Br
Bromine

Sc
Scandium

Y
Yttrium

La
Lanthanum

Ce
Cerium

Pr
Praseodymium

Bromide and Doubly Charged Rare Earth Element Interferences in Collision Cell/Kinetic Energy Distribution Mode and Standard Mode ICP-MS Analyses of Arsenic and Selenium

Nd Neodymium | Pm Promethium | Sm Samarium | Eu Europium | Gd Gadolinium | Tb Terbium | Dy Dysprosium | Ho Holmium | Er Erbium | Tm Thulium | Yb Ytterbium | Lu Lutetium

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Overview:

1. Arsenic and selenium are plagued by interferences when analyzed by ICP-MS.
2. An awareness of these interferants is necessary to produce defensible arsenic and selenium results.*

“I analyze by ICP-MS. There are very few interferences associated with ICP-MS analyses.”

“I analyze by KED/collision cell ICP-MS. I have eliminated the major interferences associated with As and Se analyses.”

“You are barking up the wrong tree. Rare Earth Elements are called rare for a reason-they are rare.”

Recent Quotes from:

A lot of analysts and project leaders we try to tell this story to.

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
Arsenic	75	100		$^{40}Ar^{35}Cl^+$ $^{40}Ca^{35}Cl^+$ $^{43}Ca^{16}O_2{}^+$ $^{23}Na^{12}C^{40}Ar^+$ $^{12}C^{31}P^{16}O_2{}^+$ $^{36}Ar^{39}K^+$
Selenium	77	7.63		$^{40}Ar^{37}Cl^+$ $^{40}Ca^{37}Cl^+$
	78	23.77	$^{38}Ar^{40}Ar^+$ $^{39}K^{39}K^+$	$^{41}K^{37}Cl^+$
	80	49.61	$^{40}Ar^{40}Ar^+$ $^{40}Ca^{40}Ca^+$	$^{45}Sc^{35}Cl^+$
	82	8.73		$^{45}Sc^{37}Cl^+$ $^{81}BrH^+$

1. **The $^{81}BrH^+$ ion interferes with the determination of selenium at 82 amu.**
2. **If bromide is present in a sample, using the default equation for correcting the Cl interference on As will give positively biased results because of the $^{81}BrH^+$ interference at ^{82}Se.....The positive bias in arsenic results when using this equation in the presence of as little as 200 ug/L bromide will result in the arsenic concentration being 40% greater than is actually present.**

Taken from Methods of Analysis by the US Geological Survey National Water Quality Lab-Determination of Dissolved Arsenic, Boron, Lithium, Selenium, Strontium, Thallium, and Vanadium using Inductively Coupled Plasma-Mass Spectrometry
Open file report 99-093

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

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

$^{82}Se^{+}{}_{corr}={}^{82}Se^{+}-1.00869*{}^{83}Kr^{+}$

ICP-MS Normal Mode Interference Correction Equations for Arsenic and Selenium when Bromine is Present in Matrix

