Image 1

Rare Earth Element Interferences in Collision Cell and Standard Mode ICP-MS Analyses of Arsenic and Selenium

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Overview:

1. Dispel the idea that Rare Earth Elements are rare

2. Look at the extent of the Rare Earth Element interference in collision cell and standard mode ICP-MS on As and Se

3. Show ways to effectively recognize and handle this interference challenge

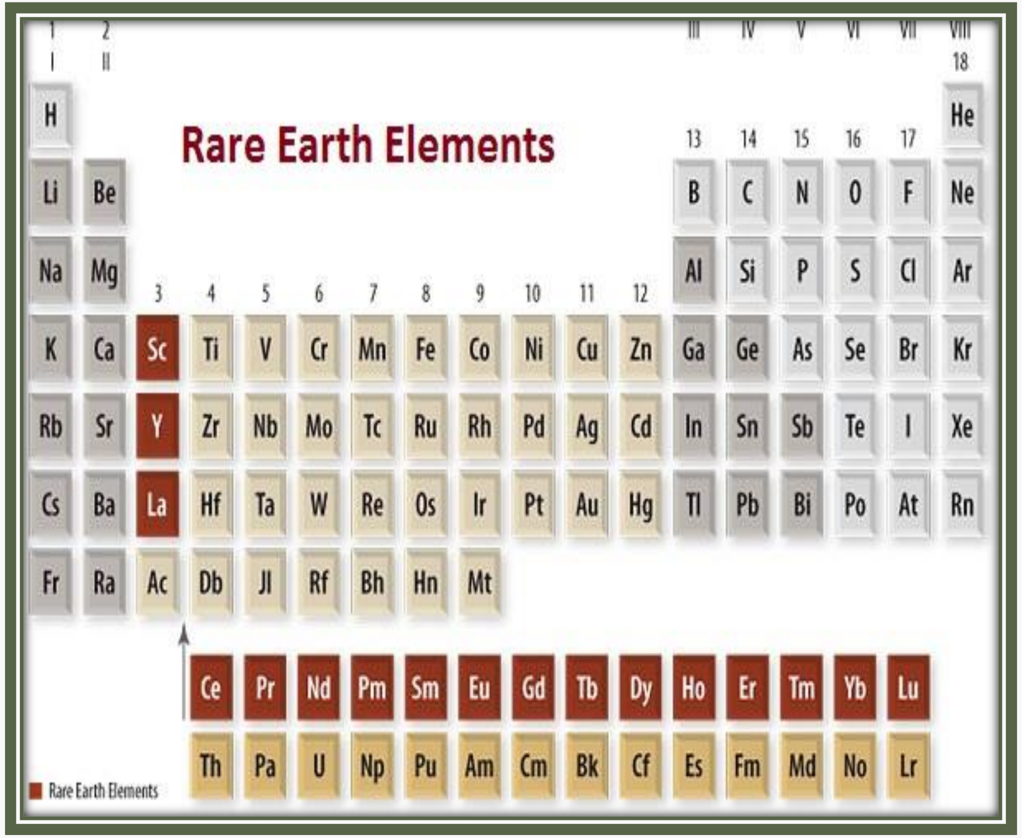


Image 2

<u>**Key Industrial Consumers and Products:**</u>

Automobile and petroleum industry

Glass industry, optics, high-quality lenses, crystal production, luminous fiber optics

High-performance electronics, high-tech weapons, satellite technology and telecommunications

Metallurgy, ceramics industry, and laser industry

Water treatment, alternative energies, marine biology

Paint and lacquer production, laboratories, drying technology, fluxing agents

Manufacture of magnets, batteries, spare parts industries

Shieldings against radioactivity

Rare Earth Technology	Application(s)	REE required
Catalysts	•Oil production •Gasoline and hybrids, diesel fuel additive •Fluid cracking •Ethane polymerization	La, Ce, Pr, Nd, Lu, Y, Sm
Rare Earth permanent magnets and ceramic magnets	•Wind and hydro power generation •Cordless power tools •Generators •Hybrids, plug-in and electric vehicles •Electric assist motors •Medical imaging •Computer disc drives •Handheld wireless devices	Nd, Pr, Dy, Tb, Sm, Tm
Phosphors	•LCD TVs and monitors •Plasma TVs and displays •Energy efficient fluorescent lights & LEDs	Y, Eu, Tb, Gd, Ce, La, Dy, Pr, Sc
Energy storage	•NiMH batteries	La, Ce, Pr, Nd
Glass additives	•Fiber optics •Optical glass for digital camera	Ce, La, Nd, Er, Gd, Yb
Polishing powders	•LCD and Plasma TVs and monitors •Silicon wafers and chips	Ce, La, Pr
Others	•Lasers •Superconductors •Nuclear applications •Fertilizers •High tech alloys	•Yb, Y, Dy, Tb, Eu, Sm, Nd •Gd •Ce, Er •various REE •Yb, Lu, Er, Tb, Gd, Eu, Sm, Nd, Pr, Ho, Sc

