



Automated Ultra-High Dilutions (>10,000x) to Extend the Applicability of ICPMS to Highly Concentrated Samples

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Who We Are



- Elemental Scientific is worldwide company based out of Omaha, NE
- Specialize in sample preparation and introduction into Inductively Coupled Plasma Optical Emission Spectrometer (ICP) and Inductively Coupled Plasma Mass Spectrometer (ICPMS)



Presentation Goals



- Dilution of Standards and Samples performed INLINE
 - Utilizing dual-loop dilution
 - Just before injection into instrument
- prepFAST MAX can dilute linearly over 40,000X range
- Calibration of ICPMS over large concentration range
- prepFAST MAX can calibrate ICPMS and analyze concentrated samples with 40,000X inline dilution

Why are we trying to achieve this?

Practical Problems

- ICP and ICPMS Instruments need to be calibrated
 - Counts per second (CPS) → Concentration (ppb)
- Analysis labs often must dilute standards and samples
 - 30+ minutes manual labor
 - Human error
 - Risk of contamination
 - High use of consumable



Can we improve this process?

prepFAST Line of Products



- prepFAST X, MX, MAX
- Autocalibration of ICP/ICPMS
- Autodilution of samples
- Auto overrange dilution
- SampleSense loading
 - Reduces sample consumption and waste
- Syringe-driven internal standard addition
- Improves laboratory productivity



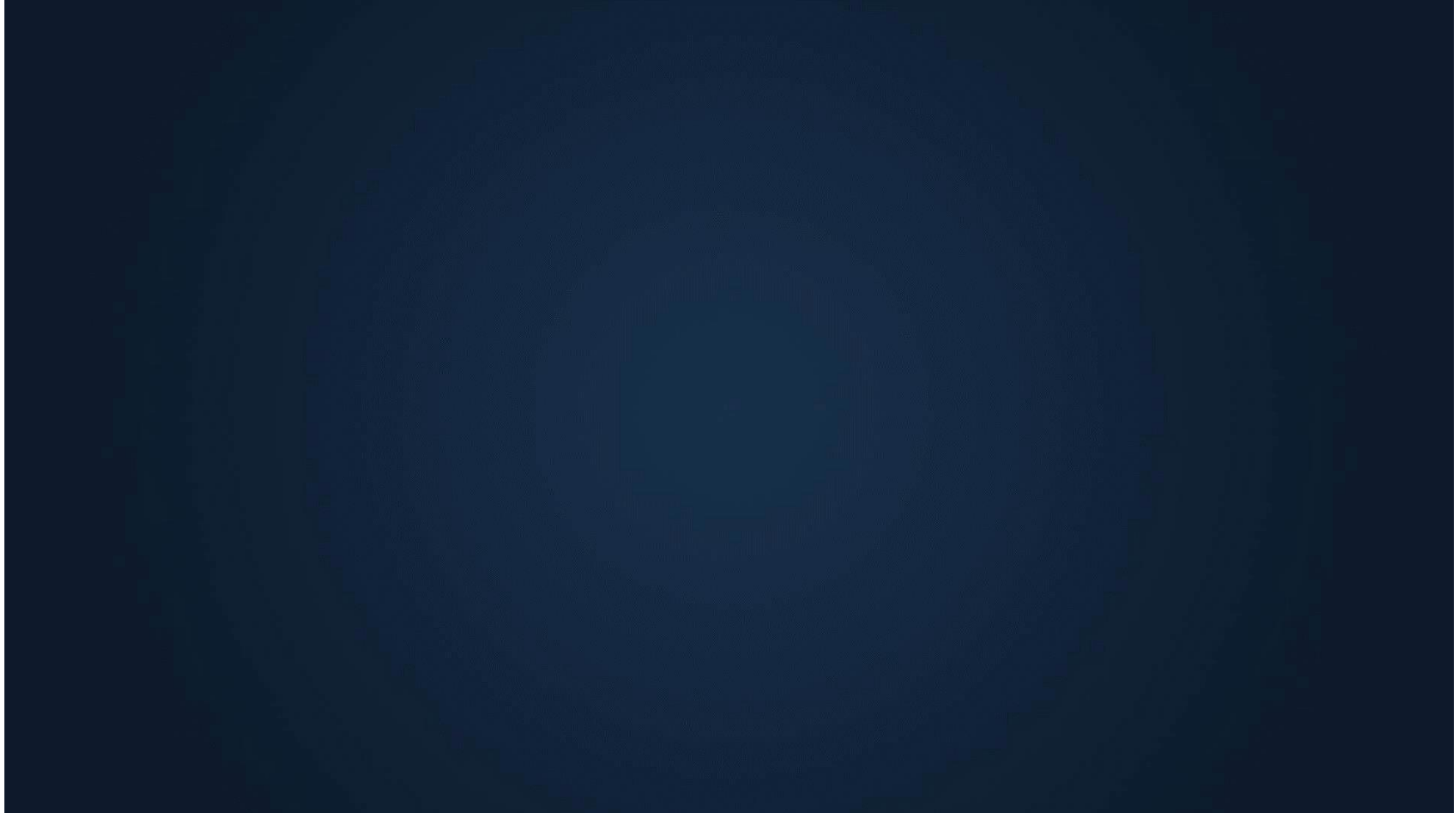
prepFAST MAX



- Newest addition to the prepFAST line (2021)
- Precision syringe sample loading
- Dual-Loop dilution for 1-40,000x dilution range
 - Undiluted or low dilution for trace elements
 - Dilute for highly concentrated elements
 - Single Instrument analysis
- High dilution factors more robust
 - Two smaller, inline dilutions



Simple Explanation of prepFAST MAX Function



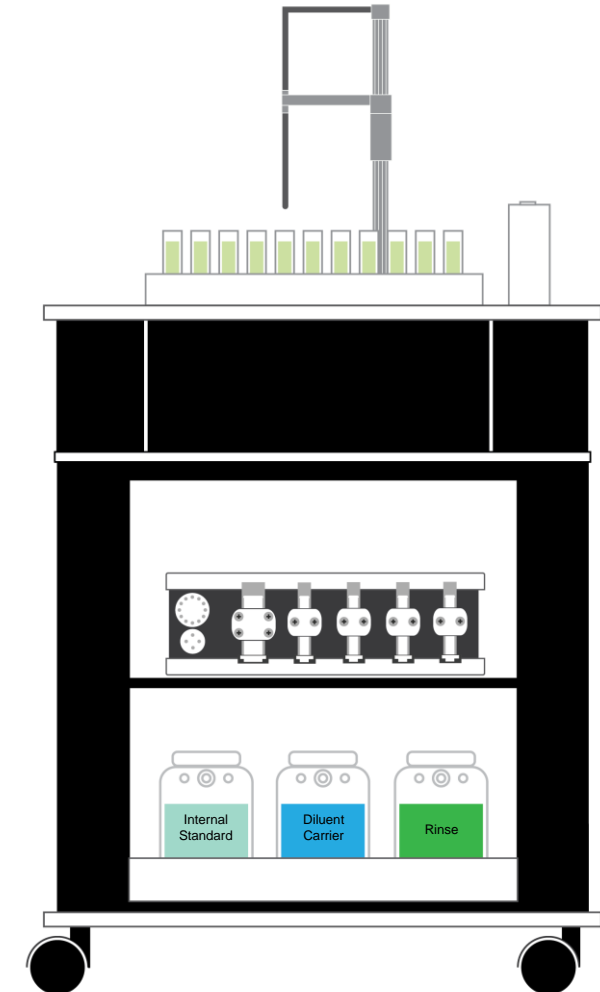
Experimental Overview



- Show linearity of Counts vs Dilution Factor
- Presenting 4 different experiments:
 - prepFAST MAX vs Manual dilutions of Lab Standard
 - Digest of Metal Standard Reference Material from NIST
 - Plating Bath samples
 - River Sediment standard from High Purity Standards

Linearity Experimental Design

- 1ppm on deck standard
 - Ba, Cd, and Mn
- Diluted at various dilution factors
 - prepFAST MAX inline dilution
 - 1X-40,000X
- Counts per Second vs Concentration (dilution factor)



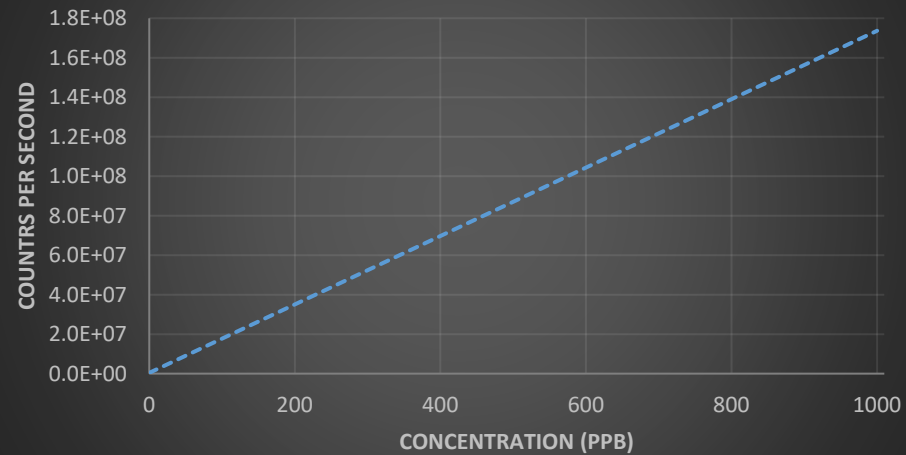
Counts per Second vs Dilution Factor

- Concentration based on 1ppm stock and dilution factor
- %Recovery based on CPS from 1X dilution factor
- 1ppm begins to max out detector

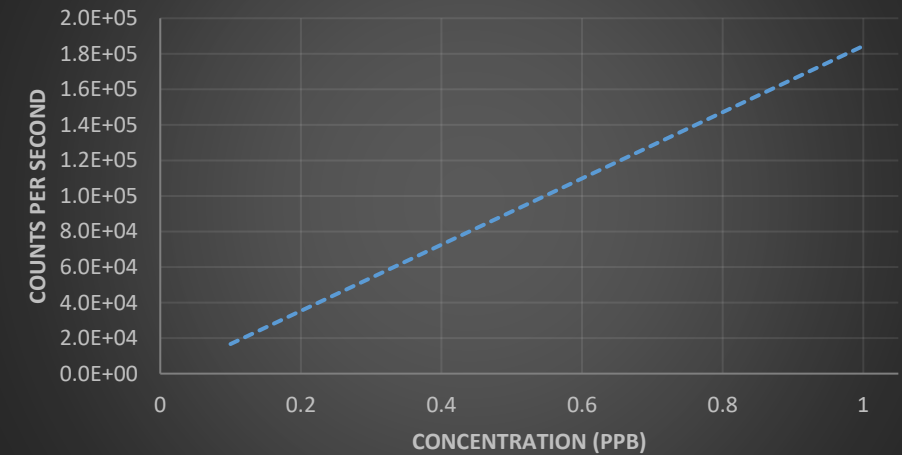
Dilution Factor	Concentration (ppb)	Ba (138) CPS	%Recovery	Mn (55) CPS	%Recovery
40,000	0.025	8003	102.0%	292	107.9%
20,000	0.05	12578	104.2%	584	108.0%
10,000	0.1	20638	98.9%	1259	116.5%
5,000	0.2	37871	99.5%	2389	110.5%
2,500	0.4	77135	106.8%	5024	116.2%
1,000	1	187815	107.0%	12220	113.0%
500	2	368801	106.1%	24096	111.4%
250	4	720164	104.1%	47177	109.1%
100	10	1860887	107.9%	121140	112.0%
50	20	3822141	110.9%	243960	112.8%
25	40	7469968	108.5%	490952	113.5%
10	100	18521181	107.6%	1205347	111.5%
5	200	36848357	107.1%	2297110	106.2%
2	500	89317831	103.8%	5635350	104.2%
1	1000	172085914	N/A	10811413	N/A

