Department of Toxic Substances Control

Hexavalent Chromium in Drinking Water

By IC-ICP-MS

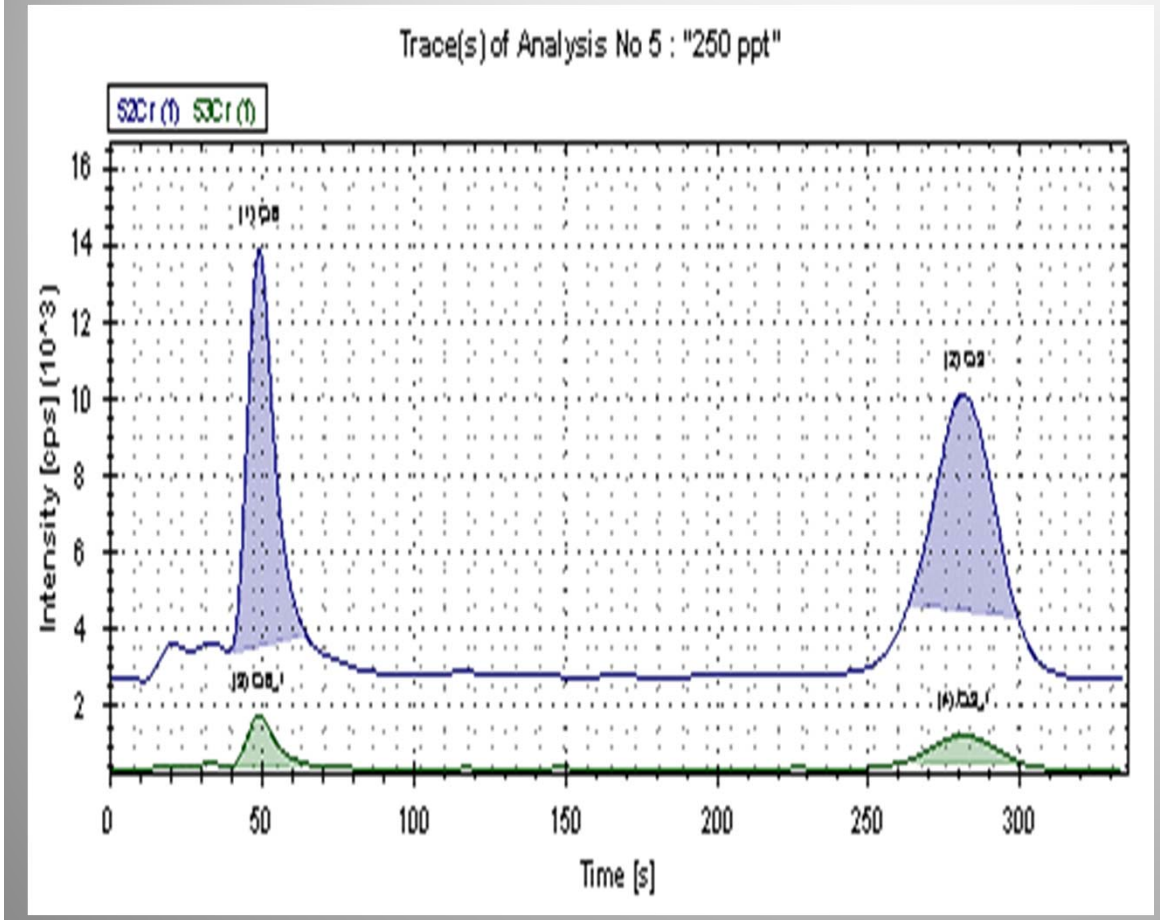
The Thermo Scientific iCAP Q with the Thermo Scientific Dionex ICS-5000+ HPIC System

