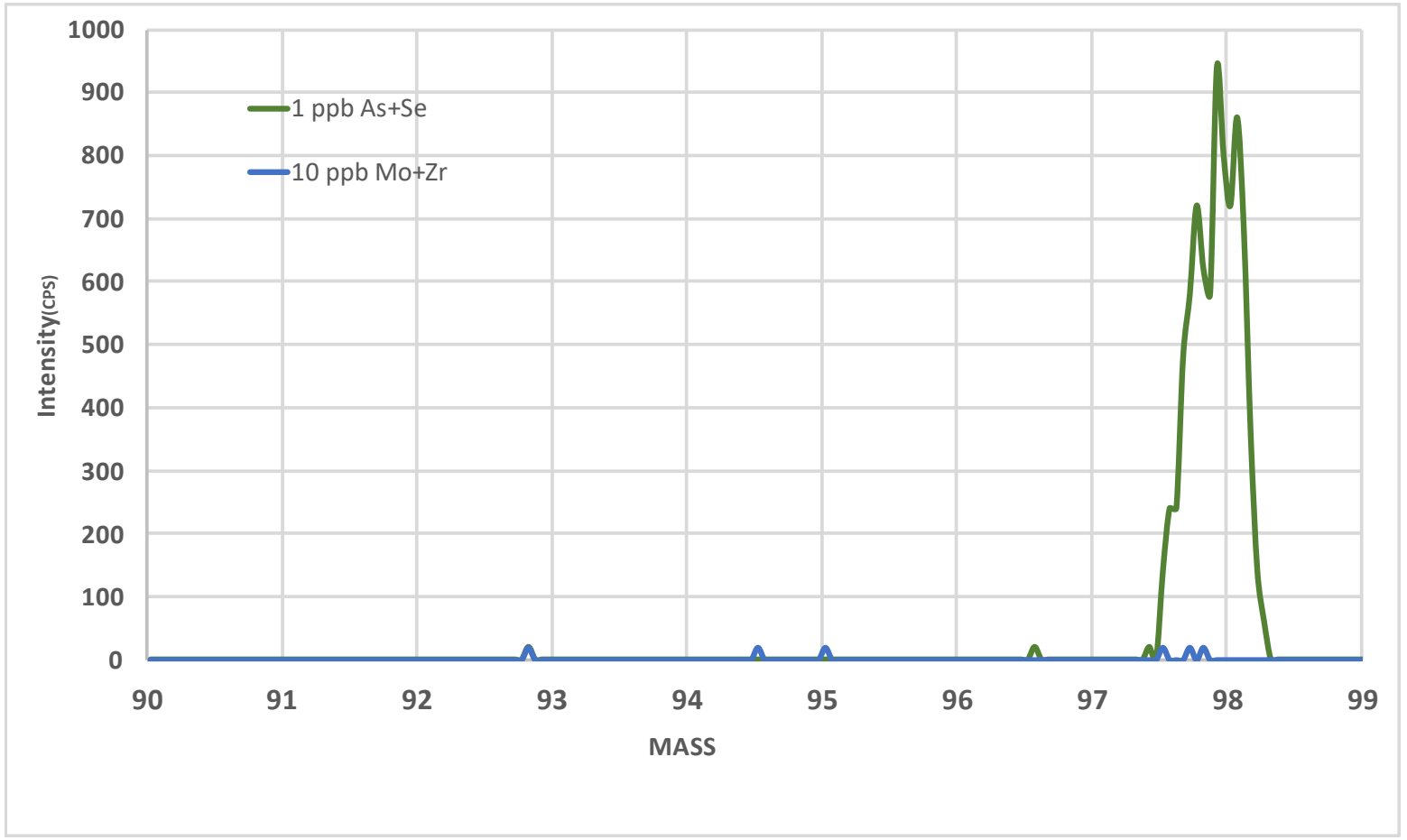
NexION 5000: The Case for Multi-quadrupole ICP-MS for O_2 Mass Shifts