Calibration of Barium (Ba)

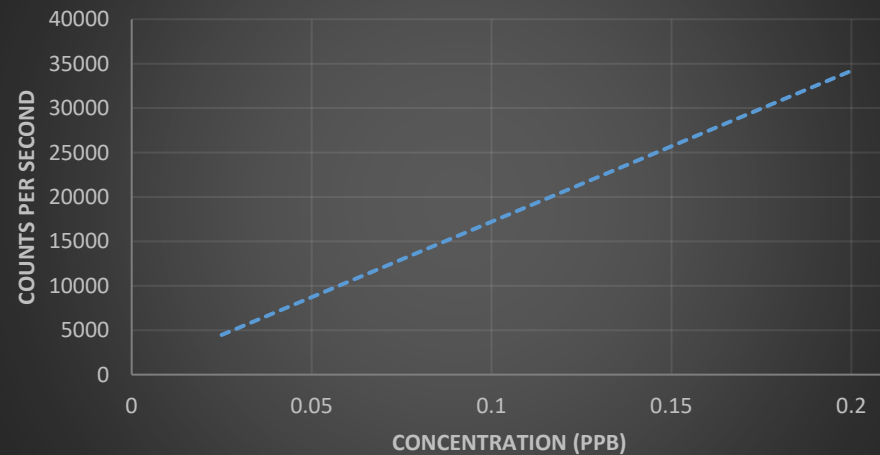
Calibration Curve



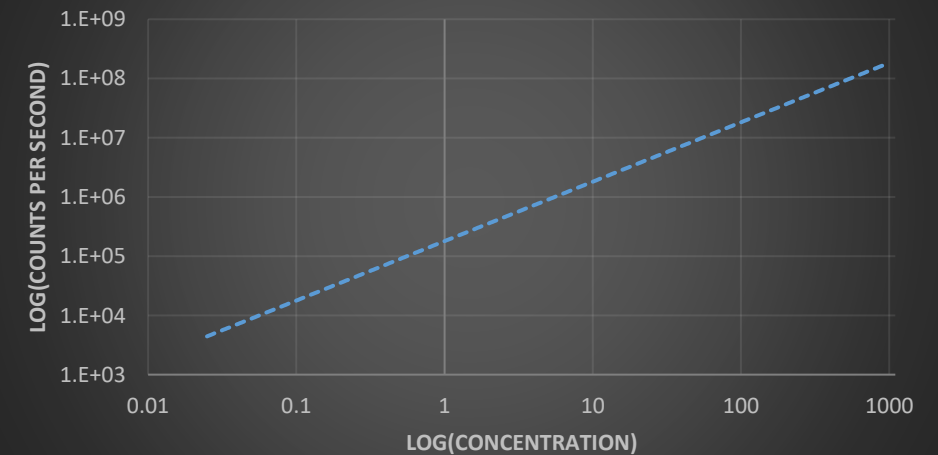
10,000X-1,000X Dilution Range



40,000X-5,000X Dilution Range

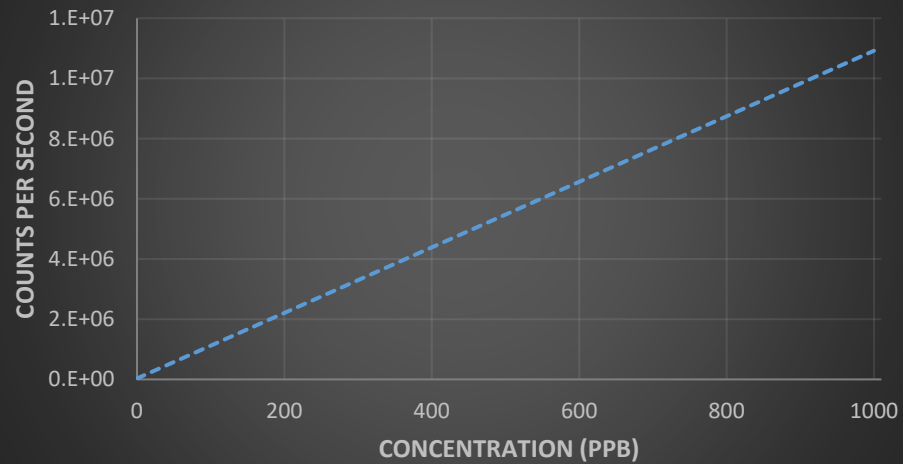


Log-Log Scale of Dilution

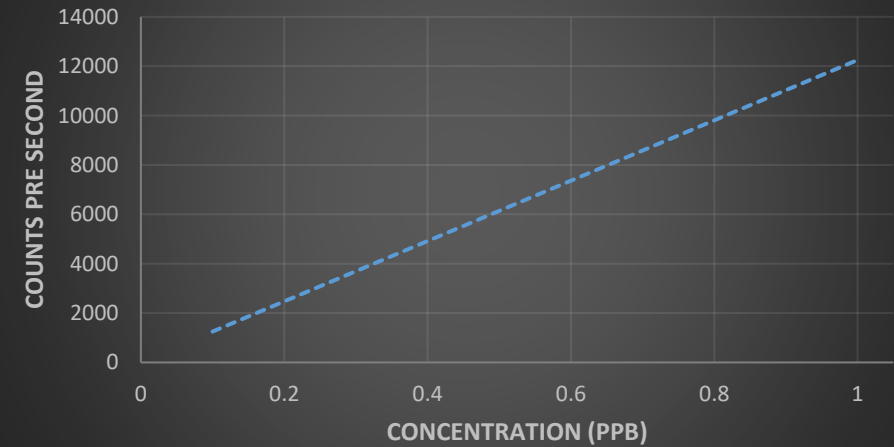


Calibration of Manganese (Mn)

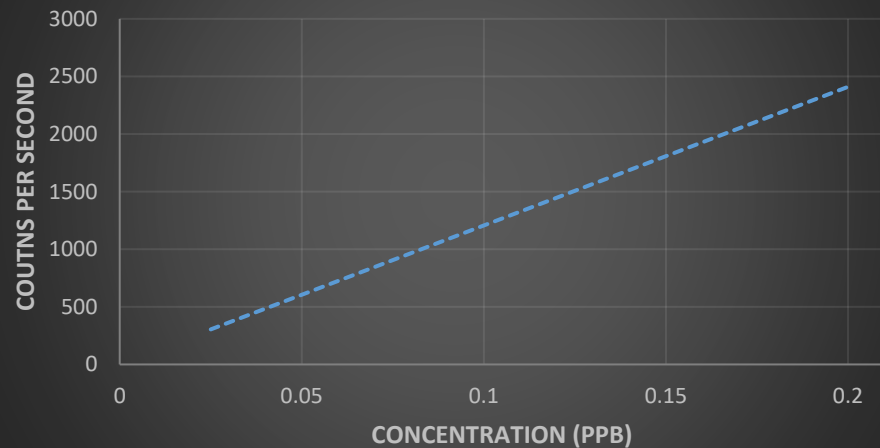
Calibration Curve



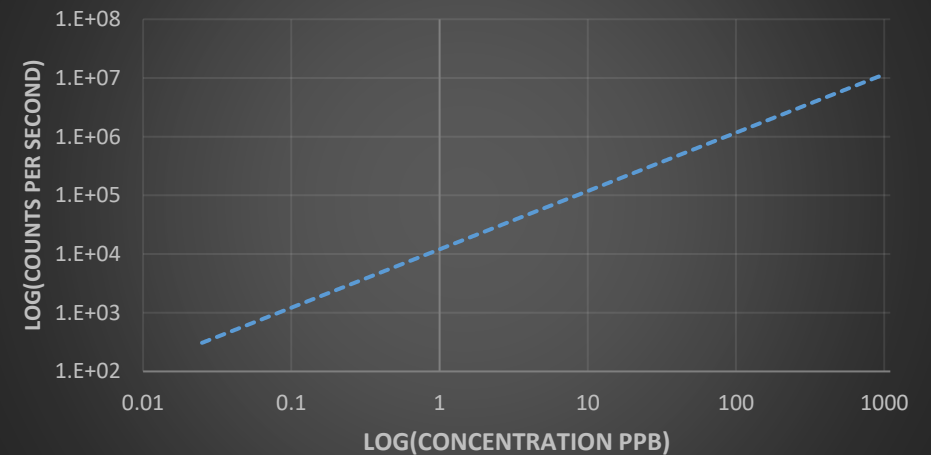
10,000X-1,000X Dilution Range



40,000X-5,000X Dilution Range

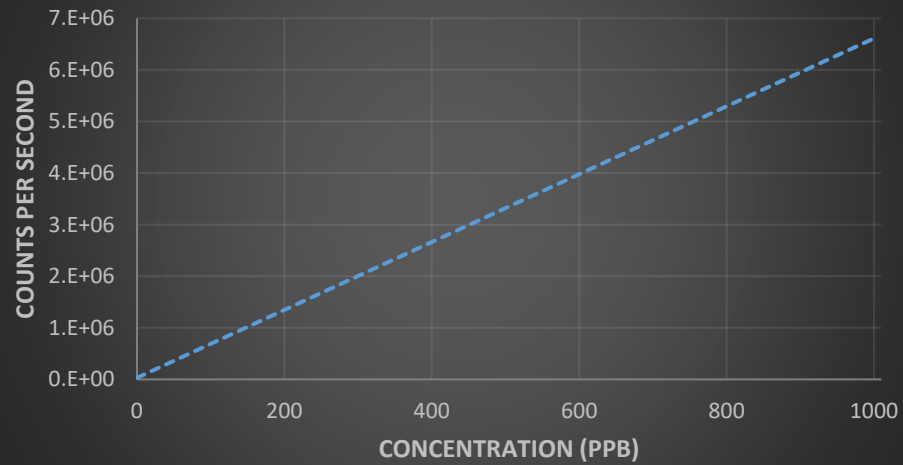


Log-Log Scale of Dilution

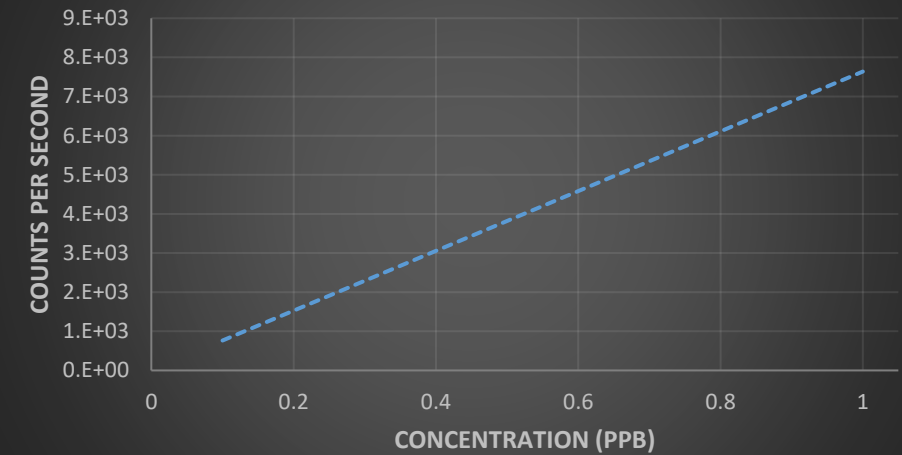


Calibration of Cadmium (Cd)