2014

Overview

- Chromium oxidation states
  - Cr^{+6}/Cr^{+3}
- Current regulations
  - 2011 US EPA recommends monitoring of Cr^{+6}
  - 7-2011 – OEHHA establishes 20 ppt PHG
  - 7-2014 – CDPH sets 10 ppb MCL
- EPA Methods – IC w/ post column derivatization
  - 1,5-diphenylcarbazide, UV detection
  - Susceptible to interference from Fe and Mn
- Direct measurement using iCap-Q ICP-MS
  - ${}_{35}Cl_{16}O_1H+$ or ${}_{40}Ar_{12}C+$ mitigated by CCT/KED
- Isotope ratio confirmation ($^{52}Cr/^{53}Cr$)
- Achieve 20 ppt report limit in drinking water

Initial Method: Isocratic (from Thermo App Note)



250 ppt Cr^{+6} & Cr^{+3} in DI

<u>Column</u>:

- Thermo Dionex IONPAC AG-7, 2x50mm
- Mobile phase: 0.3 M HNO_3
- Flow rate: 0.4 mL/minute
- Temperature: ambient
- Injection volume: 100 µL

<u>ICP-MS</u>

- RF power: 1550 W in KED mode
- Nebulizer flow: 1.05 L/min
- Dwell time: 0.05s/isotope
- Isotopes monitored:
- ^{52}Cr, ^{53}Cr (8:1 ratio)