- Q1 = 82
- Q3=90-100
- Oxygen Mass Shift:
  - O_2=1.2, RPq=0.80
- 1 ppb As+Se (Green)
- 10 ppb Mo+Zr (Blue)
- No signal at mass 94 except from $^{82}Se^{16}O$
  - Q1 setting of 82 excludes all Mo and Zr isotopes from entering cell



Note: relative intensity of SeO mass shift peaks match Se78 and Se82 abundance

NexION 5000 Multi-Quad: Arsenic Results

- 1 point calibration at 1 ppb, no Int. Std.
- Used REE ½ Mass Corrections for Standard (No Gas) and He Collision Modes
  - Potential over/under correction using ½ mass equations
- Reasonable results using O_2 mass shift to mass 91
  - No signal from Zr at Mass 91

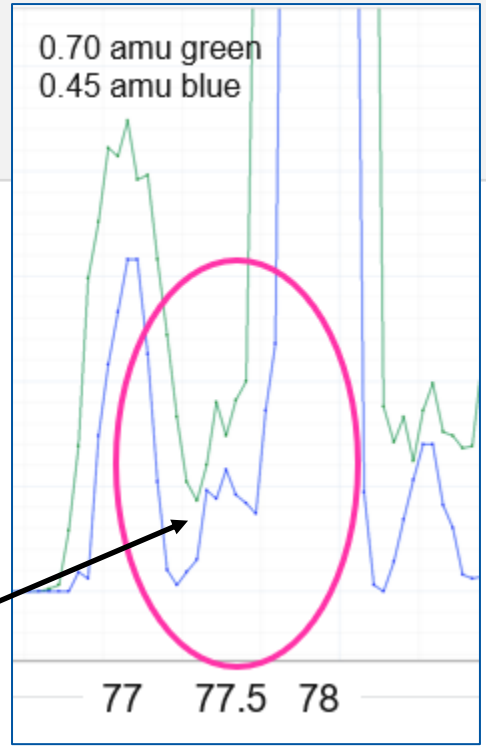
Sample Id	As Standard Mode 75/75 (ppb)	As He Collison Mode 75/75 (ppb)	Mass Shift AsO 75/91 (ppb)
1 ppb Nd	0.0021	0.0219	0.0022
1 ppb Sm	-0.0007	-0.0008	0.0001
1 ppb Gd	0.0005	0.0045	-0.0005
1 ppb Dy	0.0000	-0.0034	-0.0003
1 ppb Er	-0.0001	0.0034	-0.0004
1 ppb Ba	0.0000	0.0011	-0.0005
1 ppb Mixed REE	-0.0029	-0.0140	-0.0003
1 ppb As+Se	**0.9875**	**1.0390**	**0.9943**
1 ppb As+Se 1ppb REE mix	**0.9449**	**0.8767**	**0.9544**
1 ppb As+Se 10ppb REE mix	**0.9804**	**0.7935**	**0.9997**
1 ppb Mo+Zr	**0.0025**	**0.0011**	**0.0036**

Arsenic (ppb)	MPV (error as F-σ)	STD Mode with 1/2 Mass 75/75	He Collision With 1/2 Mass 75/75	Mass Shift AsO 75/91
T-221	17.1 (1.04)	17.0180	18.1077	17.2604
T-227	0.315 (0.04)	0.3051	0.3174	0.2879
T-231	3.16 (0.393)	2.8512	2.7617	2.5824

Note: USGS SRS Samples are natural waters with many other elements present

NexION 5000 Multi-Quad: Selenium Results

- 1 point calibration at 1 ppb (no Internal Standards)
- Mixed REE spike containing Nd, Sm, Gd, Dy, Er and Ba at equal concentrations
- Used REE ½ Mass Corrections for Standard (No Gas) and He KED (Collision) Modes
  - Only Dy correction on ^{82}Se
  - Potential over/under correction using ½ mass equations