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

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

Internal Standard ^{72}Ge

Image 1

Image 2

Image 3

Image 4

Image 5

Image 6

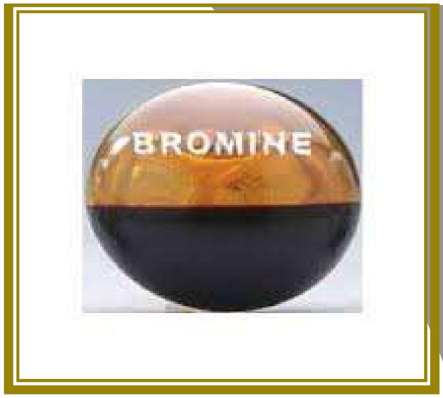


Image 7

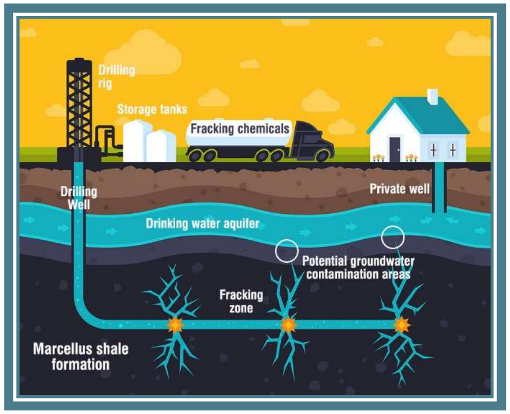


Image 8

Image 9

^{81}Br	^{75}As Default Correction Equation	^{75}As Correction Equation When Bromine is Present in Matrix	^{82}Se Default Correction Equation	^{82}Se Correction Equation When Bromine is Present in Matrix
200 ppb	ND	ND	ND	ND
1000 ppb	0.75 ppb	ND	2.4 ppb	ND
10000 ppb	7.6 ppb	ND	26 ppb	ND

Default

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

Bromine in Matrix

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

Default

$^{82}Se^{+}{}_{corr}={}^{82}Se^{+}-1.00869*{}^{83}Kr^{+}$

Bromine in Matrix

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

Sample from a Thermal Bromination Process

^{81}Br	^{75}As Default Correction Equation	^{75}As Correction Equation When Bromine is Present in Matrix	^{82}Se Default Correction Equation	^{82}Se Correction Equation When Bromine is Present in Matrix
320000 ppb	250 ppb	2.8 ppb	860 ppb	10 ppb

Sample from a City Drinking Water Source

^{81}Br	^{75}As Default Correction Equation	^{75}As Correction Equation When Bromine is Present in Matrix	^{82}Se Default Correction Equation	^{82}Se Correction Equation When Bromine is Present in Matrix
250 ppb	1.0 ppb	ND	1.2 ppb	ND

^{81}Br	^{75}As Default Correction Equation	^{75}As Correction Equation When Bromine is Present in Matrix	^{75}As KED Mode	Se Default Correction Equation	Se Correction Equation When Bromine is Present in Matrix	Se KED Mode
200 ppb	ND	ND	ND	ND	ND	ND
1000 ppb	0.75 ppb	ND	ND	2.4 ppb	ND	ND
10000 ppb	7.6 ppb	ND	ND	26 ppb	ND	ND

USEPA Method 200.8- Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma-Mass Spectrometry Revision 5.5

1.9 This method should be used by analysts experienced in the use of ICP-MS, the interpretation of spectral and matrix interferences and procedures for their correction.

2.2 Interferences relating to the techniques must be recognized and corrected for. Such corrections must include compensation for isobaric elemental interferences and interferences from polyatomic ions derived from the plasma gas, reagents or sample matrix.

4.1.3….Such interferences must be recognized, and when they cannot be avoided by the selection of alternative analytical isotopes, appropriate corrections must be made to the data. Equations for the correction of data should be established at the time of the analytical run sequence as the polyatomic ion interferences will be highly dependent on the sample matrix and chosen instrument conditions.

Table 2:

Common Molecular Ion Interferences in ICP-MS

Matrix Molecular Ions

Bromide $^{81}BrH^{+}$ ^{82}Se

Table 5:

Recommended Elemental Equations for Data Calculations

The arsenic correction calculation has a foot note:

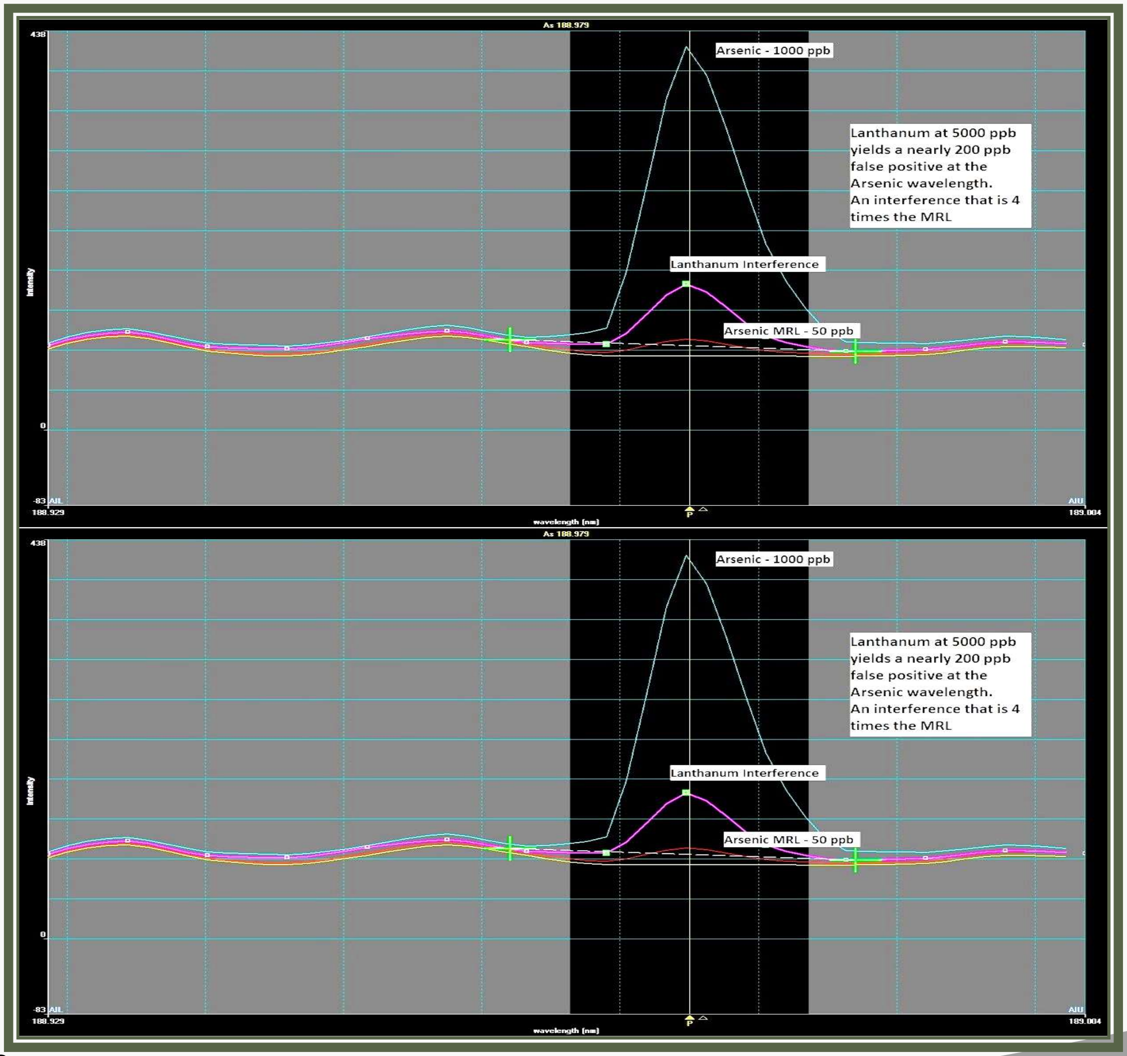
1.Isobaric mass 82 must be from Se only and not BrH^{+}.

Image10

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	28 ppb	15 ppb	ND	ND	ND
Sample 2 Total	190 ppb	72 ppb	ND	ND	ND

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

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 $^{78}Se^{+}$

How Did We Miss This?

“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. <u>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..”</u>

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 $^{104}Ru^{+}$. <u>These interferences are few and can be considerably minimized, or effectively eliminated, by optimizing the system before proceeding with the analysis.</u>

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"