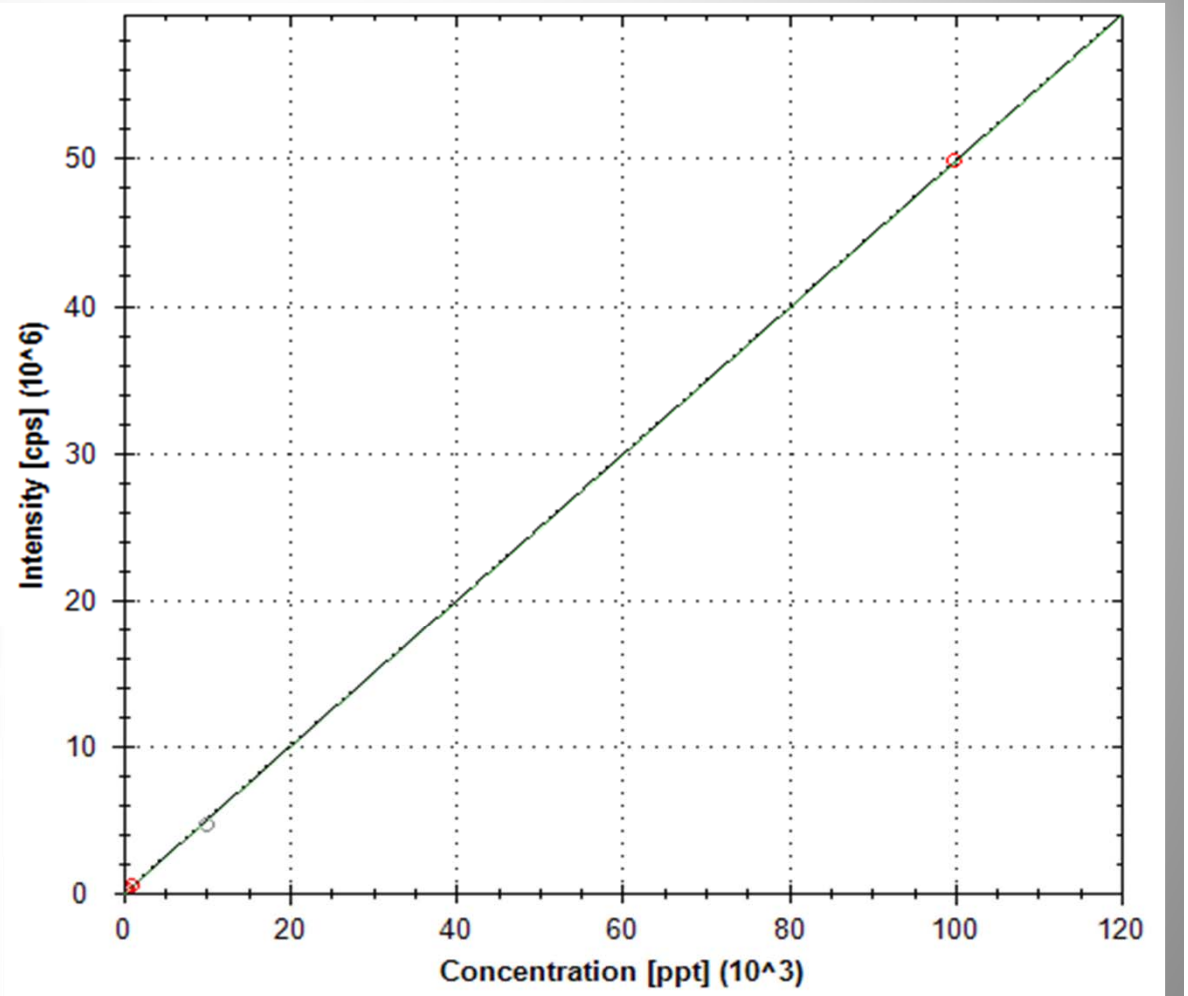
Chromium 6 retention time ~ 48 s

<u>Sample prep</u>:

- 0.1 M ammonium nitrate, pH = 4.0
- Filtered (0.45 µm)

Isocratic Linear Calibration

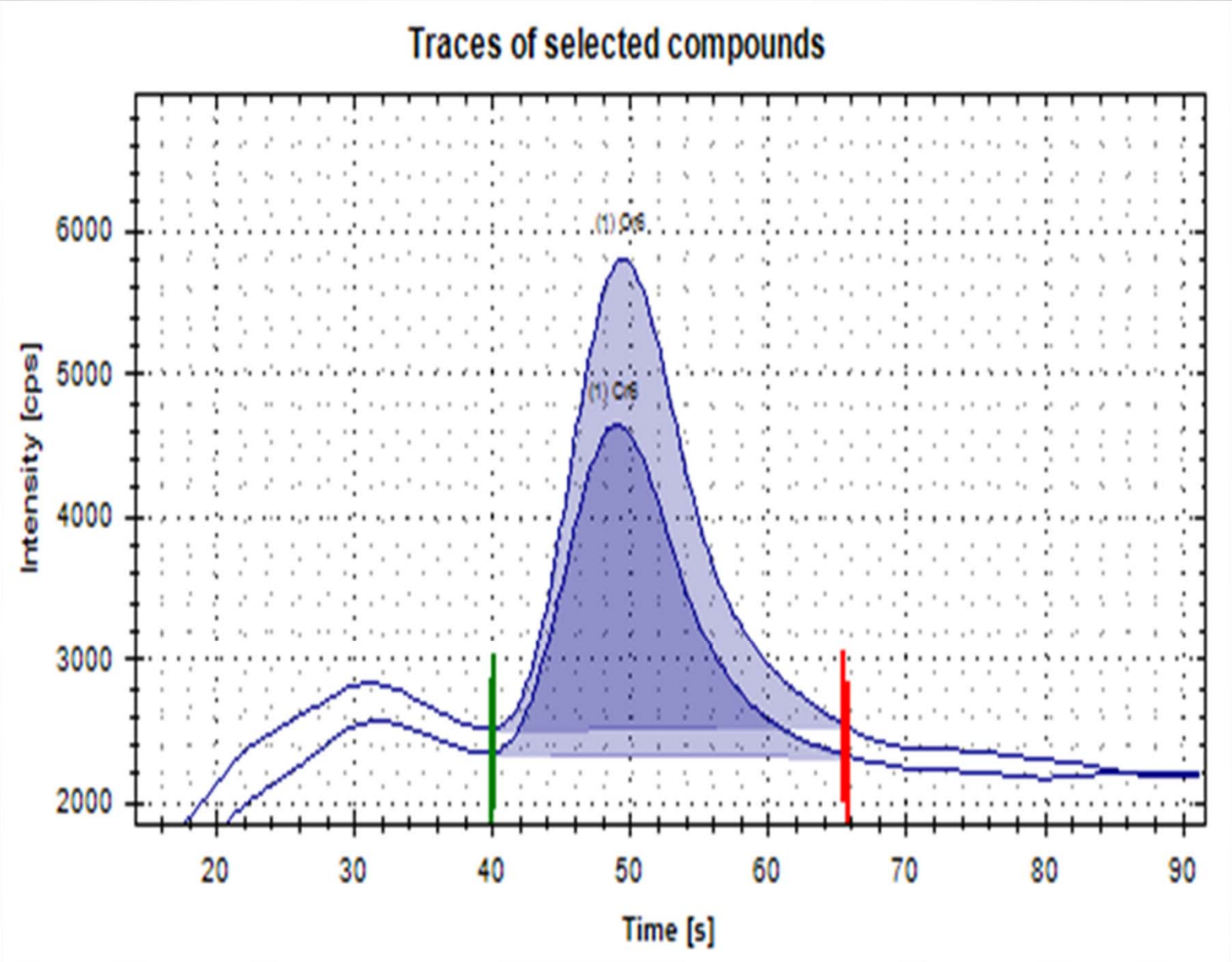
- 5 point calibration
  - 20 -1000 ppt
- $R^2 > 0.999$
- ~500 counts/ppt
- Background Equivalent Concentration
  - [(BEC = a/b)]
- BEC range = [1.8 – 25 ppt]
- *BEC 9%-125% of low standard*