Sample Id	Standard Mode Se 77/77 (ppb)	He Collison Se 77/77 (ppb)	Mass Shift SeO 77/93 (ppb)	Standard Mode Se 78/78 (ppb)	He Collison Se 78/78 (ppb)	Mass Shift SeO 78/94 (ppb)	Standard Mode Se 82/82 (ppb)	He Collison Se 82/82 (ppb)	Mass Shift SeO 82/98 (ppb)
1% nitric Blank	-0.082	-0.046	0.000	-1.107	0.015	-0.001	-0.033	0.078	-0.001
1 ppb As+Se	0.954	**0.683**	**1.054**	0.012	**0.893**	**1.015**	0.930	**1.306**	**1.040**
1 ppb As+Se 1ppb REE mix	0.846	**1.450**	**0.996**	-0.008	**0.961**	**0.968**	0.849	**1.002**	**1.008**
1 ppb As+Se 10ppb REE mix	0.914	**1.515**	**1.050**	0.127	**0.239**	**1.046**	0.521	**-10.250**	**1.024**
1 ppb Mo+Zr	-0.056	-0.085	**0.005**	-1.101	**0.032**	**0.006**	-0.025	**0.334**	**0.006**

?

$^{36}Ar_2$ peak too large in Standard Mode to separate mass 77.5 at 0.5 amu resolution

Note: Oxygen mass shift mode gives consistent accurate results for even when Zr and Mo present

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NexION 5000 Multi-Quad: Selenium Results (con't)

- USGS Reference Samples
  - Round Robin – do NOT know instrument type/mode
  - Note large errors (100% RSD) in reported MPV values for Se < 3 ppb
- Standard and He Collision mode using ½ mass corrections for Nd, Sm, Dy, Gd (not Er)

Sample Id	MPV (error F-σ)	Standard Mode Se 77/77 (ppb)	He Collison Se 77/77 (ppb)	Mass Shift SeO 77/93 (ppb)	He Collison Se 78/78 (ppb)	Mass Shift SeO 78/94 (ppb)	Standard Mode Se 82/82 (ppb)	He Collison Se 82/82 (ppb)	Mass Shift SeO 82/98 (ppb)
T-221	3.80 (0.297)	3.52	4.78	3.38	3.06	3.35	3.40	6.43	3.36
T-227	0.172 (0.122)	0.037	0.056	0.098	0.293	0.104	0.102	0.170	0.095
T-231	1.11 (1.01)	1.28	0.44	0.41	0.43	0.43	0.82	1.68	0.42
1ppb Mo+Zr		-0.057	-0.167	0.005	0.032	0.006	-0.025	0.335	0.006

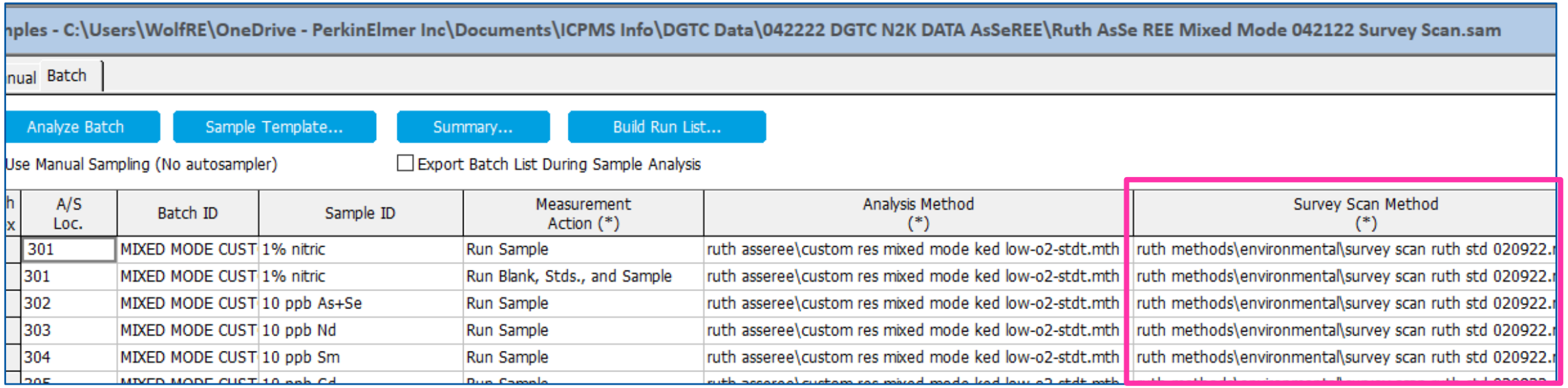
- He Collision mode with ½ Mass Corrections has some apparent over/under correction
- Oxygen Mass Shifted Results are Consistent for all 3 Se isotopes
  - No contribution to SeO signals at mass 94 and 98 from $^{94}Zr/^{94}Mo$ or ^{98}Mo isobaric overlaps
    - Setting Q1 to Se mass you are shifting eliminates Zr and Mo from entering the reaction cell