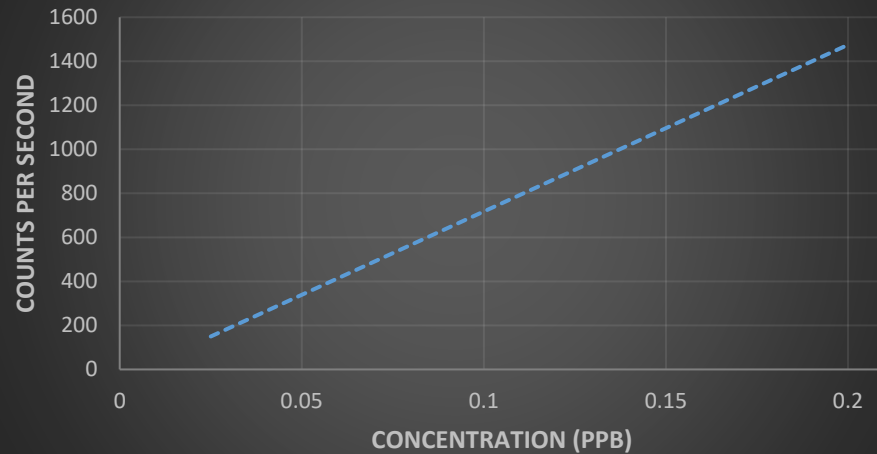
Calibration Curve (Cd)



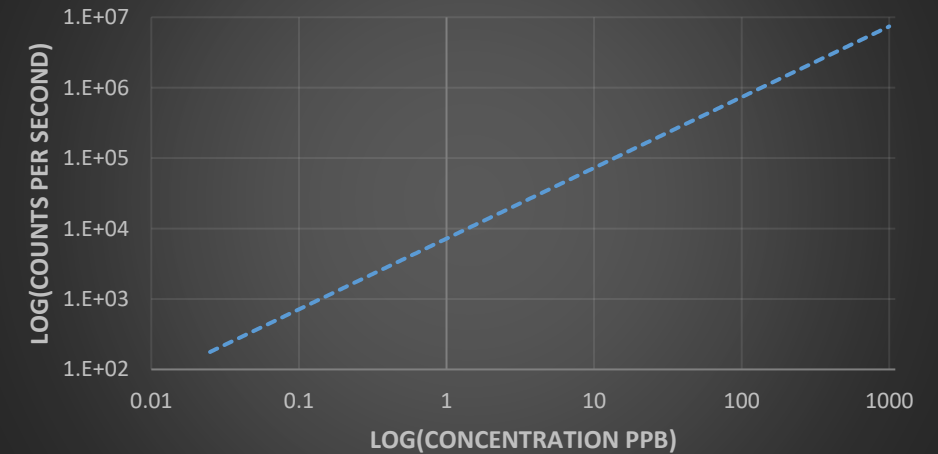
10,000X-1,000X Dilution Range



40,000X-5,000X Dilution Range



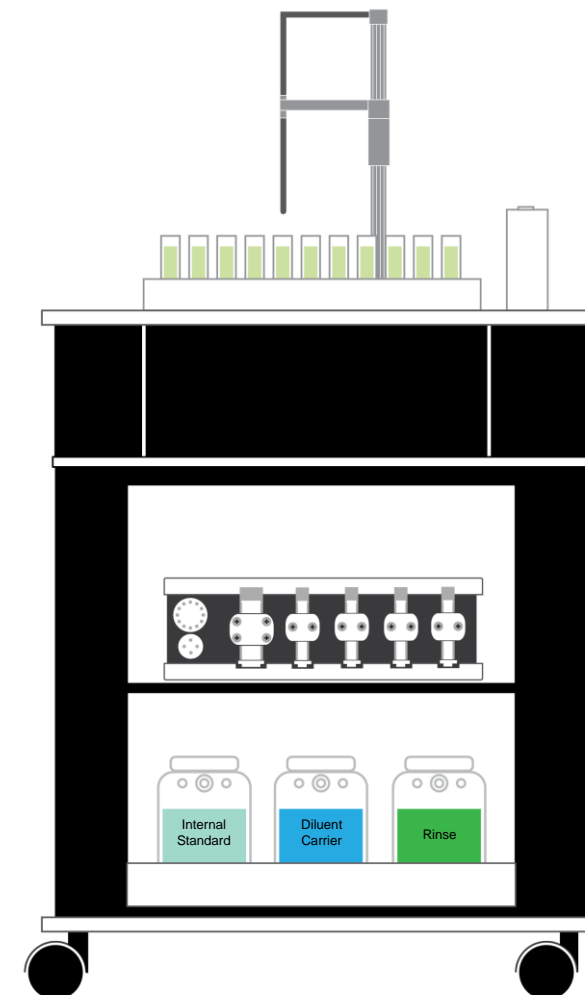
Log-Log Scale of Dilution



Lab Standard, prepFAST MAX vs Manual



- On deck concentrated standard
 - 1ppm 68A Elements from High Purity Standards
 - Aluminum, Arsenic, Barium, Beryllium, Bismuth, Boron, Cadmium, Calcium, Cerium, Cesium, Chromium, Cobalt, Copper, Dysprosium, Erbium, Europium, Gadolinium, Gallium, Holmium, Indium, Iron, Lanthanum, Lead, Lithium, Lutetium, Magnesium, Manganese, Neodymium, Nickel, Phosphorus, Potassium, Praseodymium, Rhenium, Rubidium, Samarium, Scandium, Selenium, Sodium, Strontium, Terbium, Thallium, Thorium, Thulium, Uranium, Vanadium, Ytterbium, Yttrium, Zinc
- prepFAST MAX 1x-20,000x inline dilution of standard



Lab Standard, prepFAST MAX vs Manual

- Manually diluted samples from same 1ppm Stock
 - 10X, 100X, 1,000X, 10,000X, 20,000X
 - 0.05ppb-1000ppb
- Ran as Unknowns at 1X dilution
- Compared counts of prepFAST MAX dilution vs Manual Dilutions

D.F.	Ho (165) MAX	Ho (165) Manual	%Recovery	Pb (208) MAX	Pb (208) Manual	%Recovery	Cu (63) MAX	Cu (63) Manual	%Recovery
20,000	14751	14477	101.9%	11676	11613	100.5%	1182	1134	104.2%
10,000	27486	28211	97.4%	20526	21229	96.7%	2053	2109	97.3%
1,000	290166	279846	103.7%	209938	202159	103.8%	19385	18818	103.0%
100	3035860	2869327	105.8%	2189836	2068591	105.9%	198682	187371	106.0%
10	29051424	29174117	99.6%	21038164	21092210	99.7%	1869262	1887958	99.0%
1	316459645	311535415	101.6%	225705831	222429102	101.5%	19204079	19021184	101.0%

How can we take advantage of this large inline dilution range?

Elemental Analysis of Digested Metals

- Designed to mimic metal analysis
 - Recycled or Pure
 - Major and trace metals
- NIST SRM 882 Nickel-Copper Alloy



National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material[®] 882

Nickel-Copper Alloy (65Ni-31Cu-3Al)
(granule form)

This Standard Reference Material (SRM) is intended primarily for use in validation of chemical and instrumental methods of analysis for element contents of nickel and nickel-copper alloys and materials of similar matrix. It can be used to validate value assignment of in-house reference materials. A unit of SRM 882 consists of one bottle containing approximately 100 g of granules.

Table 1. Certified Mass Fraction Values for SRM 882 Nickel-Copper Alloy

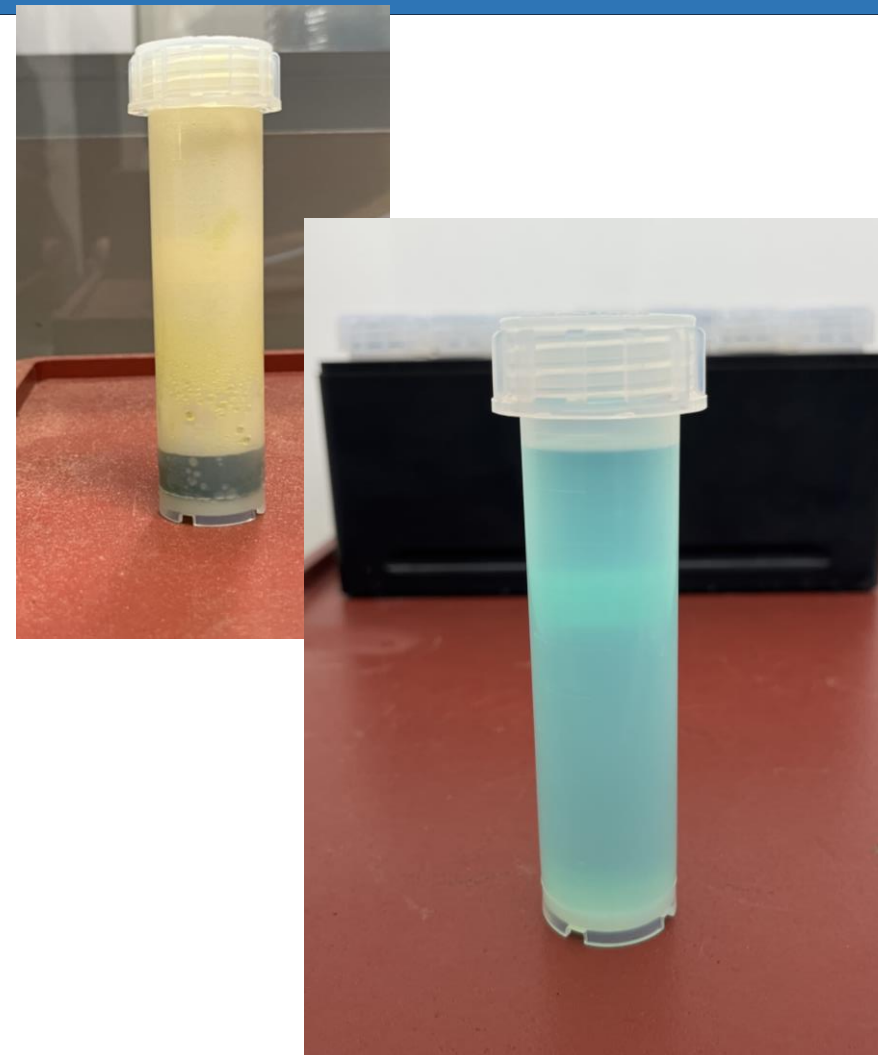
Constituent	Mass Fraction (%)	Expanded Uncertainty (%)
Aluminum (Al)	2.845	0.054
Carbon (C)	0.0065	0.0016
Copper (Cu)	31.035	0.075
Iron (Fe)	0.0093	0.0015
Nickel (Ni)	65.25	0.11
Titanium (Ti)	0.565	0.012