Rare Earth Elements are not rare

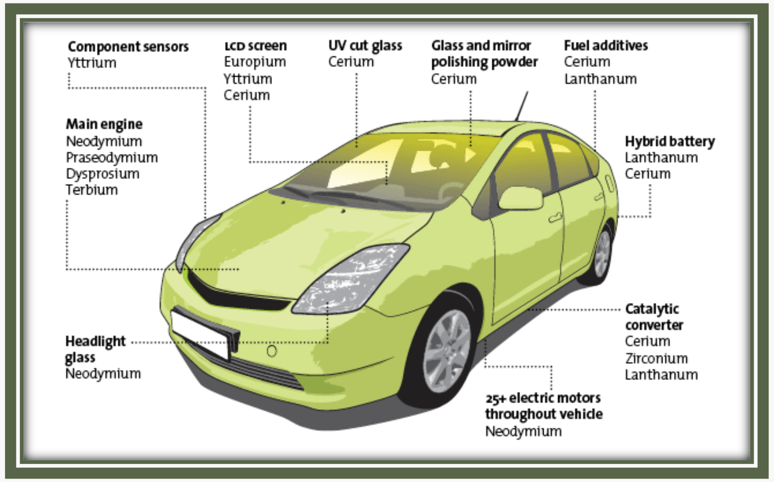


Image 3

Image 4

Image 5

Region 4 Rare Earth Element deposits

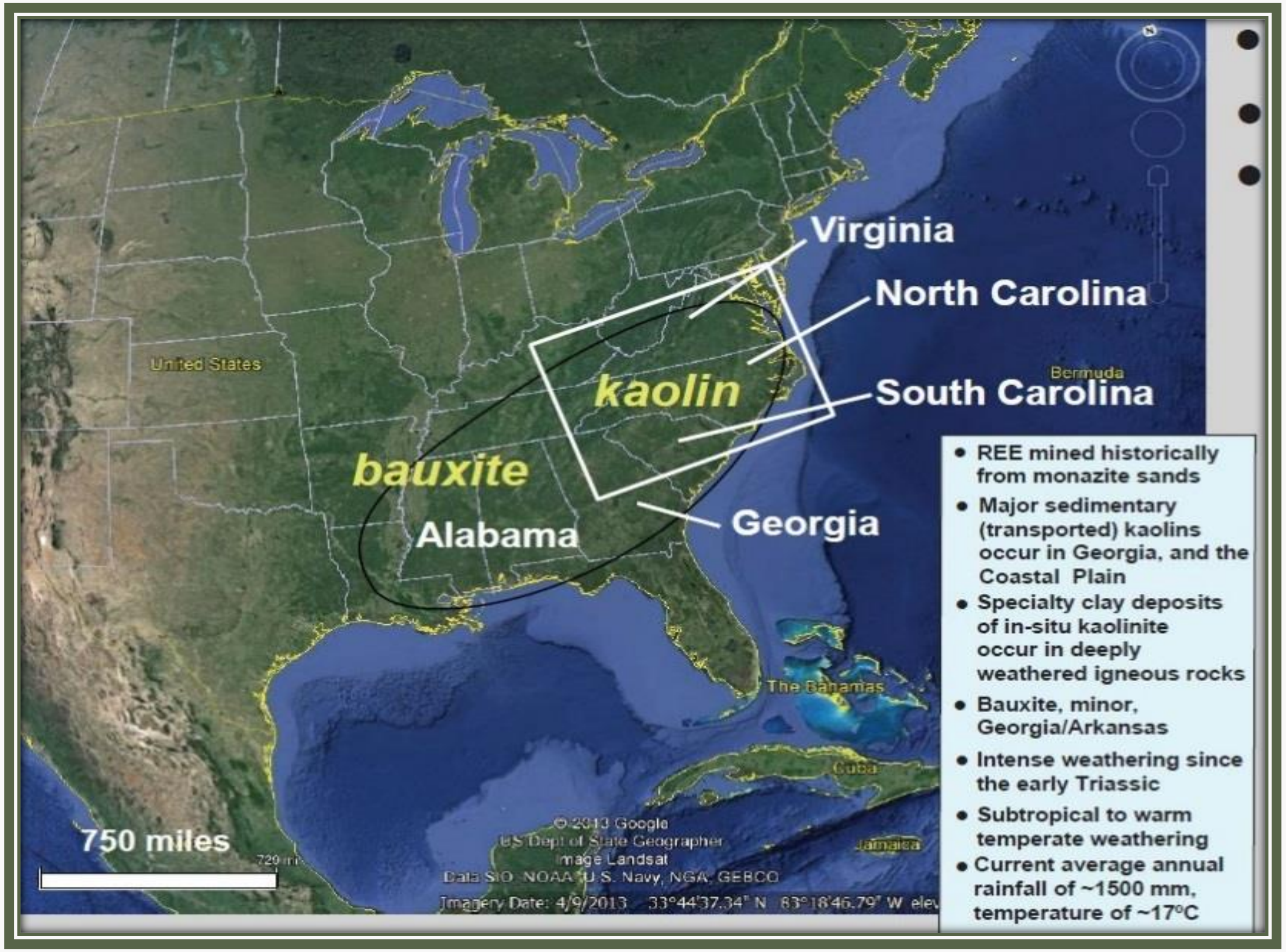


Image 6

Taken from USGS publication-
“Unconventional Resources of Rare Elements:
The Bearing of Source and Process on the Genesis of Residual Deposits”