So how do we know which values to report???

New Tool: What If You Could See ~ Concentrations of EVERY Element?

- Survey Scan feature can be enabled for all samples
  - FAST semi-quantitative analysis during quantitative data acquisition
  - New Feature for NexION ICPMS Syngistix software

- Gives approximate concentration of all elements
  - Help pinpoint potential interferences in samples, data review, reporting correct result
    - Can also be used to comment or “flag” results if interfering element present



h x	A/S Loc.	Batch ID	Sample ID	Measurement Action (*)	Analysis Method (*)	Survey Scan Method (*)
	301	MIXED MODE CUST	1% nitric	Run Sample	ruth asseree\custom res mixed mode ked low-o2-stdt.mth	ruth methods\environmental\survey scan ruth std 020922.r
	301	MIXED MODE CUST	1% nitric	Run Blank, Stds., and Sample	ruth asseree\custom res mixed mode ked low-o2-stdt.mth	ruth methods\environmental\survey scan ruth std 020922.r
	302	MIXED MODE CUST	10 ppb As+Se	Run Sample	ruth asseree\custom res mixed mode ked low-o2-stdt.mth	ruth methods\environmental\survey scan ruth std 020922.r
	303	MIXED MODE CUST	10 ppb Nd	Run Sample	ruth asseree\custom res mixed mode ked low-o2-stdt.mth	ruth methods\environmental\survey scan ruth std 020922.r
	304	MIXED MODE CUST	10 ppb Sm	Run Sample	ruth asseree\custom res mixed mode ked low-o2-stdt.mth	ruth methods\environmental\survey scan ruth std 020922.r

Reporter Tab: Shows Quant and Survey Scan Data at Same Time

- Concentrations Tab shows Quantitative results
- Can customize how sorted: as in Method, By Analyte, By Mass, By Mode

Report View

Current Sample | Raw Intensities | Net Intensities | Concentrations | Unfactored Concentrations | Internal Standards | QC | TotalQuant Intensities | TotalQuant Concentrations