Table 4. Information Mass Fraction Values for SRM 882 Nickel-Copper Alloy

Constituent	Mass Fraction (%)
Arsenic (As)	0.0001
Boron (B)	0.0001
Chromium (Cr)	0.0001
Cobalt (Co)	0.007
Lead (Pb)	0.0006
Magnesium (Mg)	0.001
Manganese (Mn)	0.0007
Selenium (Se)	0.0002
Silver (Ag)	0.0004
Tin (Sn)	0.003
Vanadium (V)	0.0001
Zinc (Zn)	0.0005

Experimental Method

- Heated, Aqua regia digest
 - 8mL acid
 - 0.302g Metal SRM
- Diluted to 50mL
- ICPMS Calibrated from 500ppb-0.05ppb
 - 1X-10,000X dilution of 500ppb Calibration Standard
- Repeated twice and all data compiled



Major Elemental Composition in Digest

- prepFAST MAX inline dilution
 - Calibration and Sample
- Analyzed major elements at dilution factor that brings counts within calibration curve range

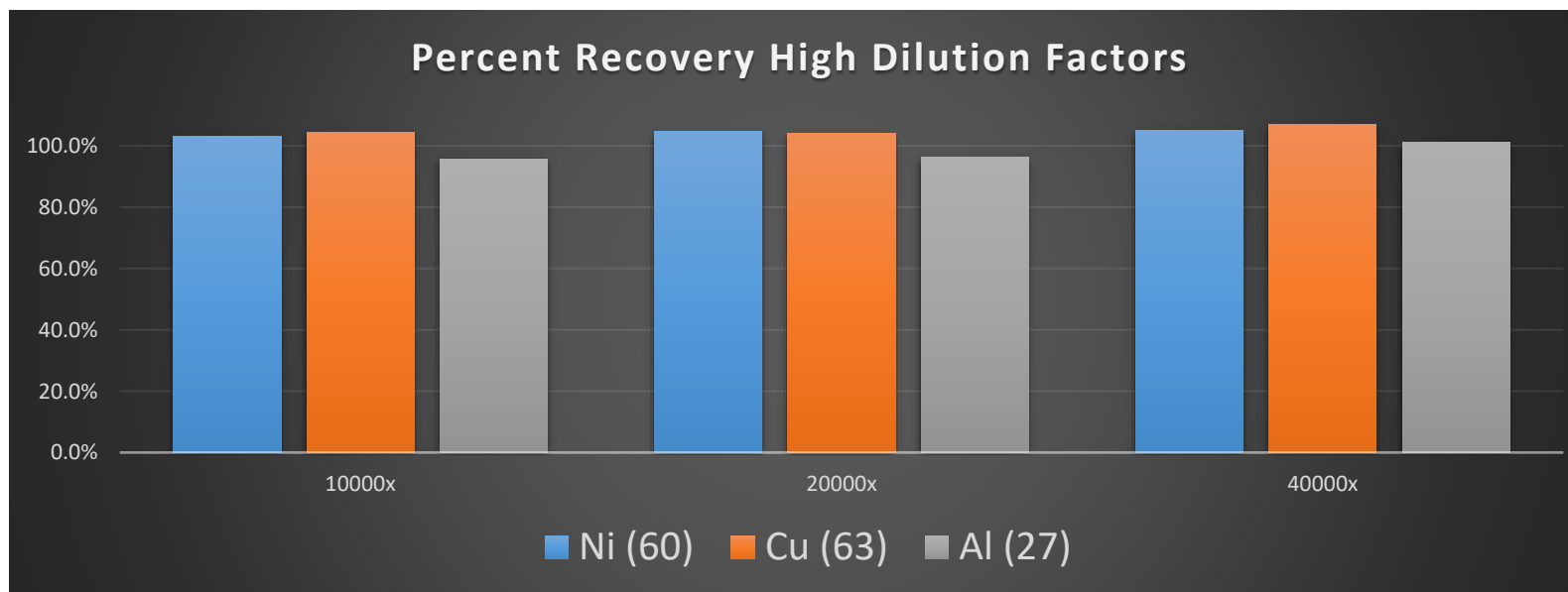
Element	Mass Fraction (%)	Concentration in Digest (ppb)	Minimum DF	Reported ppb at Min DF	%Recovery
Ni (60)	65.25 \pm 0.11	3,941,000 \pm 6,000	10,000	4,067,000	103.2%
Cu (63)	31.035 \pm 0.075	1,874,500 \pm 4,500	10,000	1,959,000	104.5%
Al (27)	2.845 \pm 0.054	171,800 \pm 3,300	1,000	171,700	99.9%
Ti (48)	0.565 \pm 0.012	34,100 \pm 730	100	37,500	110.0%

What if we increase the dilution factor?

Further prepFAST MAX Dilutions



Element	Concentration in Digest (ppb)	Reported ppb at 10,000X	%Recovery	Reported ppb at 20,000X	%Recovery	Reported ppb at 40,000X	%Recovery
Ni (60)	3,941,000 \pm 6,000	4,022,000	103.2%	4,128,000	104.7%	4,138,000	105%
Cu (63)	1,874,500 \pm 4,500	1,959,000	104.5%	1,949,000	104%	2,004,000	106.9%
Al (27)	171,800 \pm 3,300	164,600	99.9%	165,400	96.2%	173,500	101%



What about all of the other components?

Minor Elemental Composition in Digest

Element	Concentration in digest (ppb)	Reported ppb
Fe	560 \pm 91	661
As	6	12
B	6	158
Cr	6	10
Co	423	1683
Pb	36	37
Mg	60	195
Mn	42	49
Se	12	52
Ag	24	19
Sn	181	138
V	6	25
Zn	30	51

- Ran at 10X dilution
- Agreement of trace elements
- ppb detection with ICPMS is common
- Performed alongside 1,000's ppm of elements

Mass Fraction Summary

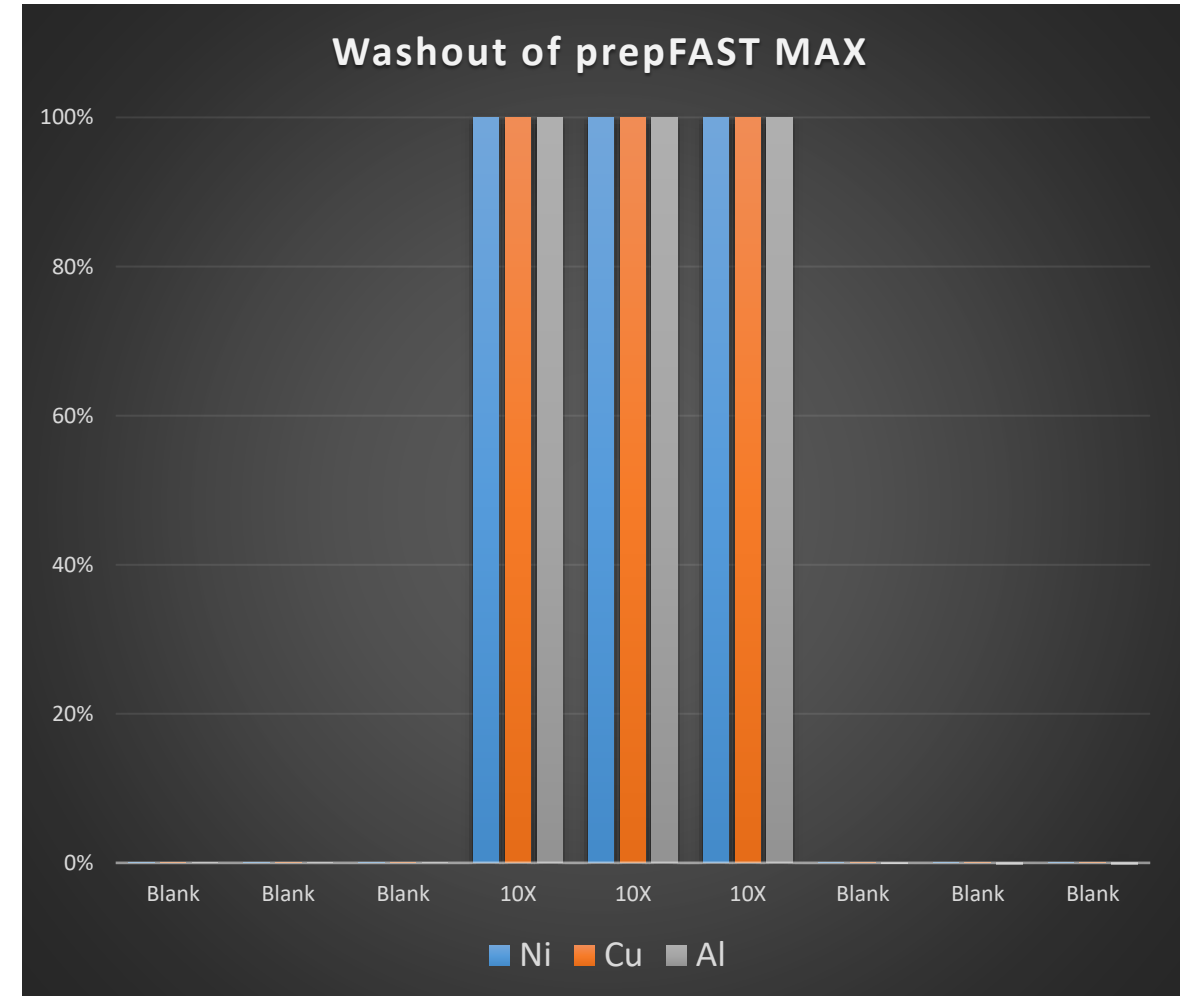


- Great agreement between CoA and our analysis
- Thousands of ppm down to a several ppb
- prepFAST MAX utilized ultra-high Inline Dilution to allow for analysis on single instrument

Element	CoA Mass Fraction (%)	Analysis Mass Fraction (%)
Al	2.845 ±0.054	2.843
Cu	31.035 ±0.075	32.43
Fe	0.0093 ±0.0015	0.011
Ni	65.25 ±0.11	67.33
Ti	0.565 ±0.012	0.62
As	0.0001	0.0002
B	0.0001	0.0026
Cr	0.0001	0.0002
Co	0.007	0.028
Pb	0.0006	0.0006
Mg	0.001	0.003
Mn	0.0007	0.0008
Se	0.0002	0.0009
Ag	0.0004	0.0003
Sn	0.003	0.0023
V	0.0001	0.0004
Zn	0.0005	0.0008

Metal Digest Wash Out

- Blanks ran in between all samples
- >10,000X washout after top point
 - 400ppm Ni
 - 200ppm Cu
 - 16ppm Al



Plating Bath Samples

- Customer sent samples of 3 plating bath solutions
 - Interested in Cr, Fe, Ni, and Zn concentrations
 - Originally ran on an Agilent ICP OES for customer
 - Also decided to test for Mn and Pb with ICPMS
 - Thousands of ppm
- Analyzed at 10,000X and 100X dilution factors