f(x) = b*x + a

Parameter	Value	Confidence Delta at 90%	StdErr	Rel. StdErr [%]
b	497.826	+/-0.38182733	0.265	0.053
a	-2,021.345	+/-15,589.01974385	10,827.212	-535.644
R	0.99999943			
BEC	-4.060 ppt			

Tap Water with 20 ppt Cr^{+6} Spike



Isocratic Method Detection Limit

1	2	3	4	5	6	7	8	Avg	SD	MDL
24.0	24.8	23.2	23.9	24.1	24.3	24.0	24.6	24.1	0.485	1.45

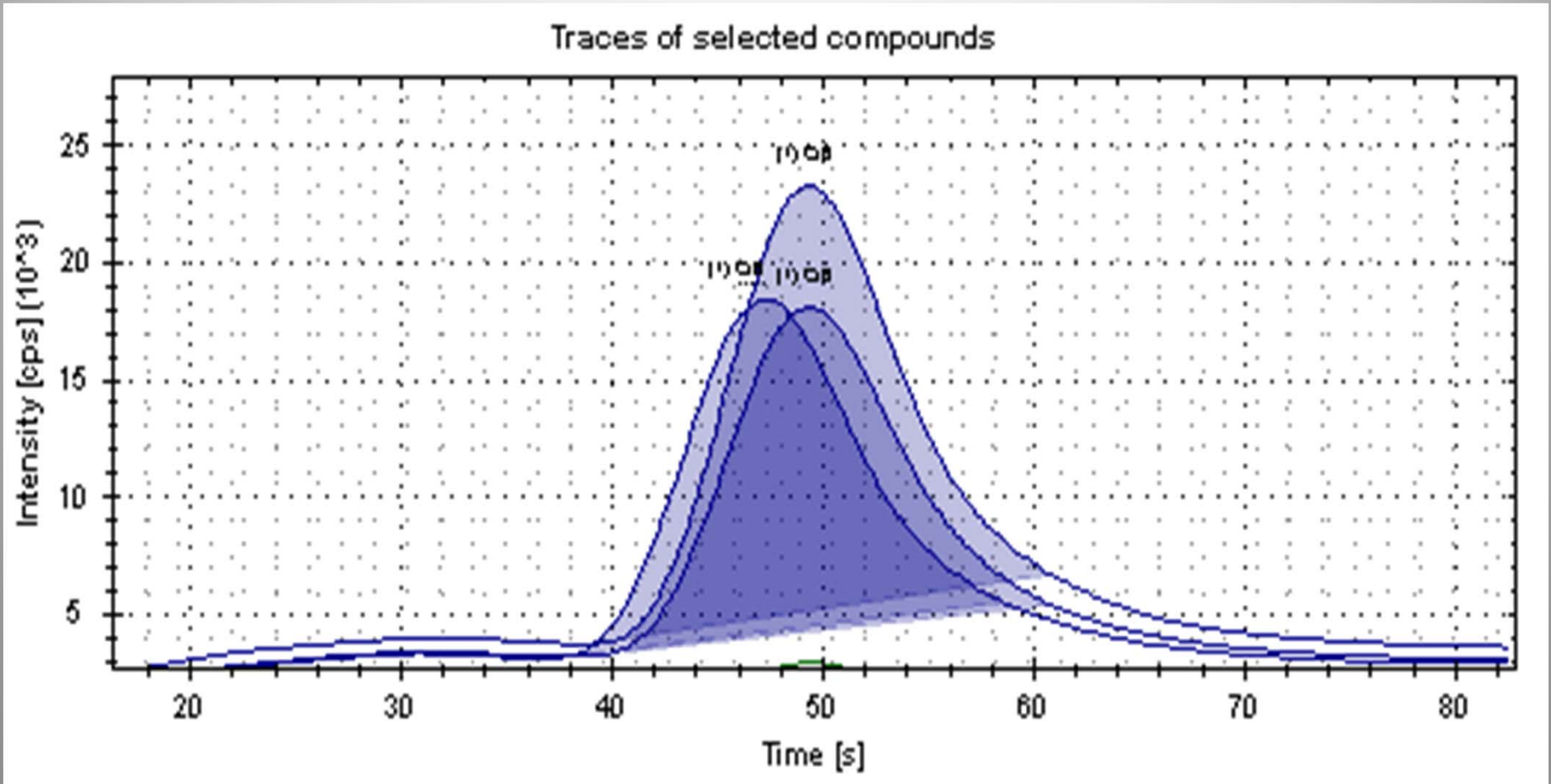
MDL determination using DI spiked with 20 ppt Cr^{+6}, t=2.998