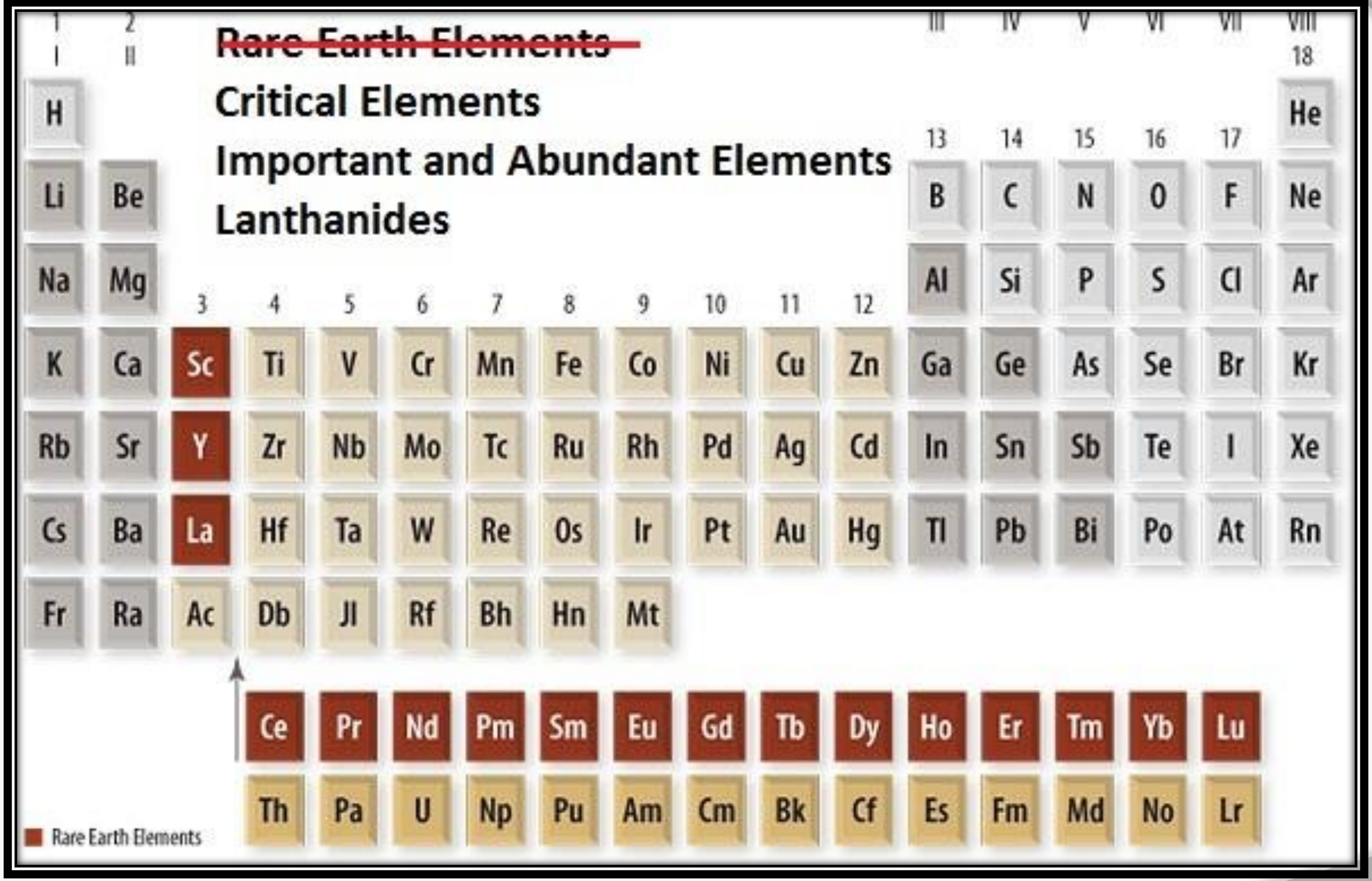

~~Rare Earth Elements~~
Critical Elements
Important and Abundant Elements
Lanthanides
H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl Ar
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba La Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po At Rn
Fr Ra Ac Db Jl Rf Bh Hn Mt
Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lr
Rare Earth Elements