Plating Bath Concentrations



Concentration (ppm) of Elements in Plating Solutions

Sample	Dilution Factor	Cr (52)	Mn (55)	Fe (56)	Ni (60)	Cu (63)	Zn (66)	Pb (208)
3205	10000	4377 \pm 1.9%					3425 \pm 2.5%	
	100		0.63 \pm 2.4%	15.4 \pm 2.5%	1.4 \pm 1.6%	0.25 \pm 2.0%		0.035 \pm 5.2%
3225	10000			4024 \pm 1.6%			9923 \pm 2.0%	
	100	13.2 \pm 2.3%	85.9 \pm 2.6%		5.4 \pm 1.4%	1.5 \pm 4.2%		12.6 \pm 3.7%
200UB	10000	6579 \pm 2.8%						
	100		0.012 \pm 3.1%	0.54 \pm 2.3%	0.41 \pm 1.8%	0.026 \pm 2.9%	0.50 \pm 2.2%	0.007 \pm 3.7%

Comparison of prepFAST MAX to Manual dilutions



- Previously manually diluted samples 100x and analyzed on an Agilent ICP

	Cr	%RSD	Fe	%RSD	Ni	%RSD	Zn	%RSD
3205 prepFAST MAX	4377	1.9	15.4	2.5	1.4	1.6	3425	2.5
3205 Manual	4086	0.3	13.8	0.5	3.0	13.5	2828	0.2
3225 prepFAST MAX	13.2	2.3	4024	1.6	5.4	1.4	9923	2.0
3225 Manual	11.2	3.4	3624	0.4	6.2	1.3	7342	0.4
200UB prepFAST MAX	6579	2.8	0.54	2.3	0.41	1.8	0.50	2.2
200UB Manual	6671	0.9	0.2	4.3	0.3	77.8	-0.7	30.5

River Sediment SRM



- 1ppm on deck standard in 4% HNO_3
 - 1X-10,000X dilution to calibrate ICPMS
- High Purity Standards CRM-RS-A
 - River Sediment CRM
 - Ran as an Unknown with Auto Over-range Dilution Enabled



7221 Investment Drive • North Charleston, SC 29418
843.767.7900 • info@highpuritystandards.com • www.highpuritystandards.com

Certificate of Analysis

Certified Reference Material

Product Description: River Sediment Solution A

Product Number: CRM-RS-A-500
Lot Number: 2028136-500
Matrix: 4% HNO_3
Purity: 99.97%-99.9999%



Certified Values:

Element	($\mu\text{g/mL}$)	SRM ID	Element	($\mu\text{g/mL}$)	SRM ID
Al	250 ± 3	3101a	Mn	8.0 ± 0.1	3132
As	0.60 ± 0.03	3103a	Na	50.0 ± 0.5	3152a
Ba	0.500 ± 0.005	3104a	Ni	0.500 ± 0.005	3136
Ca	300 ± 3	3109a	Pb	7.00 ± 0.07	3128
Cd	0.100 ± 0.002	3108	Sb	0.50 ± 0.02	3102a
Co	0.100 ± 0.002	3113	Se	0.020 ± 0.002	3149
Cr	300 ± 3	3112a	Th	0.020 ± 0.001	3159
Cu	1.00 ± 0.01	3114	Tl	0.010 ± 0.001	3158
Fe	1200 ± 7	3126a	U	0.0100 ± 0.0005	3164
K	150 ± 2	3141a	V	0.250 ± 0.005	3165
Mg	70.0 ± 0.7	3131a	Zn	15.0 ± 0.2	3168a

Certified values are based on gravimetric and volumetric preparation, and verified against NIST SRM 3100 series when available via inductively coupled plasma optical emission spectrometry (ICP-OES) and/or inductively coupled plasma mass spectrometry (ICP-MS) using an internal laboratory-developed method. The uncertainty in the certified value is calculated for a 95% confidence interval and coverage factor k is about 2.

* Refer to Traceability Information, Section 4

River Sediment %Recovery



- Low concentration elements within calibration range
- prepFAST MAX re-runs sample at dilution factor

Element	Concentration (ppm)	%Recovery at 1X	%Recovery Auto over range
Ni (60)	0.5	109.8%	
Cu (63)	1	101.7%	
Cd (111)	0.1	104.4%	
Th (232)	0.02	93.5%	
U (238)	0.01	91.4%	
Al (27)	250	O/R	107.4%
Mn (55)	8	O/R	104.7%
Fe (56)	1200	O/R	99.0%

Conclusions

- Shown the prepFAST MAX can dilute linearly over 40,000X range
 - Calibrate ICPMS linearly as well
- Dilution of Standards and Samples performed INLINE
- prepFAST MAX can be utilized to analyze concentrated samples on ICPMS



Questions

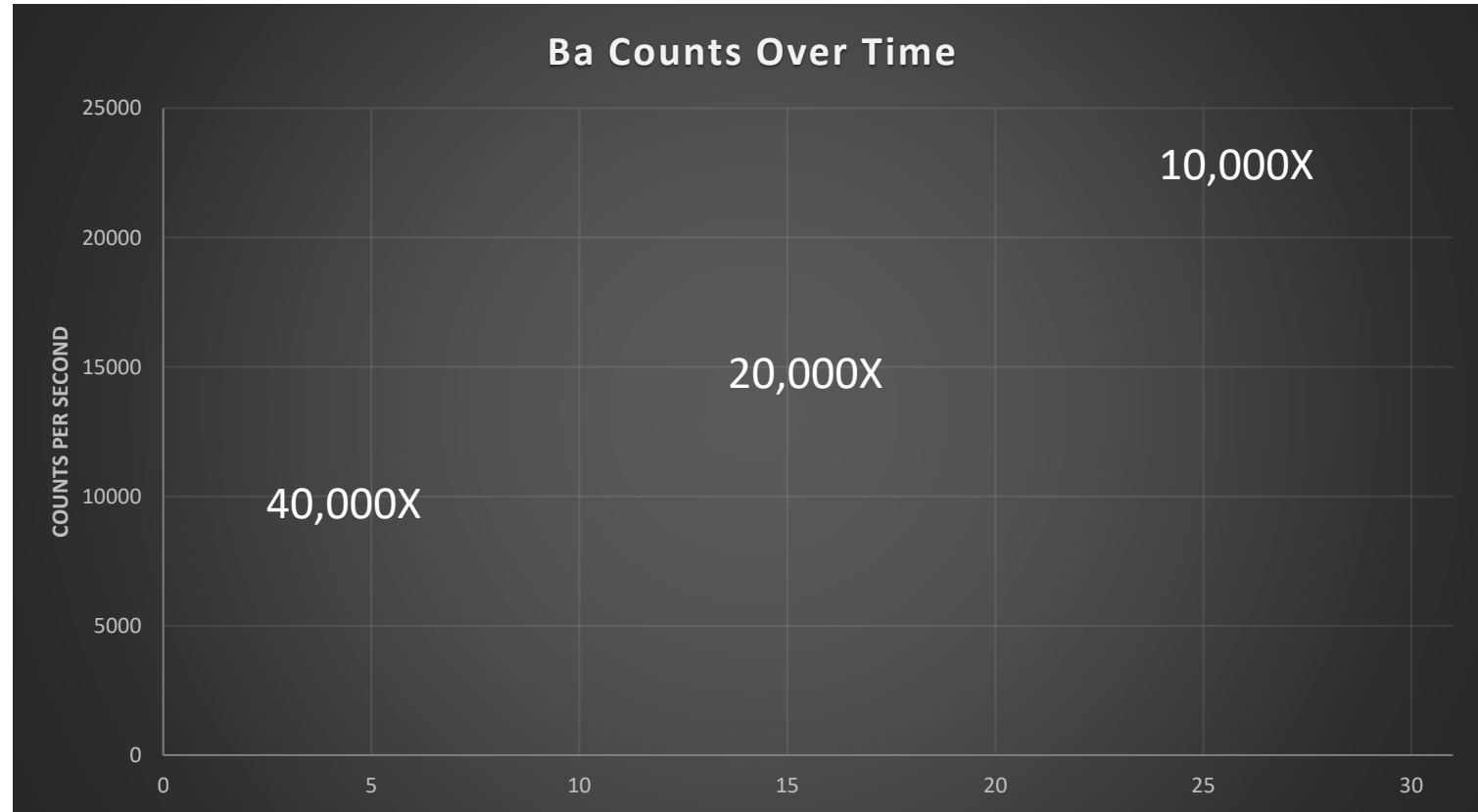


Experimental Instrumentation

- All analysis was performed on a Thermo iCAP TQ ICPMS
- Quartz Cyclonic spray chamber
- PFA ICN nebulizer
- Quartz torch with 2.0mm injector



Ba reproducibility over time



prepFAST MAX vs Manual Dilution



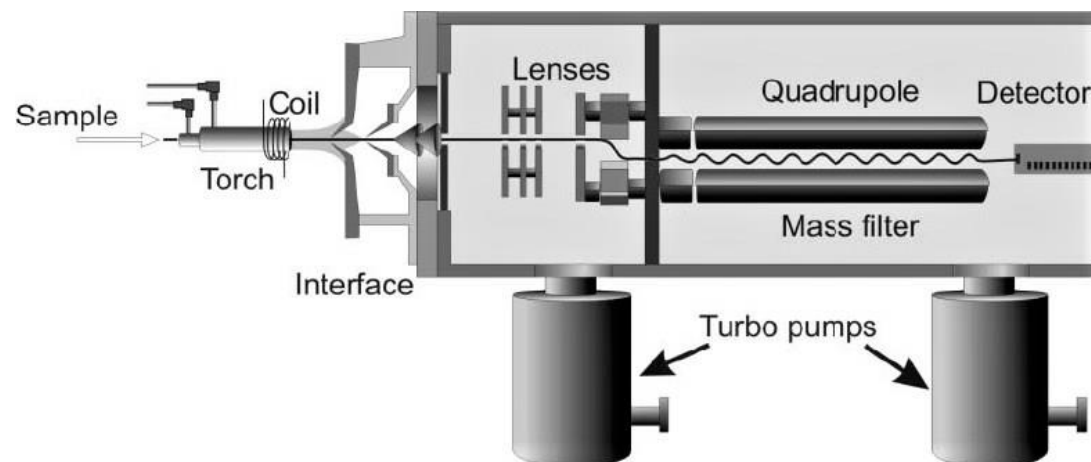
- Manually diluted digest: 10, 100, 1,000, and 10,000X

Element	Concentration in Digest (ppb)	prepFAST MAX ppb at Min DF	%RSD	Manual dilution ppb	%RSD
Ni (60)	3,941,000 \pm 6,000	4,067,000	6.0%	3,857,000	3.6%
Cu (63)	1,874,500 \pm 4,500	1,959,000	5.9%	1,863,000	3.0%
Al (27)	171,800 \pm 3,300	171,700	6.3%	166,300	3.3%
Ti (48)	34,100 \pm 730	37,500	5.2%	34,000	3.1%
Fe (56)	560 \pm 91	661	1.8%	643	3.2%
Pb (208)	36	37	6.4%	34	5.4%
Zn (66)	30	51	4.2%	56	4.1%
Ag (107)	24	19	4.1%	19	3.5%