Isocratic Method, Accuracy and Precision

Sample	Spike	Result	Average Recovery	RSD
74.3 ppt Cr^{+6}	20 ppt Cr^{+6}	96.0	109%	2.4%
	250 ppt Cr^{+6}	370	118%	0.8%
	750 ppt Cr^{+6}	940	115%	0.5%

Tap water spiked at various concentrations (n=7)

Retention Time-drift and Intensity Variance



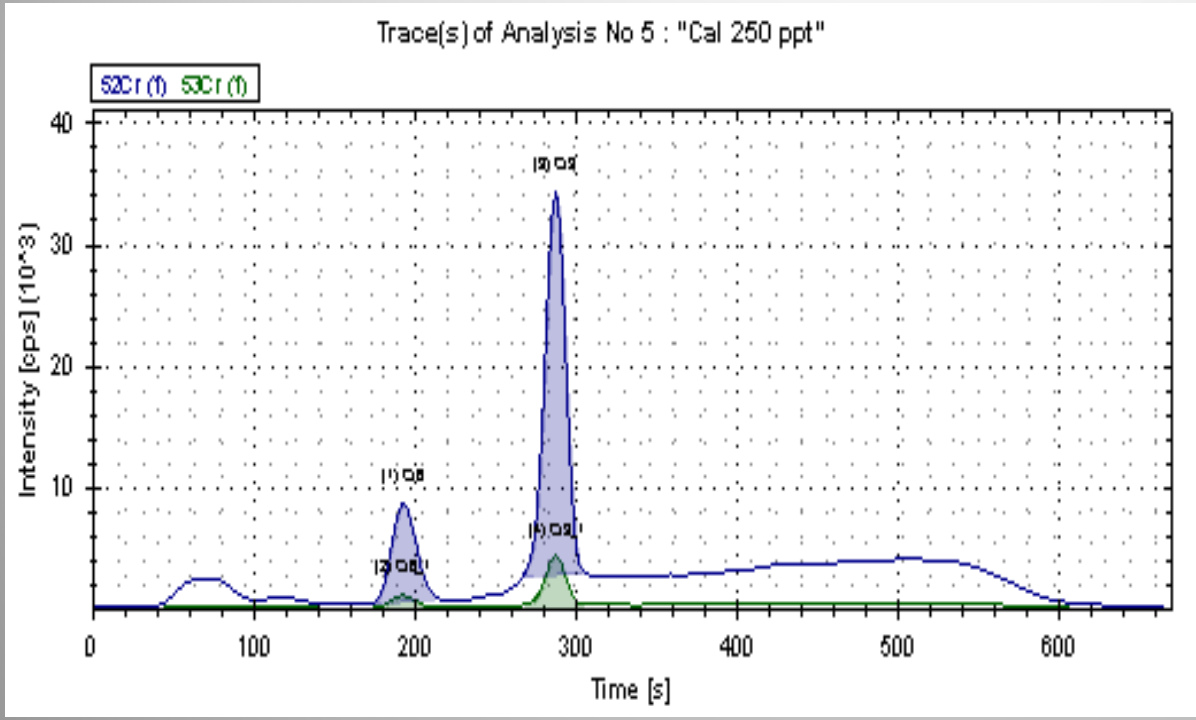
250 ppt Cr^{+6} in DI, injected every ten samples