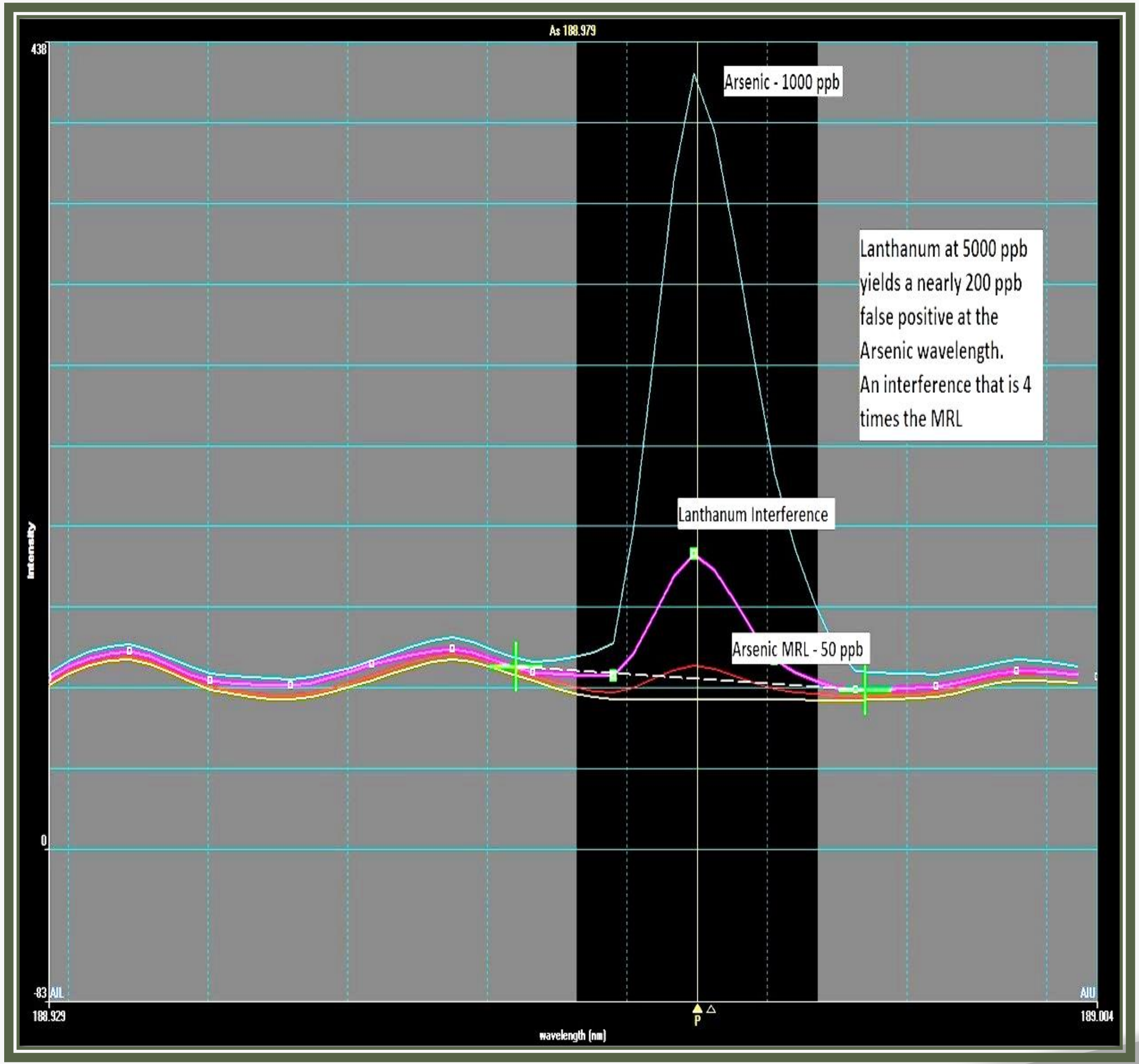
Image 7

Image 8

Data Review Request

Monitoring Well	Arsenic Method 6010 ICP	Arsenic Method 6020 ICP-MS Collision Cell	Arsenic Method 7062 Hydride	Arsenic Speciation	Arsenic Triple Quad
Sample 1 Total	27.8 ppb	15.4 ppb	<0.4 ppb	0.12 ppb	<1.0 ppb
Sample 2 Total	188 ppb	72 ppb	<0.4 ppb	0.38 ppb	<1.0 ppb

The method quality control results were all acceptable.



Lanthanum is a direct spectral overlap on arsenic at ICP-OES wavelength 189

PE ICP-OES 8300
USEPA Region 4 SESD ICS
Brittany Stuart, Chemist

What could possibly interfere with As and Se in ICP-MS?

What doesn't interfere with As and Se in ICP-MS?

Element	Mass	% Abundance	Dimer	Chlorides/ Hydrides	Doubly Charged
Arsenic	75	100		$^{40}Ar^{35}Cl^{+}$ $^{40}Ca^{35}Cl^{+}$ $^{43}Ca^{16}O_2^{+}$ $^{23}Na^{12}C^{40}Ar^{+}$ $^{12}C^{31}P^{16}O_2^{+}$ $^{36}Ar^{39}K^{+}$	$^{150}Sm^{++}$ $^{150}Nd^{++}$
Selenium	77	7.63		$^{40}Ar^{37}Cl^{+}$ $^{40}Ca^{37}Cl^{+}$	$^{154}Sm^{++}$ $^{154}Gd^{++}$
	78	23.77	$^{38}Ar^{40}Ar^{+}$ $^{39}K^{39}K^{+}$	$^{41}K^{37}Cl^{+}$	$^{156}Gd^{++}$ $^{156}Dy^{++}$
	80	49.61	$^{40}Ar^{40}Ar^{+}$ $^{40}Ca^{40}Ca^{+}$	$^{45}Sc^{35}Cl^{+}$	$^{160}Gd^{++}$ $^{160}Dy^{++}$
	82	8.73		$^{45}Sc^{37}Cl^{+}$ $^{81}BrH^{+}$	$^{164}Dy^{++}$ $^{164}Er^{++}$

Definition of Doubly Charged:

If an ion is singly charged, its position in the mass spectrum corresponds to its mass.

If an ion is doubly charged, it will appear in the spectrum at half its mass. At this mass it will interfere with isotopes of different elements.

For Example:

$^{150}Nd^{++}$ on $^{75}As^{+}$ or $^{156}Gd^{++}$ on $^{78}Se^{+}$

“Oxides (MO^+) and doubly charged species ($M2^+$) can be significantly reduced through proper tuning of the plasma and torch conditions and by good plasma design. Oxides are far more problematic in ICP-MS than doubly charged species since there are very few elements that generate significant levels of doubly charged species and these can be easily avoided..”

Taken from ICP-MS Inductively Coupled Plasma Mass Spectrometry A Primer from Agilent Technologies

Double charged ions are detected by the instrument as apparent isobars at half their actual mass…..There are no software corrections for this type of spectral interference, but optimization procedures used to set instrument operating conditions attempt to set double-charge formation to be a low fraction (less than 3 percent) of the single-charge ions present. Double-charge formation effects tend to be small or non existent when determining higher mass element concentrations, such as $^{75}As^{+}$. Natural abundance of double charged ions of the Lanthanide elements are low (Ryabchikov et al,. 1959).

Taken from "Arsenic and Thallium Data in Environmental Samples: Fact or Fiction?" Susan D. Chapnick, Leonard C. Pitts, Nancy C. Rothman Remediation Autumn 2010.