Rare Earth Elements are Not Rare

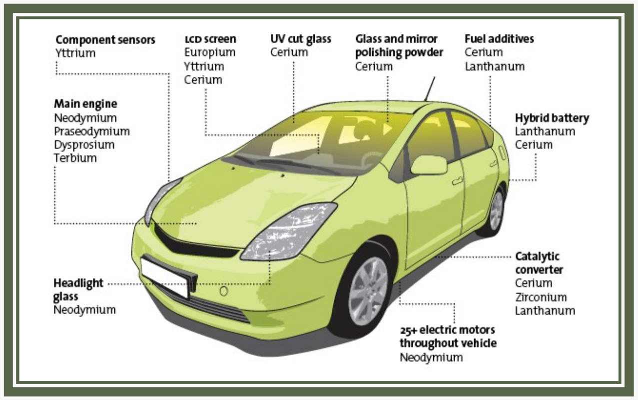


Image 11

Image 12

Image 13

Region 4 Rare Earth Element Deposits

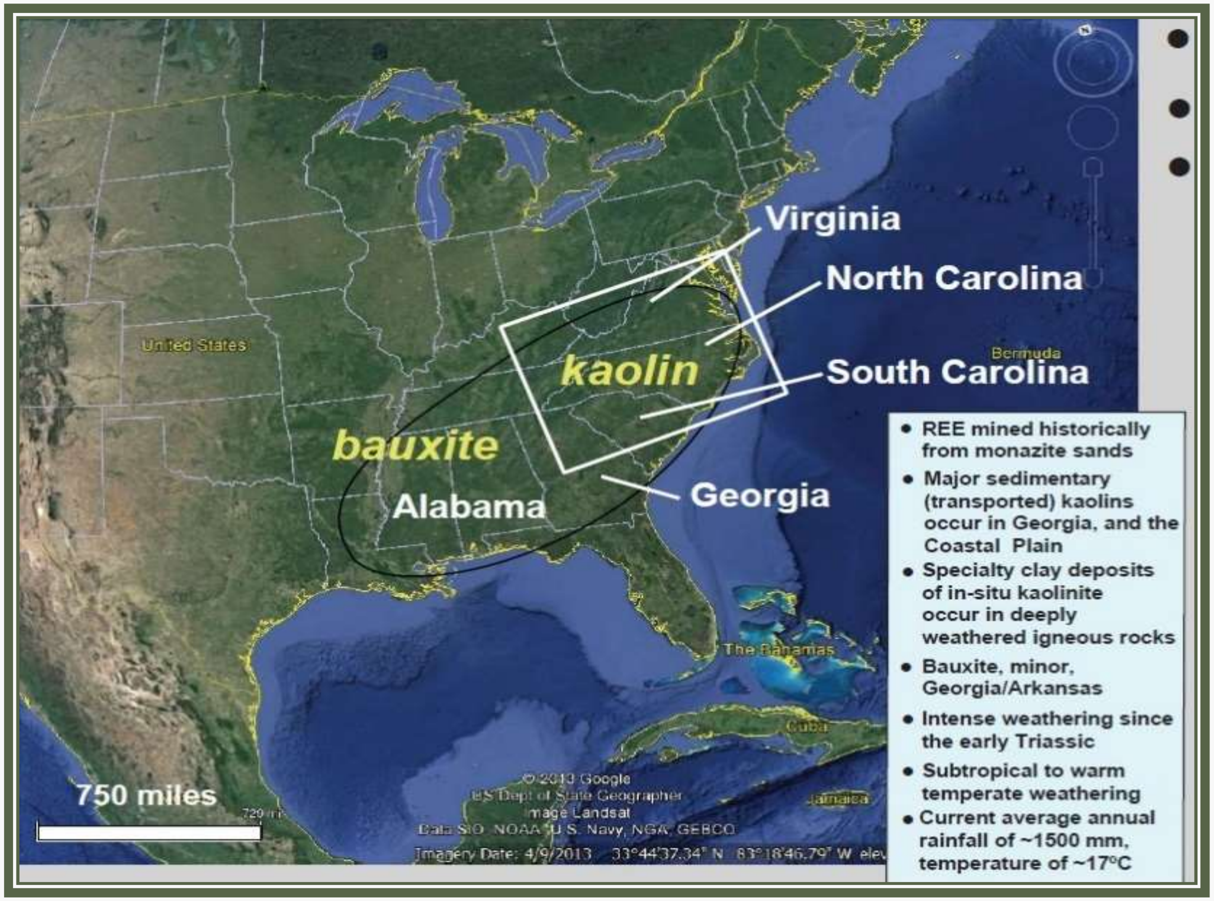


Image 14

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

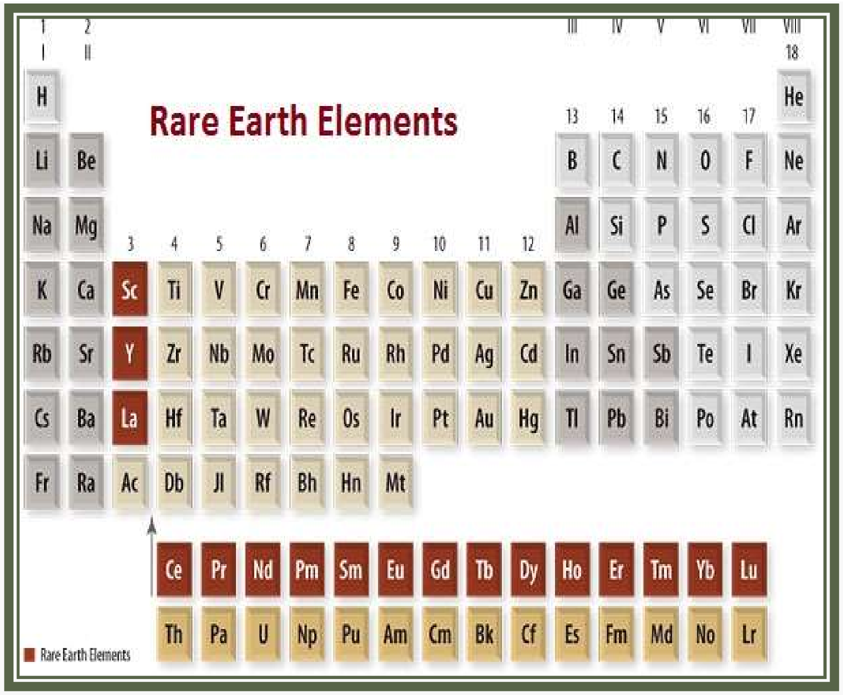


Image 15

<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

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	ND	ND
1000 ppb Nd	44	ND
1000 ppb Sm	29	ND
1000 ppb Gd	ND	620
1000 ppb Dy	ND	1.5
1000 ppb Pr	ND	-13

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

What can we do to minimize this problem?

It was suggested to minimize doubly charged by:
Cooling Plasma
Lowering Nebulizer Flow

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

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

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

REE	^{75}As Uncorr	^{75}As Corr	^{78}Se Uncorr
10 ppb Nd	0.37	ND	ND
100 ppb Nd	3.5	ND	ND
500 ppb Nd	18	ND	ND
1000 ppb Nd	33	ND	ND
500 ppb Nd +20 ppb ICV	36 180% Recovery	18 90% Recovery	18 90% Recovery

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

REE	^{75}As Uncorr	^{75}As Corr	^{78}Se Uncorr
10 ppb Sm	ND	ND	ND
100 ppb Sm	2.5	ND	ND