Inductively Coupled Plasma Mass Spectrometer (ICPMS)

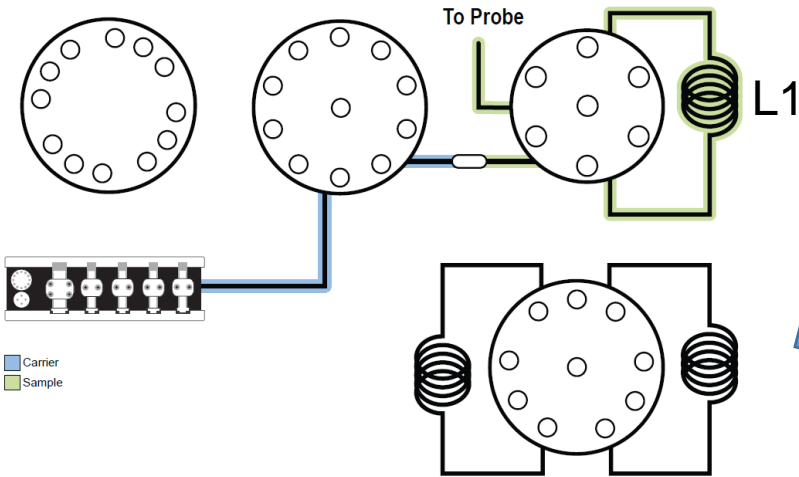


- Uses an inductively coupled plasma to generate positive ions
- Quadrupole then separates ions based on mass:charge ratio
- Low detection limits
- Rapid analysis times
- Multi-element detection



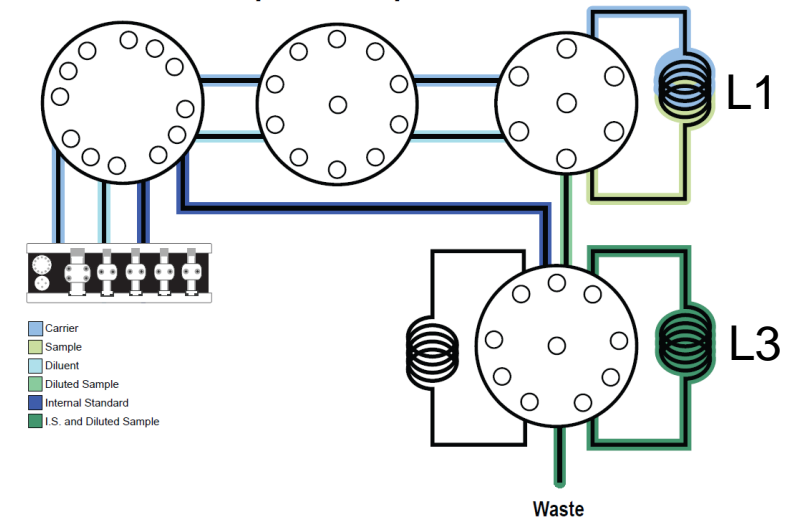
Simple explanation of prepFAST MAX Function

Load Sample



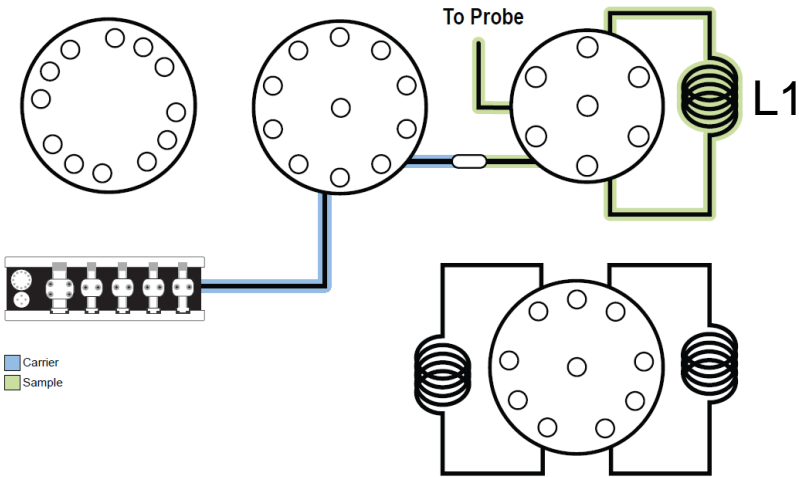
Small Dilutions

Dilute From Loop 1 to Loop 3

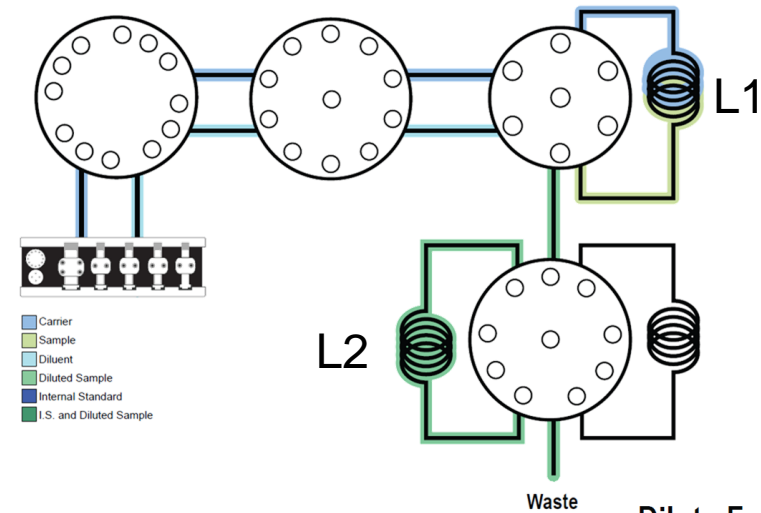


Simple explanation of prepFAST MAX Function

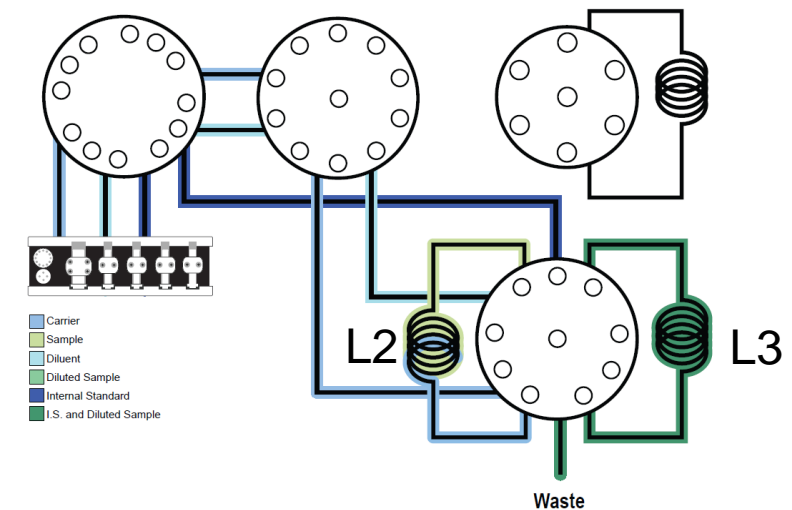
Load Sample



Dilute Into Loop 2



Dilute From Loop 2 to Loop 3



Lab Standard, prepFAST MAX vs Manual

- Manually diluted samples from same 1ppm Stock
 - 10X, 100X, 1,000X, 10,000X, 20,000X
 - 0.05ppb-1000ppb
- Ran as Unknowns at 1X dilution
- Concentration calculated from calibrated ICPMS

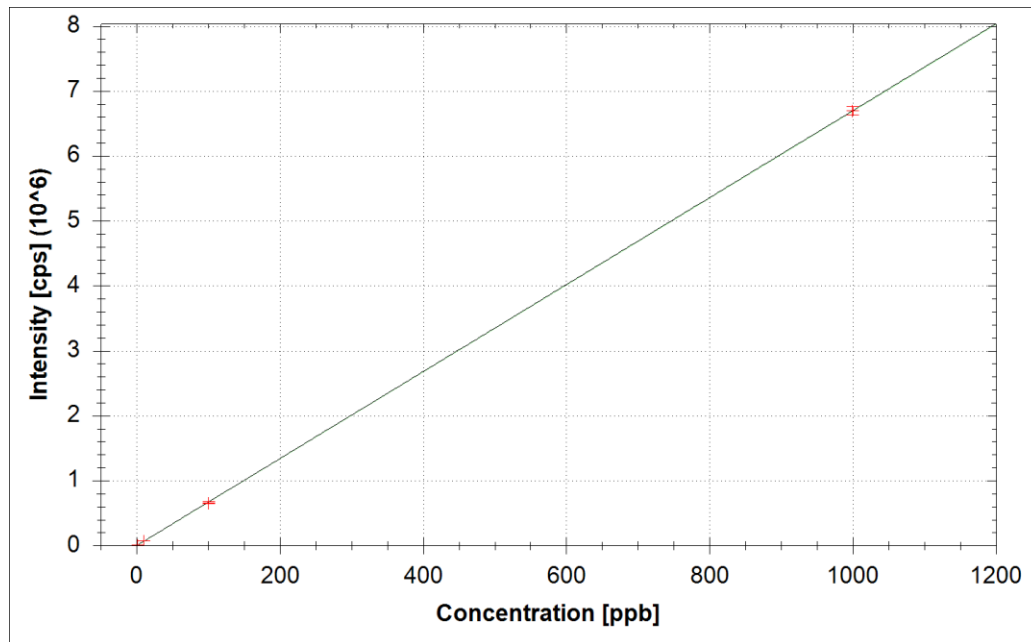
Concentration (ppb)	Co (59)	Ni (60)	Cu (63)	Ho (165)	Pb (208)
0.05	0.050	0.050	0.050	0.048	0.049
0.1	0.099	0.102	0.103	0.094	0.094
1	0.985	0.996	1.008	0.933	0.940
10	9.98	9.99	10.13	9.57	9.60
100	98.6	99.7	101.0	97.3	97.1
1000	995	996	1002	1039	1048

Autocalibration of ICPMS

Nickel (Ni 60)