A doubly charged ion will cause a spectral interference at half the m/z of the singly charged ion, e.g. $^{138}Ba^{++}$ on $^{69}Ga^{+}$ or $^{208}Pb^{++}$ on $^{104}Ru^{+}$. **These interferences are few and can be considerably minimized, or effectively eliminated, by optimizing the system before proceeding with the analysis.**

Taken from ICP-MS, or ICP-AES and AAS?-a comparison Varian, ICP-MS-1 April 1994

"Associated with oxide-based spectral overlaps are doubly charged spectral interferences. These are species that are formed when an ion is generated with a double positive charge, as opposed to a normal single charge, and produces a peak at half its mass. Like the formation of oxides, the level of doubly charged species is related to the ionization conditions in the plasma and can usually be minimized by careful optimization of the nebulizer gas flow, rf power, and sampling position within the plasma."

Taken from A Beginner's Guide to ICP-MS, Part XII-A Review of Interferences Spectroscopy 17(10) October 2002

Initial Look at Rare Earth Element Interference on As and Se in ICP-MS

Rare Earth Element	^{75}As Uncorr	^{78}Se Uncorr
1000 ppb Eu	0.171	-0.050
1000 ppb Nd	44.009	-0.075
1000 ppb Sm	29.079	-0.074
1000 ppb Gd	0.097	618.118
1000 ppb Dy	0.074	1.534

PE NexION 300D ICP-MS
KED Mode
USEPA Region 4 SESD ICS
Ernie Walton, Chemist

Rare Earth Element	Standard Source	^{75}As Uncorr	^{78}Se Uncorr
Nd 200 ppb	HPS	6.299	0.155
Nd 200 ppb	SPEX	6.639	0.034
Sm 50 ppb	HPS	1.171	0.166
Sm 50 ppb	SPEX	1.175	-0.170
Gd 20 ppb	HPS	0.011	10.638
Gd 20 ppb	SPEX	0.006	10.836
Dy 10 ppb	HPS	0.011	0.158
Dy 10 ppb	SPEX	0.0003	0.124
Eu 200 ppb	HPS	0.152	-0.025
Eu 200 ppb	SPEX	0.146	-0.123
Er 200 ppb	HPS	-0.014	0.070
Er 200 ppb	SPEX	0.008	0.109

SPEX Standards

Image 9


Image 10

High Purity Standards

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What can we do to minimize this problem?

Determine a correction by empirically measuring the signals and mathematically calculating the ratios.

These corrections are similar to an IEC calculation for optical ICP. You must have a clean source for the interfering element.

Analyze at levels you are likely to see in the samples of concern.

NexION 300D

Sample ID: 500ppb Nd
Sample Date/Time: Tuesday, March 03, 2015 16:03:17
Method File: C:\NexIONData\Method\EPA NexION KED-FAST As Se.mth
Dataset File: C:\NexIONData\DataSet\030315\500ppb Nd.017
Tuning File: c:\nexiondata\masscal\epa_default.tun
Optimization File: c:\nexiondata\conditions\epa_default.dac
Sample Description: 1X
Sample File: C:\NexIONData\Sample\022315.sam
Batch ID: 030315
Autosampler Position: 104

Analyte	Mass	Blank Intensity	Meas. Intensity	Intens. RSD	Conc. Mean	Conc. SD	Conc. RSD
Ge	72	64928.598	81836.450	1.8 %			%
Ge	74	99700.860	101268.135	1.9 %			%
In-1	115	379108.891	359212.670	4.1 %			%
As	75	3.667	5536.406	2.6 %	17.709864	1.1907	6.7 %
2010_As	75	3.659	31.005	295.1 %	0.095979	0.3032	315.9 %
Se	76	23619.185	22786.841	3.5 %			%
Se	77	-3.716	-1.050	1.7 %			%
Se	78	37.333	30.333	8.3 %	-0.157345	0.0616	39.2 %
2070_Se	78	37.328	30.293	8.3 %	-0.158463	0.0615	38.8 %
Br	79	20.333	26.667	4.3 %			%
Se	82	3.667	6.000	44.1 %	0.152486	0.1554	101.9 %
Se-1	82	3.600	4.536	58.6 %	0.066976	0.1576	235.3 %
Br	81	37.000	36.333	4.2 %			%
Kr	83	6.333	6.333	36.5 %			%
Nd	146	1.667	1928143.675	1.3 %			%
Nd	143	3.000	1221979.124	2.2 %			%
Nd	145	1.000	900358.476	1.6 %			%
Sm	147	1.000	28.000	18.9 %			%
Sm	149	0.667	17.667	18.2 %			%
Eu	151	0.667	2.667	57.3 %			%
Eu	153	1.000	1.667	34.6 %			%
Gd	155	0.333	6.000	28.9 %			%
Gd	157	1.333	9.667	15.8 %			%
Dy	161	6.667	4888.170	3.4 %			%
Dy	163	12.333	131.334	6.4 %			%
Er	166	11.333	3884.862	3.6 %			%

As75/Nd146 = (5536.406-3.667) / (1928143.675-1.667)

= 5532.739 / 1928143.008

= 0.0028695

As75corr=As75uncorr-0.0028695*Nd146

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Rare Earth Element	^{75}As Uncorr	^{75}As Corr	^{78}Se Uncorr
10 ppb Nd	0.374	0.007	-0.293
100 ppb Nd	3.493	-0.016	-0.089
500 ppb Nd	17.709	0.095	-0.157
1000 ppb Nd	33.466	-0.361	-0.159
500 ppb Nd +20 ppb ICV	35.6 178% Recovery	18.3 92% Recovery	17.7 89% Recovery