500 ppb Sm	12	ND	ND
1000 ppb Sm	24	1.1	ND
500 ppb Sm +20 ppb ICV	31 155% Recovery	19 95% Recovery	18 90% Recovery

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

REE	^{75}As Uncorr	^{75}As Corr	^{78}Se Uncorr	^{78}Se Corr
10 ppb Gd	ND	ND	5.7	ND
100 ppb Gd	ND	ND	55	ND
500 ppb Gd	ND	ND	280	5.1
1000 ppb Gd	ND	ND	570	6.9
500 ppb Gd +20 ppb ICV	20 100% Recovery	20 100% Recovery	310 1550% Recovery	18 90% Recovery

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

REE	^{75}As Uncorr	^{75}As Corr	^{78}Se Uncorr
10 ppb Er	ND	ND	ND
100 ppb Er	ND	ND	ND
500 ppb Er	ND	ND	ND
1000 ppb Er	ND	ND	ND
500 ppb Er +20 ppb ICV	19 95% Recovery	19 95% Recovery	19 95% Recovery

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

REE	^{75}As Uncorr	^{75}As Corr	^{78}Se Uncorr
10 ppb Eu	ND	ND	ND
100 ppb Eu	ND	ND	ND
500 ppb Eu	ND	ND	ND
1000 ppb Eu	ND	ND	ND
500 ppb Eu +20 ppb ICV	19 95% Recovery	19 95% Recovery	19 95% Recovery

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

REE	^{75}As Uncorr	^{75}As Corr	^{78}Se Uncorr	^{78}Se Corr
10 ppb Mixed REEs	0.62	ND	5.9	ND
100 ppb Mixed REEs	6.2	ND	57	ND
500 ppb Mixed REEs +20 ppb ICV	50 250 Recovery	21 105% Recovery	300 1500% Recovery	15 75% Recovery