☐ Show RSDs ☑ Show Calibration Rows

	Sample Id	R	QC Status	As 75 Helium K... (ppb)	As (75) S... (ppb)	Se (78) 78 Helium K... (ppb)	Se (78) S... (ppb)	Se (82) 82 Helium K... (ppb)	Se (82) S... (ppb)	AsO (91) 91 Oxygen D... (ppb)	SeO (93) 93 Oxygen D... (ppb)	SeO (94) 94 Oxygen D... (ppb)	SeO (98) 98 Oxygen D... (ppb)
1	1% Nitric	R											
2	10 ppb As+Se	R		10.000	10.000	10.000	10.000	10.000	10.000	10.000	10.000	10.000	10.000
3	Calibration Curves	R											
4	1% nitric	R		0.006	0.006	0.230	0.511	0.119	0.051	0.005	0.009	0.013	0.010
5	10 ppb As+Se	R		10.259	10.331	10.511	10.431	10.254	10.660	10.240	9.720	10.175	9.855
6	10 ppb Nd	R		-0.276	-0.072	0.156	0.599	0.105	0.045	0.004	0.028	0.042	0.201
7	10 ppb Sm	R		-0.153	-0.058	0.216	0.747	0.130	0.033	0.001	0.012	0.022	0.088
8	10 ppb Gd	R		0.004	-0.001	-1.045	0.492	-0.060	0.026	-0.001	-0.003	-2.944E-10	-0.069
9	10 ppb Dy	R		-0.001	-0.001	0.189	0.698	-5.480	-0.544	-0.002	0.003	0.001	0.010
10	10 ppb Ba	R		-0.002	-1.264E-4	0.194	0.842	-0.023	0.012	-0.002	-0.012	-0.001	-0.034
11	10 ppb Er	R		-0.002	-4.658E-4	0.298	1.026	0.345	0.079	-0.002	-0.012	0.001	0.081

TotalQuant Concentrations tab

- Shows semi-quant results in selected units for all elements in periodic table

Report View

Current Sample | Raw Intensities | Net Intensities | Concentrations | Unfactored Concentrations | Internal Standards | QC | TotalQuant Intensities | TotalQuant Concentrations

Hide columns without measured data

Sample ID	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se
1% nitric _survey	26.679	0.003	0.009	0.006	0.040	0.001	0.005	0.026	0.174
1% Nitric_survey	28.069	0.003	1.072	0.006	0.046	0.001	0.009	0.013	0.087
10 ppb As+Se_survey	27.934	0.003	1.041	0.004	0.041	0.002	0.000	13.715	11.641
1% nitric _survey	27.516	0.004	1.092	0.006	0.048	0.001	0.001	0.010	0.157
10 ppb As+Se_survey	27.232	0.004	0.005	0.008	0.048	0.001	0.010	14.486	12.356
10 ppb Nd_survey	26.342	0.003	0.003	0.007	0.041	0.001	0.008	0.103	0.139
10 ppb Sm_survey	28.731	0.002	0.003	0.005	0.451	0.000	0.058	0.069	0.157
10 ppb Gd_survey	26.463	0.004	0.006	0.004	0.032	0.001	0.010	0.003	0.192
10 ppb Dy_survey	28.231	0.003	1.052	0.001	0.068	0.000	0.000	0.000	1.411

More info at: https://resources.perkinelmer.com/lab-solutions/resources/docs/tch-totalquant-analysis-in-nexion-icp-mass-spectrometers.pdf

TotalQuant Concentrations tab

- Indicates concentrations of REEs in my spikes and reference QC samples
  - Helps indicate potential interferences
  - Supports selection of isotope/mode to report
- 10 ppb check shows fairly good accuracy (±15%)

Report View

Current Sample | Raw Intensities | Net Intensities | Concentrations | Unfactored Concentrations | Internal Standards | QC | TotalQuant Intensities | TotalQuant Concentrations