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Rare Earth Element	^{75}As Uncorr	^{75}As Corr	^{78}Se Uncorr
10 ppb Sm	0.220	-0.025	-0.181
100 ppb Sm	2.509	-0.027	-0.273
500 ppb Sm	12.171	0.130	-0.156
1000 ppb Sm	24.187	1.062	-0.210
500 ppb Sm +20 ppb ICV	30.7 154% Recovery	18.7 94% Recovery	17.7 89% Recovery

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Rare Earth Element	^{75}As Uncorr	^{75}As Corr	^{78}Se Uncorr	^{78}Se Corr
10 ppb Gd	0.007	0.007	5.670	-0.242
100 ppb Gd	0.010	0.010	55.232	0.077
500 ppb Gd	0.000	0.000	281.728	5.126
1000 ppb Gd	0.013	0.009	566.691	6.850
500 ppb Gd +20 ppb ICV	19.5 98% Recovery	19.5 98% Recovery	305.852 1529% Recovery	18.4 92% Recovery

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Rare Earth Element	^{75}As Uncorr	^{75}As Corr	^{78}Se Uncorr
10 ppb Dy	-0.000	-0.000	-0.077
100 ppb Dy	-0.003	-0.003	-0.018
500 ppb Dy	-0.002	-0.002	0.569
1000 ppb Dy	-0.002	-0.002	1.697
500 ppb Dy +20 ppb ICV	18.5 93% Recovery	18.5 93% Recovery	19.7 99% Recovery

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KED Mode
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Rare Earth Element	^{75}As Uncorr	^{75}As Corr	^{78}Se Uncorr
10 ppb Er	0.005	0.005	-0.278
100 ppb Er	0.003	0.003	-0.300
500 ppb Er	0.005	0.005	-0.073
1000 ppb Er	0.009	0.009	-0.166
500 ppb Er +20 ppb ICV	19.2 96% Recovery	19.2 96% Recovery	18.9 95% Recovery

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Rare Earth Element	^{75}As Uncorr	^{75}As Corr	^{78}Se Uncorr
10 ppb Eu	0.000	0.000	-0.137
100 ppb Eu	0.013	0.013	-0.170
500 ppb Eu	0.064	0.063	-0.171
1000 ppb Eu	0.126	0.126	-0.395
500 ppb Eu +20 ppb ICV	19.1 96% Recovery	19.1 96% Recovery	19.3 97% Recovery

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Rare Earth Element	^{75}As Uncorr	^{75}As Corr	^{78}Se Uncorr	^{78}Se Corr
10 ppb Mixed REEs	**0.619**	**0.007**	**5.957**	**0.149**
100 ppb Mixed REEs	**6.203**	**0.283**	**56.638**	**0.720**
500 ppb Mixed REEs +20 ppb ICV	**50.4 130% Recovery**	**21.2 106% Recovery**	**301.0 565% Recovery**	**15.3 77% Recovery**

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ICP-MS Normal Mode Default Interference Correction Equations for Arsenic and Selenium

$^{75}As_{corr}={}^{75}As^{+}-3.127*({}^{40}Ar^{37}Cl^{+}-(0.874*{}^{82}Se^{+}))$

$^{75}As_{corr}={}^{75}As^{+}-3.127*({}^{40}Ar^{37}Cl^{+}-(0.322*{}^{78}Se^{+}))$

$^{82}Se^{+}_{corr}={}^{82}Se^{+}-1.00869*{}^{83}Kr^{+}-(0.000468659*{}^{81}Br^{+})$

Internal Standard ^{72}Ge

Mass 72	$^{144}Nd^{++}$, $^{144}Sm^{++}$
Mass 75	$^{150}Nd^{++}$, $^{150}Sm^{++}$
Mass 77	$^{154}Gd^{++}$, $^{154}Sm^{++}$
Mass 81	$^{162}Er^{++}$, $^{162}Dy^{++}$
Mass 82	$^{164}Er^{++}$, $^{164}Dy^{++}$
Mass 83	$^{166}Er^{++}$

Rare Earth Element	^{75}As Uncorr	^{75}As Corr	^{82}Se Uncorr	^{82}Se Corr
10 ppb Nd	0.118	0.099	-0.012	-0.019
100 ppb Nd	0.953	0.842	0.011	-0.005
500 ppb Nd	4.604	4.040	-0.005	-0.019
1000 ppb Nd	9.230	8.081	-0.016	-0.009
500 ppb Nd +20 ppb ICV	22.9 115%% Recovery	21.2 106% Recovery	18.2 91% Recovery	18.3 91% Recovery

$$^{75}As^+_{corr}={}^{75}As^+-3.127*({}^{40}Ar^{37}Cl^+-(0.874*{}^{82}Se^+))$$

$$^{82}Se^+_{corr}={}^{82}Se^+-1.00869*{}^{83}Kr^+-(0.000468659*{}^{81}Br^+)$$

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Rare Earth Element	^{75}As Uncorr	^{75}As Corr	^{82}Se Uncorr	^{82}Se Corr
10 ppb Sm	0.074	-0.452	0.000	0.038
100 ppb Sm	0.593	-4.663	-0.021	-0.037
500 ppb Sm	2.998	-23.442	-0.007	0.009
1000 ppb Sm	5.967	-45.672	-0.028	-0.028
500 ppb Sm +20 ppb ICV	22.3 112% Recovery	-6.094421 Recovery	19.2 96% Recovery	19.2 96% Recovery