PE NexION 300D ICP-MS
KED Mode
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Ernie Walton, Chemist

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	$^{144}Gd^{++}$, $^{144}Sm^{++}$
Mass 81	$^{162}Er^{++}$, $^{162}Dy^{++}$
Mass 82	$^{164}Er^{++}$, $^{164}Dy^{++}$
Mass 83	$^{166}Er^{++}$

REE	^{75}As Uncorr	^{75}As Corr	^{82}Se Uncorr	^{82}Se Corr
10 ppb Nd	ND	ND	ND	ND
100 ppb Nd	0.95	0.84	ND	ND
500 ppb Nd	4.6	4.0	ND	ND
1000 ppb Nd	9.2	8.1	ND	ND
500 ppb Nd +20 ppb ICV	23 115%% Recovery	21 105% Recovery	18 90% Recovery	18 90% Recovery

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

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

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

REE	^{75}As Uncorr	^{75}As Corr	^{82}Se Uncorr	^{82}Se Corr
10 ppb Sm	ND	ND	ND	ND
100 ppb Sm	0.59	-4.7	ND	ND
500 ppb Sm	3.0	-23	ND	ND
1000 ppb Sm	6.0	-46	ND	ND
500 ppb Sm +20 ppb ICV	22 112% Recovery	-6.1 Recovery	19.2 96% Recovery	19.2 96% Recovery

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

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

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

REE	^{75}As Uncorr	^{75}As Corr	^{82}Se Uncorr	^{82}Se Corr
10 ppb Gd	ND	ND	ND	ND
100 ppb Gd	ND	-0.35	ND	ND
500 ppb Gd	ND	-1.7	ND	ND
1000 ppb Gd	ND	-3.6	ND	ND
500 ppb Gd +20 ppb ICV	20 100% Recovery	17 85% Recovery	19 95% Recovery	19 95% Recovery

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

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

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

REE	^{75}As Uncorr	^{75}As Corr	^{82}Se Uncorr	^{82}Se Corr
10 ppb Dy	ND	0.52	1.9	1.9
100 ppb Dy	ND	4.8	18	18
500 ppb Dy	ND	24	91	91
1000 ppb Dy	ND	48	180	180
500 ppb Dy +20 ppb ICV	20 100% Recovery	42 210% Recovery	110 550% Recovery	110 550% Recovery

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

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

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

REE	^{75}As Uncorr	^{75}As Corr	^{82}Se Uncorr	^{82}Se Corr
10 ppb Er	ND	ND	ND	-1.9
100 ppb Er	ND	ND	0.891	-20
500 ppb Er	ND	1.2	4.7	-100
1000 ppb Er	ND	2.5	9.5	-200
500 ppb Er +20 ppb ICV	20 100% Recovery	20 100% Recovery	24 120% Recovery	-80 Recovery

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

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

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

REE	^{75}As Uncorr	^{75}As Corr	^{82}Se Uncorr	^{82}Se Corr
10 ppb Eu	ND	ND	ND	ND
100 ppb Eu	ND	ND	ND	ND
500 ppb Eu	ND	ND	ND	ND
1000 ppb Eu	ND	ND	ND	ND
500 ppb Eu +20 ppb ICV	20 100% Recovery	18 90% Recovery	20.0 100% Recovery	20.0 100% Recovery

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

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

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

REE	^{75}As Uncorr	^{75}As Corr	^{82}Se Uncorr	^{82}Se Corr
10 ppb Mixed REEs	ND	ND	1.9	ND
100 ppb Mixed REEs	1.6	0.94	19	-1.2
500 ppb Mixed REEs	7.7	4.4	94	-8.6
500 ppb Mixed REEs +20 ppb ICV	26 130% Recovery	22 110% Recovery	113 565% Recovery	10 50% Recovery

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

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

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

REE Collision Cell	^{75}As Uncorr	^{75}As with correction	^{78}SE Uncorr	^{78}Se with correction
Sample 4x dilution	3.8mg/kg	1.8 mg/kg	8.9 mg/kg	2.4 mg/kg

REE Standard Mode	^{75}As Uncorr	^{75}As with correction	^{82}Se Uncorr	^{82}Se with correction
Sample 4x dilution	8.9 mg/kg	1.7 mg/kg	3.6 mg/kg	2.6 mg/kg