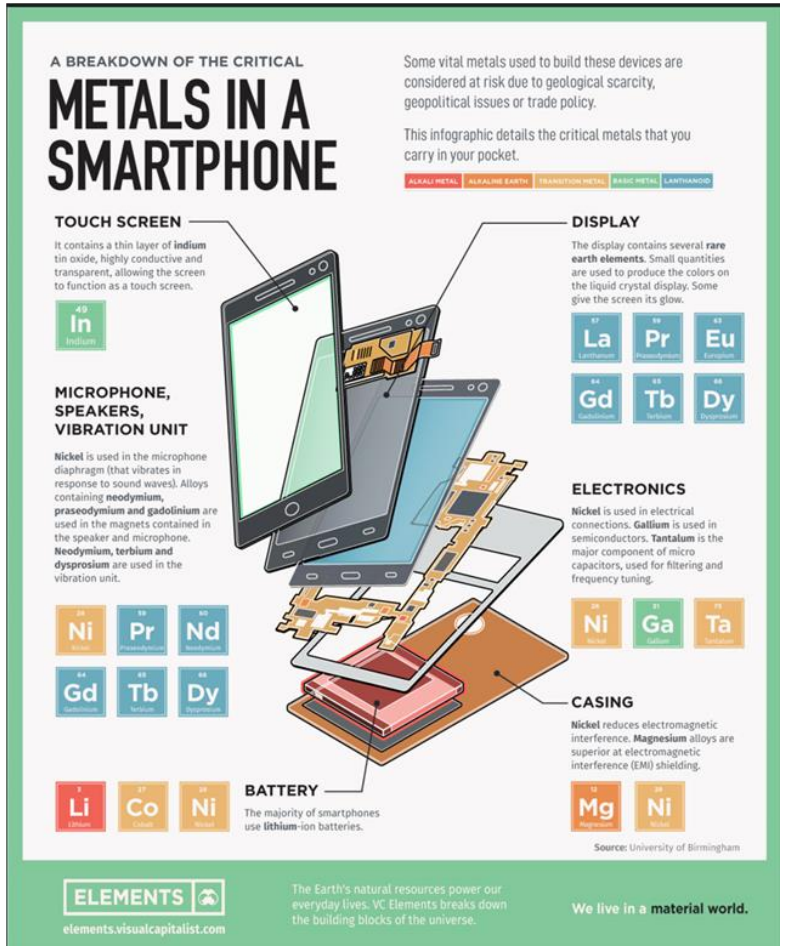
☑ Hide columns without measured data

Sample ID	Cs	Ba	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er
10 ppb As+Se 50 ppb REE_survey	0.001	44.193	0.001	0.000	0.001	44.710	44.271	0.002	41.403	34.316	43.383	0.012	42.498
T-221_survey	0.016	25.332	0.493	0.752	0.130	0.479	0.081	0.014	0.077	6.380	0.044	0.009	0.019
T-227_survey	0.027	24.928	0.412	0.603	0.104	0.467	0.080	0.024	0.100	8.384	0.073	0.012	0.031
T-231_survey	0.024	79.848	0.236	0.336	0.064	0.238	0.040	0.010	0.029	2.378	0.016	0.003	0.006
blank_survey	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.059	0.000	0.000	0.000
1 ppb As+Se_survey	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.059	0.000	0.000	0.000
1 ppb As+Se 10 ppb REE_survey	0.001	8.724	0.000	0.000	0.000	8.998	8.653	0.000	8.454	8.028	8.091	0.003	7.984
10 ppb As+Se 50 ppb REE_survey	0.001	52.174	0.001	0.000	0.001	47.091	47.063	0.003	43.839	38.004	44.779	0.005	43.756
10 ppb TQ check_survey	8.795	8.811	8.528	8.841	8.539	8.656	8.271	9.103	8.679	9.039	8.728	8.638	8.625

Can change order of elements to focus on key items during analysis and export all data …

Conclusions

- No one-size fits all solution to REE^{2+} interferences
- Options required to ensure good quality data
  - Different gas modes (Standard, He Collision, Reaction Gases)
  - Ability to use ½ Mass corrections when appropriate
    - Must include how validated and tested
    - Consider ALL REEs present and potential for isotopic fractionation
    - Flexibility for non-traditional internal standards
  - Use Mass Shift if/when appropriate
    - Multi-Quad systems superior for elimination of interferences
  - SurveyScan tool to identify other potential interferences
    - Data can support selection of alternate conditions or isotopes reported
- Methods 200.8/6020 need to be performance based
- Operator training/skill/experience critical
  - Blind use of ½ mass corrections could cause new problems



Source: https://www.visualcapitalist.com/visualizing-the-critical-metals-in-a-smartphone/

Thank You and Questions