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$$^{75}As_{corr} = {}^{75}As^{+} - 3.127*({}^{40}Ar^{37}Cl^{+} - (0.874*{}^{82}Se^{+}))$$

$$^{82}Se^{+}_{corr} = {}^{82}Se^{+} - 1.00869*{}^{83}Kr^{+} - (0.000468659*{}^{81}Br^{+})$$

Rare Earth Element	^{75}As Uncorr	^{75}As Corr	^{82}Se Uncorr	^{82}Se Corr
10 ppb Gd	0.025	-0.019	0.033	0.029
100 ppb Gd	0.017	-0.345	0.010	0.009
500 ppb Gd	0.018	-1.680	-0.003	-0.023
1000 ppb Gd	0.005	-3.613	-0.026	-0.068
500 ppb Gd +20 ppb ICV	20.0 100% Recovery	16.7 84% Recovery	19.3 97% Recovery	19.3 97% Recovery

$$^{75}As_{corr} = {}^{75}As^{+} - 3.127*({}^{40}Ar^{37}Cl^{+} - (0.874*{}^{82}Se^{+}))$$

$$^{82}Se^{+}_{corr} = {}^{82}Se^{+} - 1.00869*{}^{83}Kr^{+} - (0.000468659*{}^{81}Br^{+})$$

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Rare Earth Element	^{75}As Uncorr	^{75}As Corr	^{82}Se Uncorr	^{82}Se Corr
10 ppb Dy	0.003	0.518	1.889	1.890
100 ppb Dy	0.003	4.837	18.293	18.282
500 ppb Dy	0.005	23.972	90.938	90.922
1000 ppb Dy	0.002	47.653	180.738	180.766
500 ppb Dy +20 ppb ICV	19.9 100% Recovery	42.4 212% Recovery	111.4 555% Recovery	111.4 555% Recovery

$$^{75}As_{corr}={}^{75}As^{+}-3.127*({}^{40}Ar^{37}Cl^{+}-(0.874*{}^{82}Se^{+}))$$

$$^{82}Se^{+}{}_{corr}={}^{82}Se^{+}-1.00869*{}^{83}Kr^{+}-(0.000468659*{}^{81}Br^{+})$$

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Rare Earth Element	^{75}As Uncorr	^{75}As Corr	^{82}Se Uncorr	^{82}Se Corr
10 ppb Er	0.011	0.0487	0.106	-1.944
100 ppb Er	-0.004	0.248	0.891	-20.055
500 ppb Er	-0.000	1.233	4.663	-100.545
1000 ppb Er	0.001	2.489	9.466	-205.387
500 ppb Er +20 ppb ICV	19.7 99% Recovery	19.7 99% Recovery	24.4 122% Recovery	-79.7 Recovery

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$$^{75}As_{corr} = {}^{75}As^{+} - 3.127*({}^{40}Ar^{37}Cl^{+} - (0.874*{}^{82}Se^{+}))$$

$$^{82}Se^{+}{}_{corr} = {}^{82}Se^{+} - 1.00869*{}^{83}Kr^{+} - (0.000468659*{}^{81}Br^{+})$$

Lanthanide Element	^{75}As Uncorr	^{75}As Corr	^{82}Se Uncorr	^{82}Se Corr
10 ppb Eu	0.000	0.007	-0.053	-0.059
100 ppb Eu	0.008	0.033	0.020	-0.040
500 ppb Eu	0.020	0.035	-0.014	0.000
1000 ppb Eu	0.043	0.060	-0.010	-0.042
500 ppb Eu +20 ppb ICV	19.6 98% Recovery	18.4 92% Recovery	20.0 100% Recovery	20.0 100% Recovery

$$^{75}As_{corr}={}^{75}As^{+}-3.127*({}^{40}Ar^{37}Cl^{+}-(0.874*{}^{82}Se^{+}))$$

$$^{82}Se^{+}_{corr}={}^{82}Se^{+}-1.00869*{}^{83}Kr^{+}-(0.000468659*{}^{81}Br^{+})$$

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Rare Earth Element	^{75}As Uncorr	^{75}As Corr	^{82}Se Uncorr	^{82}Se Corr
10 ppb Mixed REEs	0.175	0.129	1.93	-0.182
100 ppb Mixed REEs	1.560	0.940	18.794	-1.171
500 ppb Mixed REEs	7.712	4.387	93.587	-8.595
500 ppb Mixed REEs +20 ppb ICV	25.9 130% Recovery	22.2 111% Recovery	113.4 565% Recovery	10.4 52% Recovery

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$$^{75}As_{corr} = {}^{75}As^{+} - 3.127*({}^{40}Ar^{37}Cl^{+} - (0.874*{}^{82}Se^{+}))$$

$$^{82}Se^{+}_{corr} = {}^{82}Se^{+} - 1.00869*{}^{83}Kr^{+} - (0.000468659*{}^{81}Br^{+})$$

Rare Earth Element Collision Cell	^{75}As Uncorr	^{75}As with correction	^{78}SE Uncorr	^{78}Se with correction
Sample 4x dilution	3.75mg/kg	1.81 mg/kg	8.9 mg/kg	2.39 mg/kg

Rare Earth Element Standard Mode	^{75}As Uncorr	^{75}As with correction	^{82}Se Uncorr	^{82}Se with correction
Sample 4x dilution	8.87 mg/kg	1.71 mg/kg	3.62 mg/kg	2.61 mg/kg

	Collision Cell Uncorr	Collision Cell Lanthanide Doubly Charged Corrected	Standard Mode Corrected
Arsenic	3.7 mg/kg	1.81 mg/kg	1.7 mg/kg
Selenium	8.9 mg/kg	2.39 mg/kg	2.6 mg/kg