	Collision Cell Uncorr	Collision Cell Rare Earth Element Doubly Charged Corrected	Standard Mode Corrected
Arsenic	3.8 mg/kg	1.8 mg/kg	1.7 mg/kg
Selenium	8.9 mg/kg	2.4 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**
$^{75}As^{+}$	$^{40}Ar^{35}Cl^{+}$, $^{150}Dy^{++}$, $^{150}Sm^{++}$
$^{40}Ar^{37}Cl^{+}$	$^{77}Se^{+}$, $^{154}Gd^{++}$, $^{154}Sm^{++}$
$^{82}Se^{+}$	$^{82}Kr^{+}$, $^{164}Er^{++}$, $^{164}Dy^{++}$, $^{81}Br^{1}H^{+}$

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

$$^{75}As_{corr} = {}^{75}As^{+} - 3.1005 * (({}^{40}Ar^{37}Cl^{+} - 0.00457 * {}^{147}Sm147^{+} - 0.000326 * {}^{157}Gd^{+}) -(0.874 * ({}^{82}Se^{+} - 0.00293 * {}^{163}Dy^{+}))) - 0.00177 * {}^{146}Nd^{+} - 0.00144 * {}^{147}Sm^{+}$$

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

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

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

$$^{82}Se^{+}_{corr} = {}^{82}Se^{+} - (1.0087 * ({}^{83}Kr^{+} - 0.00248 * {}^{166}Er^{+})) - (0.000469 * ({}^{81}Br^{+} - 0.00236 * {}^{163}Dy^{+})) - (0.00293 * {}^{163}Dy^{+}) - (0.000109 * {}^{166}Er^{+})$$

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

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

$$^{75}As_{corr} = {}^{75}As^{+} - 3.1005 * (({}^{40}Ar^{37}Cl^{+} - 0.00457 * {}^{147}Sm^{+} - 0.000326 * {}^{157}Gd^{+}) -(0.322 * ({}^{78}Se^{+} - 0.00307 * {}^{157}Gd^{+}))) - 0.00177 * {}^{146}Nd^{+} - 0.00144 * {}^{147}Sm+$$

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

Image 16

Image 11

Image 17

Image 18

Image 19

Image 20

Conclusions:

Arsenic and selenium are subject to interferences from bromine and Rare Earth Element doubly charged formation when analyzed by ICP-MS. It is not unusual to find the presence of bromine or REEs in environmental samples.

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

Procedures USEPA Region4 SESD/ASB/ICS has initiated to address this challenge:

- -Monitoring all samples for bromine and Rare Earth Elements in the sample matrix
- -Attempting to create correction factors that will consistently 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
- -Beginning to look at ½ mass corrections
- -Talking with project managers to let them know what we are doing and what they should be asking for from ICP-MS/ICP analyses