$R^2 = 1.0000$

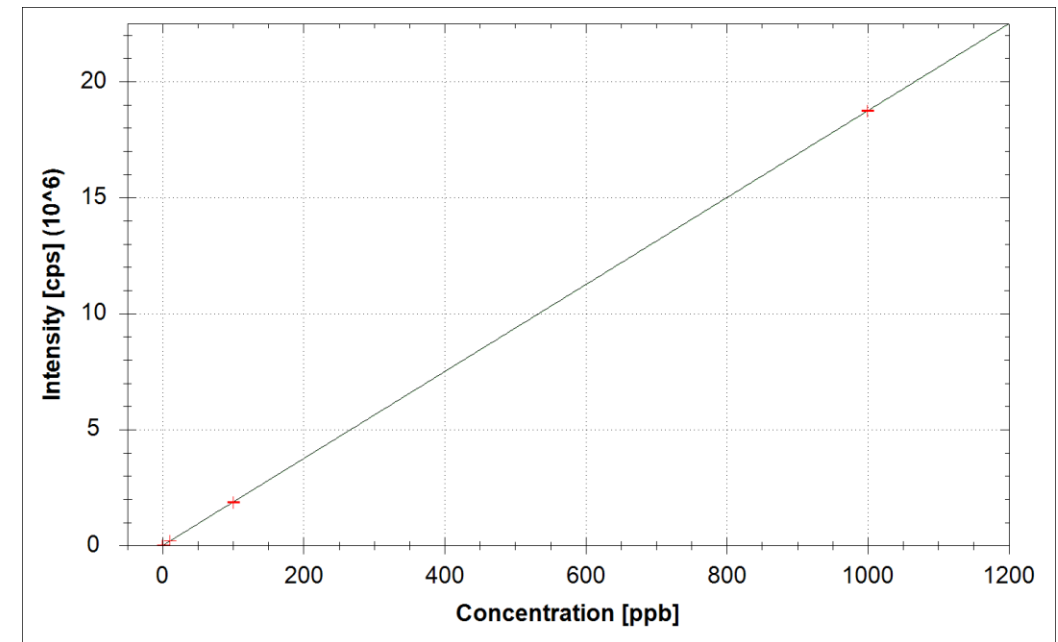
LoD = 0.0067 ppb



Copper (Cu 63)

$R^2 = 1.0000$

LoD = 0.0067 ppb

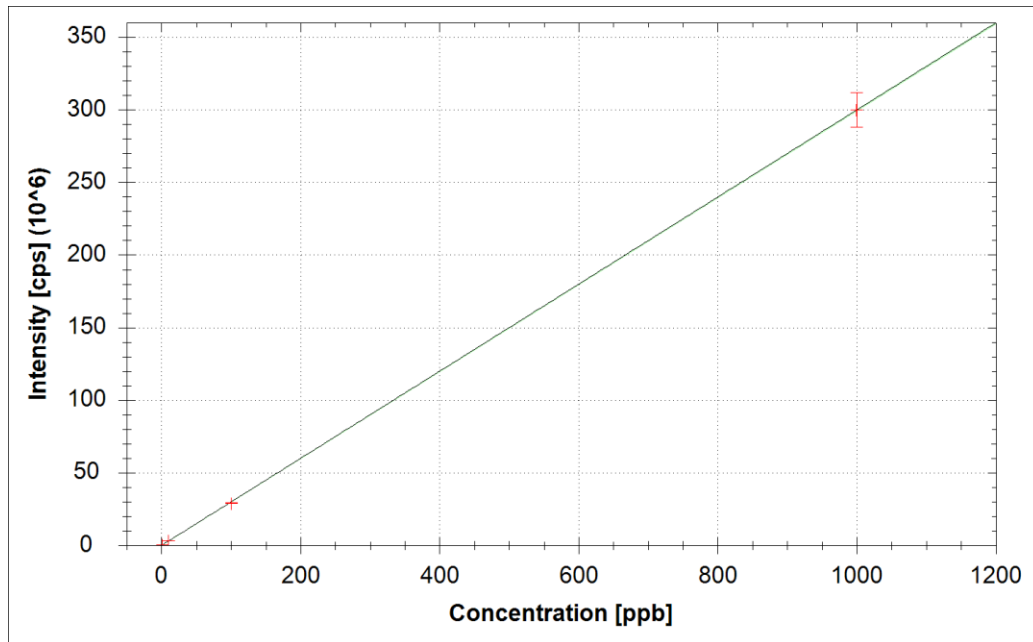


Autocalibration of ICPMS

Holmium (Ho 165)

$R^2 = 1.0000$

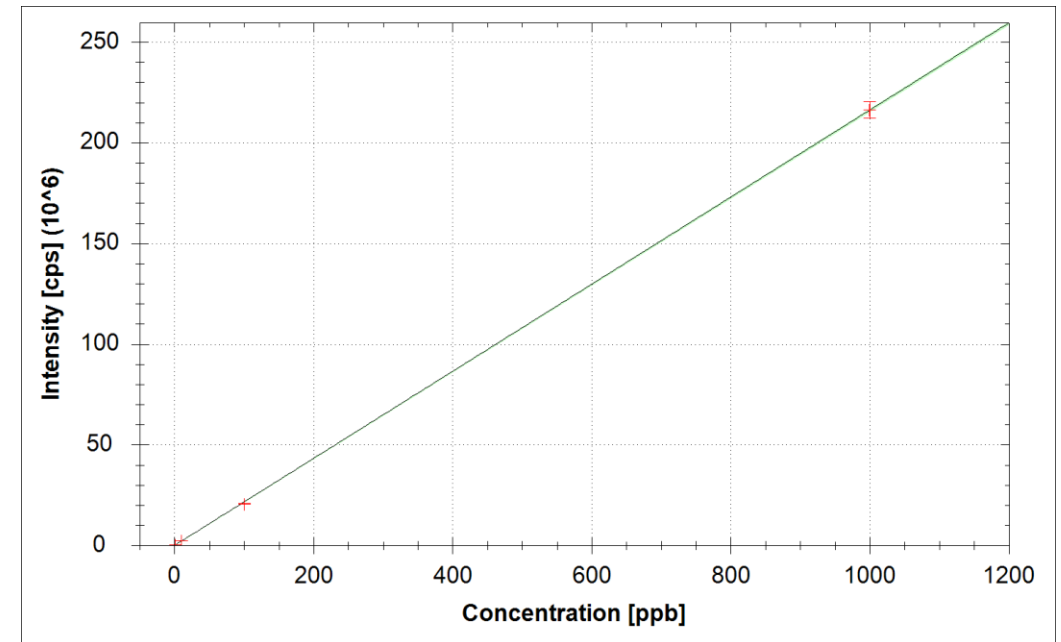
LoD = 0.0003 ppb



Lead (Pb 208)

$R^2 = 1.0000$

LoD = 0.0008 ppb



- 10 samples at 20,000x, 10,000x
- 3 samples at 1000x, 100x, 10x, 1x
- Software calculates concentration of elements in stock based on dilution factor

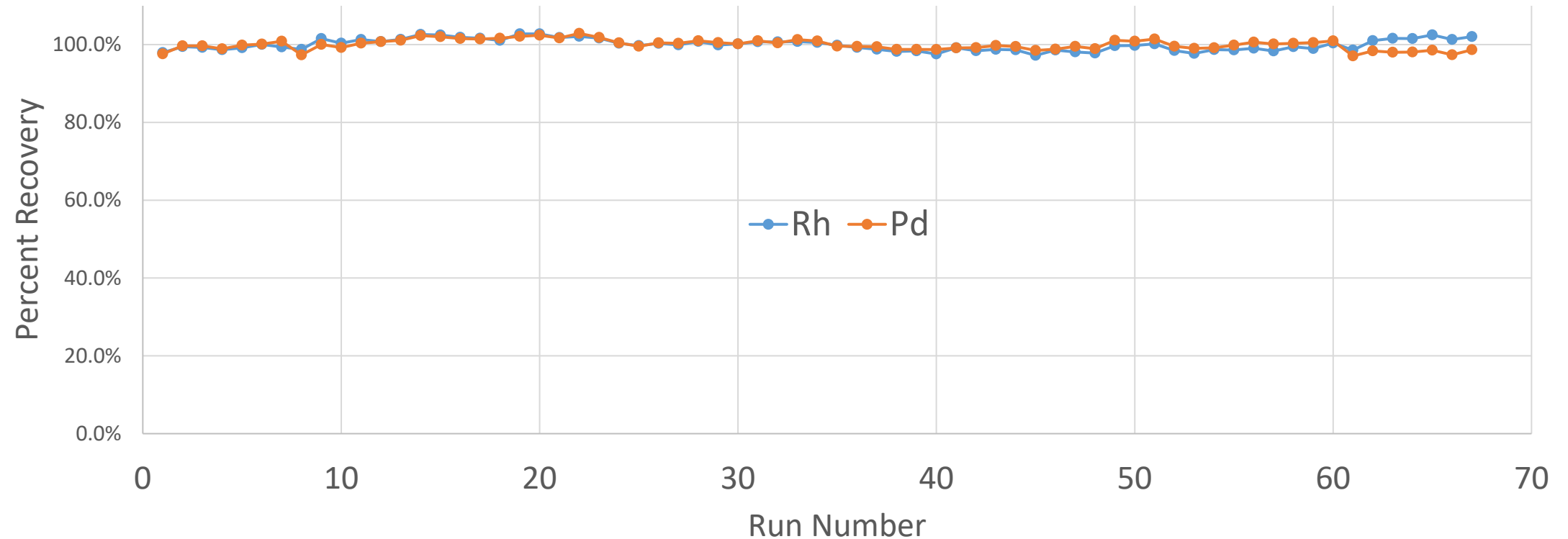
%Recovery



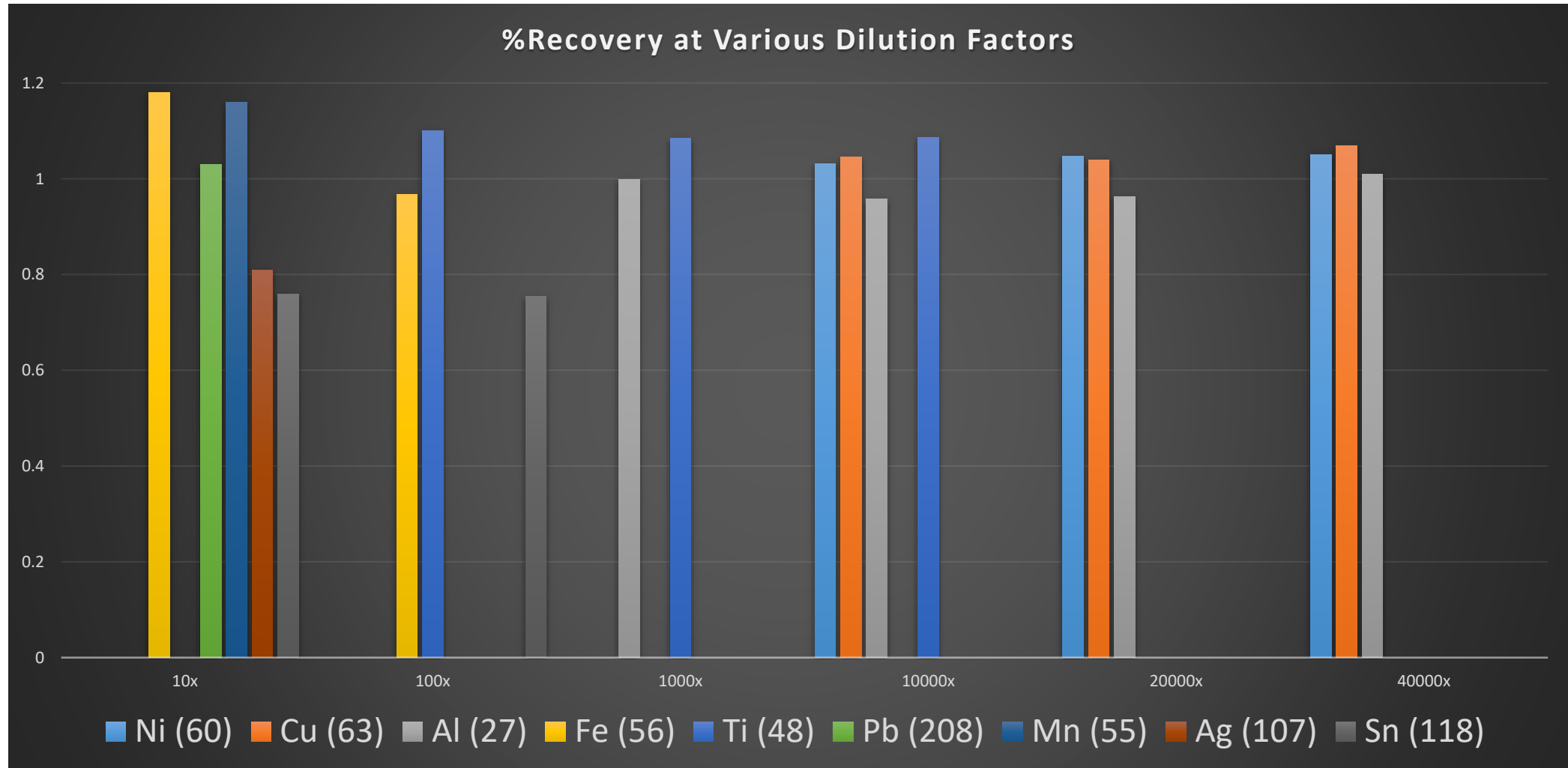
Dilution Factor	%Rec Co(59)	%Rec Ni(60)	%Rec Cu(63)	%Rec Ho(165)	%Rec Pb(208)
20000	101.0%	98.9%	103.3%	97.3%	97.7%
10000	95.4%	95.1%	99.0%	91.1%	90.4%
1000	101.4%	101.7%	103.3%	96.7%	96.9%
100	103.9%	104.2%	105.4%	101.3%	99.8%
10	97.6%	98.4%	100.2%	96.9%	96.6%
1	99.9%	99.7%	100.0%	105.6%	106.0%