Sample Matrix	
Al	15400 mg/kg
Ca	6500 mg/kg
Fe	3700 mg/kg
Mg	450 mg/kg
Na	50 mg/kg
S	5200 mg/kg
La	38 mg/kg
Nd	12 mg/kg
Sm	2.5 mg/kg
Gd	3.3 mg/kg
Dy	2.3 mg/kg
Er	1.0 mg/kg
Cu	100 mg/kg
Ba	270 mg/kg
Pb	140 mg/kg
Sr	1000 mg/kg
Zn	90 mg/kg

Soil sample from a military base

$$^{75}As_{corr} = {}^{75}As^{+} - 3.127 * ({}^{40}Ar^{37}Cl^{+} - (0.874 * {}^{82}Se^{+}))$$

Mass	Possible Interferences
$^{75}As^{+}$	$^{40}Ar^{35}Cl^{+}$, $^{150}Dy^{++}$, $^{150}Sm^{++}$
$^{40}Ar^{37}Cl^{+}$	$^{77}Se^{+}$, $^{154}Gd^{++}$, $^{154}Sm^{++}$
$^{82}Se^{+}$	$^{82}Kr^{+}$, $^{164}Er^{++}$, $^{164}Dy^{++}$, $^{81}BrH^{+}$

$$^{75}As_{corr} = {}^{75}As^+ - 3.127 * ({}^{40}Ar^{37}Cl^+ - (0.874 * {}^{82}Se^+))$$

$$^{75}As_{corr} = {}^{75}As^+ - 3.1005 * (({}^{40}Ar^{37}Cl^+ - 0.0045721 * {}^{147}Sm147^+ - 0.00032621 * {}^{157}Gd^+) - (0.874 * ({}^{82}Se^+ - 0.0029296 * {}^{163}Dy^+))) - 0.0017728 * {}^{146}Nd^+ - 0.0014422 * {}^{147}Sm^+$$

$$^{82}Se^{+}_{corr} = {}^{82}Se^{+} - 1.0087 * {}^{83}Kr^{+} - (0.00046866 * {}^{81}Br^{+})$$

Mass	Possible Interferences
$^{82}Se^{+}$	$^{82}Kr^{+}$, $^{81}Br^{1}H^{+}$, $^{164}Er^{++}$, $^{164}Dy^{++}$
$^{83}Kr^{+}$	$^{166}Er^{++}$
$^{81}Br^{+}$	$^{162}Er^{++}$, $^{162}Dy^{++}$

$$^{82}Se^{+}_{corr} = {}^{82}Se^{+} - 1.0087 * {}^{83}Kr^{+} - (0.00046866 * {}^{81}Br^{+})$$

$$^{82}Se^{+}_{corr} = {}^{82}Se^{+} - (1.0087 * ({}^{83}Kr^{+} - 0.0024829 * {}^{166}Er^{+})) - (0.00046866 * ({}^{81}Br^{+} - 0.0023575 * {}^{163}Dy^{+})) - (0.002926 * {}^{163}Dy^{+}) - (0.00010935 * {}^{166}Er^{+})$$

An alternate calculation for As if elevated Br is present.

$$^{75}As_{corr} = {}^{75}As^{+} - 3.127 * ({}^{40}Ar^{37}Cl^{+} - (0.322 * {}^{78}Se^{+}))$$

Mass	Possible Interferences
$^{75}As^{+}$	$^{40}Ar^{35}Cl^{+}$, $^{150}Dy^{++}$, $^{150}Sm^{++}$
$^{40}Ar^{37}Cl^{+}$	$^{77}Se^{+}$, $^{154}Gd^{++}$, $^{154}Sm^{++}$
$^{78}Se^{+}$	$^{38}Ar^{40}Ar^{+}$, $^{156}Gd^{++}$, $^{156}Dy^{++}$

$$^{75}As_{corr} = {}^{75}As^{+} - 3.127 * ({}^{40}Ar^{37}Cl^{+} - (0.322 * {}^{78}Se^{+}))$$

$$^{75}As_{corr} = {}^{75}As^{+} - 3.1005 * (({}^{40}Ar^{37}Cl^{+} - 0.0045721 * {}^{147}Sm^{+} - 0.00032621 * {}^{157}Gd^{+}) - (0.322 * ({}^{78}Se^{+} - 0.0030692 * {}^{157}Gd^{+}))) - 0.0017728 * {}^{146}Nd^{+} - 0.0014422 * {}^{147}Sm^{+}$$

Ocean Dredging
Dump Sites
Battery Dump Sites
Plating Sites
Mills
Transformer Sites
Chemical Sites
Mountain Top Mining Sites
Pesticide Sites
Phosphate Mines
Military Bases
Fertilizer Sites

Image 11

Image 11

Image 12

Image 13

Image 14

Image 15

Conclusions:

-Rare Earth Elements are not rare in environmental samples.

-Arsenic and selenium are subject to interferences from Rare Earth Element doubly charged formation when analyzed by Collision Cell and Standard Mode ICP-MS.

-The analytical community should be informed of this challenge that could lead to false positive/high bias results or false negative/low bias results on As and Se.

Procedures Region 4 SESD/ASB/ICS has initiated to address this challenge:

-Monitoring all samples for Rare Earth Elements matrix presence

-Creating correction factors that will work with collision cell ICP-MS and Standard Mode ICP-MS

-Working /talking with Perkin Elmer, Agilent, LTIG, and other EPA analysts to address this problem

-Talking with project managers to let them know what we are doing and what they should be asking for from ICP-MS/ICP analyses.