References and Acknowledgements

1. Garbarino, John, R., Determination of Dissolved Arsenic, Boron, Lithium, Selenium, Strontium, Thallium, and Vanadium Using Inductively Coupled Plasma-Mass Spectrometry, U.S. Geological Survey Open File Report 99-093 Denver Colorado, 1999
2. Hinners, Thomas A., Pergnatis, Spiros A., and Heithmar, Edward M., Assessment of Internal Standards for Arsenic In ICP-MS, U.S. Environmental Protection Agency, National Exposure Research Laboratory, characterization Research Division, P.O. Box 93478. Las Vegas, NV 89193-3478
3. Jackson, Brian P., Liba. Amir, Nelson, Jenny Advantages of reaction cell ICP-MS on doubly charges interferences for arsenic and selenium analysis in foods, J. Anal At. Spectrom. The Royal Society of Chemistry 2014
4.Hinners, Thomas A., Heithmar, Edward M., Butler, Larry C., Performance of Inductively Coupled Plasma Mass Spectrometry Method 6020, Environmental Monitoring Systems Laboratory, P.O. box 93478, Las Vegas, Nevada 89193-3478; Hurd, Michael L., Office of Emergency and Remedial Response 401 M. Street, S.W., Washington, District of Columbia 20460; Dobb, Dave E., Laing, Guy A., Lockheed Engineering and Sciences Company, 1050 East Flamingo Road, Suite 120, Las Vegas, Nevada 89119.
5. X,Pang, D,Li, A. Peng Application of rare-earth elements in the agriculture of China and its environmental behavior in soil. Research Center of Eco-Environmental Science, Chinese Academy of Sciences, Beijing, China.
6. Wyttenbach, A., Furrer, V., Schleppi, P., and Tobler, L.Rare earth elements in soil and in soil-grown plants, @1998 Kluwer Academic Publishers. Printed in the Netherlands
7.Nakano,Kazumi and Shikamori,Yasuyuki Removal of REE++ interference on arsenic and selenium:Agilent 8800 ICP-QQQ Application Handbook
8.Long, Keith R., Van Gosen, Bradley, S., Foley, Nora, K., and Cordier, Daniel, 2010, The Principal Rare Earth Elements Deposits of the United States-A Summarry of Domestic Deposits and a Global Perspective: U.S. Department of the Interior, U.S. Geological Survey Scientific Investigations Report 2010-5220
9.Gunderson, Karen, MPH,CIH, JDSI, May17, 2006,Problems with Arsenic detection: When NIOSH and EPA Methods Fail: Power Point Presentatio
10.Beres, Steven, Dionne, Luc, Neubauer, Kenneth, and Thomas, Robert, May 2, 2005 Reducing the Impact of Spectral Interferences on the Determination of Precious Metals in Complex Geological Matrices Using DRC ICP-MS:Spectroscopy
11. Gray, Patrick, J., B.S., 2011, Nanoparticle Characterization, Fundamental Studies and Computer Simulations of Dynamic Reaction Cell Inductively Couples Plasma Mass Spectrometry: Dissertation Ohio State University
12. King, Hobart,REE-Rare Earth Elements and their Uses:Http://geology.com/articles/rare-earth-elements/
13. IAMGOLD Corporation, April 2012,Rare Earth Elements 101
14. Long, S.E., Martin, T.D., and Martin, E.R., Creed, J.T., Brockhoff, C.A., 1994, Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma-Mass Spectrometry, Revision 5.4

References and Acknowledgements

15. Segneri, Brittany, Deprozio, Jodi, Reinhardt, Timothy, Feb 24-26, 2014, Geologic Provenance of Rare Earth Eleemnts in the United States, and their Potential Collocation with Geothermal Resources:Thirty-Ninth workshop on Geothermal Reservoir Engineering Stanford University, Stanford California

16. Mindak, William, R., Elemental Analysis Manual: Section 3.6.4 Inductively Coupled Plasma-Mass Spectrometer, Version 1(June 2008), http://www.fda.gov/Food/FoodScienceResearch/LaboratoryMethods/ucm205

17. Folger, Tim, The Secret Ingredients of Everything, National Geographic Magazine, June 2011, NGM.com http://ngm.nationalgeographic.com/print/2011/06/rare-earth-elements/folger

18. Chapnick, Susan, D., Pitts, Leonard, C.,Rothman, Nancy C., Arsenic and Thallium Data in Environmental Samples: Fact or Fiction?, 2010 Wiley Periodicals, Inc. http://wileyonlinelibrary.com.DOI:10.1002/rem.20260

19. Tantalus Rare Earths Ag http://www.tre-ag.com/commodities/applications.aspx?sc_lang=en

20. SW847 Method 6020

21. 5.Long, Keith R., Van Gosen, Bradley, S., Foley, Nora, K., and Cordier, Daniel, 2010, The Geology of Rare Earth Elements Report 2010-5220,

22. Office of Research and Development-Rare Earth Elements: A Review of Production, Processing, Recycling, and Associated Environmental Issues EPA 600/R-12/572/December 2012/ www.epa.gov/ord19

REE-Rare Earth Elements and their Uses

23. http://geology.com/articles/rare-earth-elements/

24. http://www.cbsnews.com/news/rare-earth-elements-not-so-rare-after-all/

25. Nakano, Kazumi, Hachioji, Takakura-machi, Study of a novel interference correction method for doubly-charged ions to improve trace analysis for As and Se in environmental samples by ICP-MS, European Winter Conference on Plasma Spectrochemistry Munster, Germany Feb 22-26, 2015.

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