Internal Standard of Lab Samples

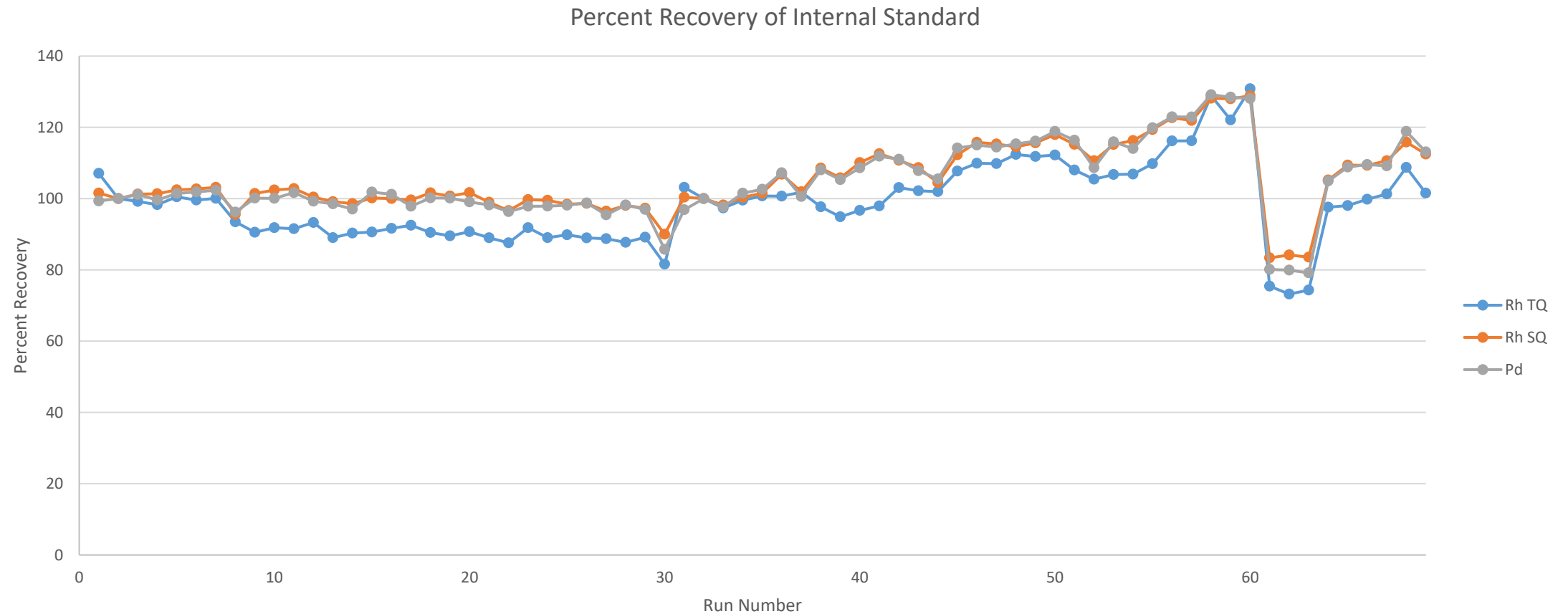
Percent Recovery of Internal Standards



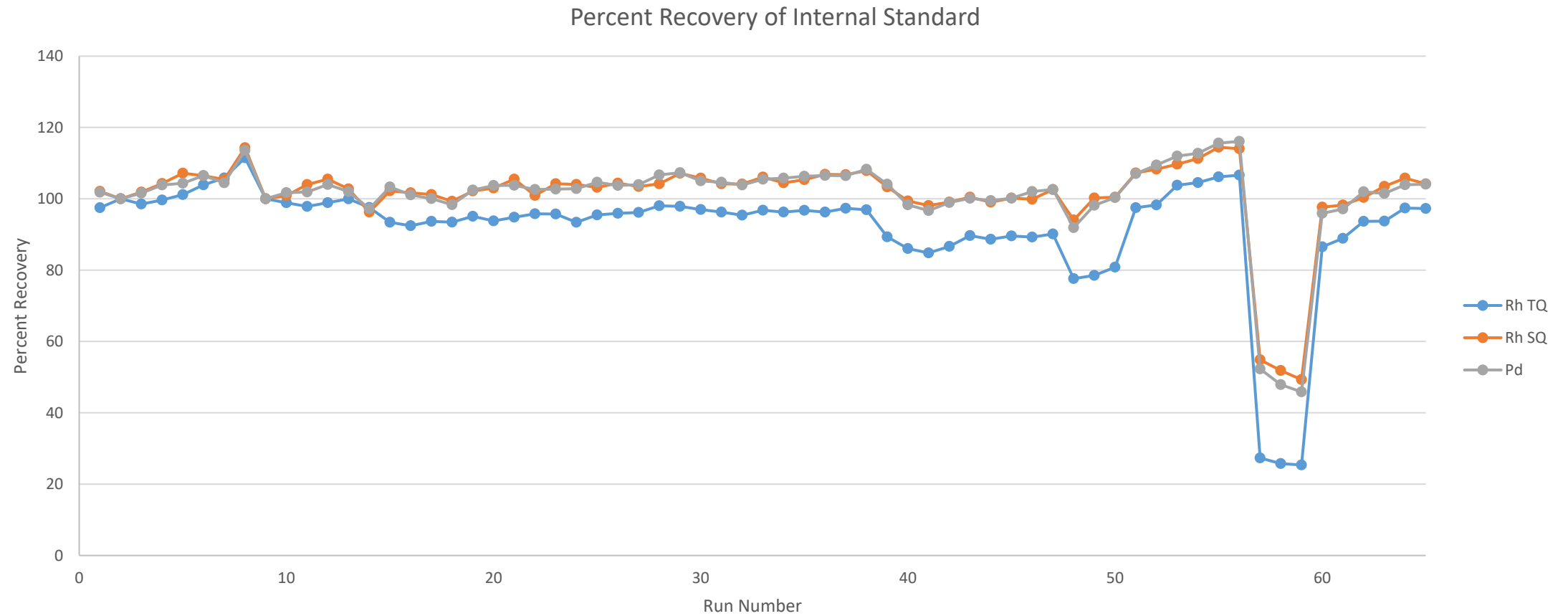
Percent Recovery



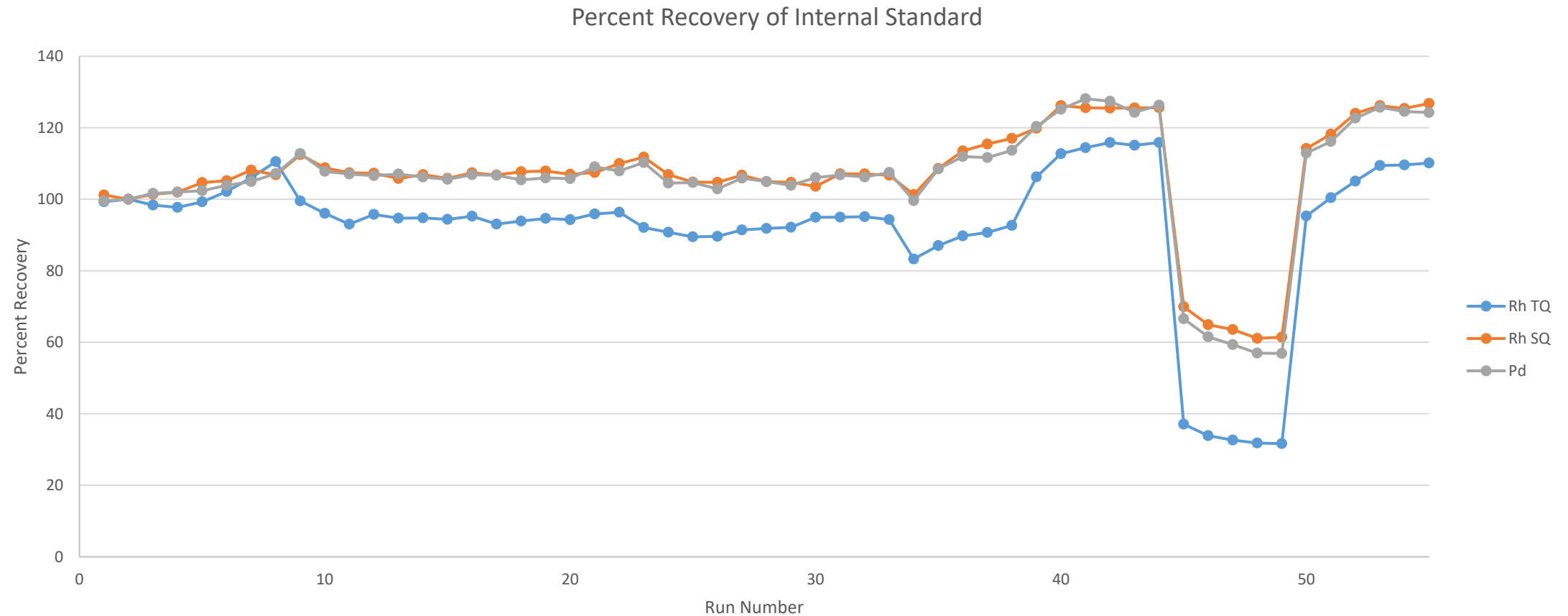
Internal Standard of Digest 1



Internal Standard of Digest 2



Internal Standard of Manual Dilutions of Digest



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- Connor Lejcher
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