Matrix Issues

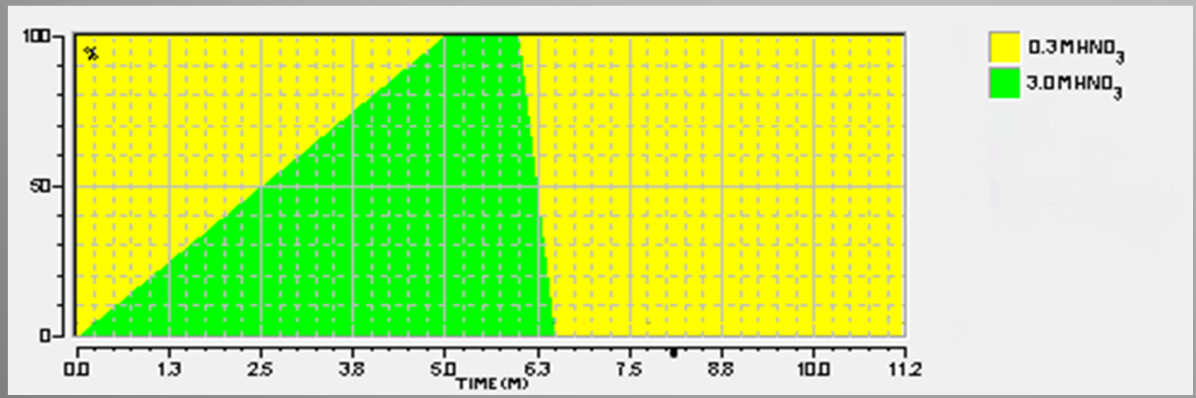
- Drift in retention time and intensity
  - When injecting matrix, not present with DI only
- Marked improvement using fresh vials for every injection
- AS-7 column (2x250mm) for better separation
- Increase injection volume and dwell time
- Apply gradient
- Examine sample preparation

Gradient Method

250 ppt Cr^{+6} & Cr^{+3} in DI



Gradient Plot



Column:

Thermo Dionex IONPAC AS-7, 2x250mm

Mobile phase:

0.3 M HNO_3 /3.0 M HNO_3

Ramp from 100% 0.3 M to 100% 3.0 M at 5 minutes, hold for 1 minute, then equilibrate with 100% 0.3 M for 4.5 minutes

Flow rate: 0.4 mL/minute

Temperature: ambient

Injection volume: 200 µL

ICP-MS

RF power: 1550 W in KED mode

Nebulizer flow: 1.05 L/min

Dwell time: 0.1s/isotope

Isotopes monitored:

^{52}Cr, ^{53}Cr (8:1 ratio)

Chromium 6 retention time ~ 195 s

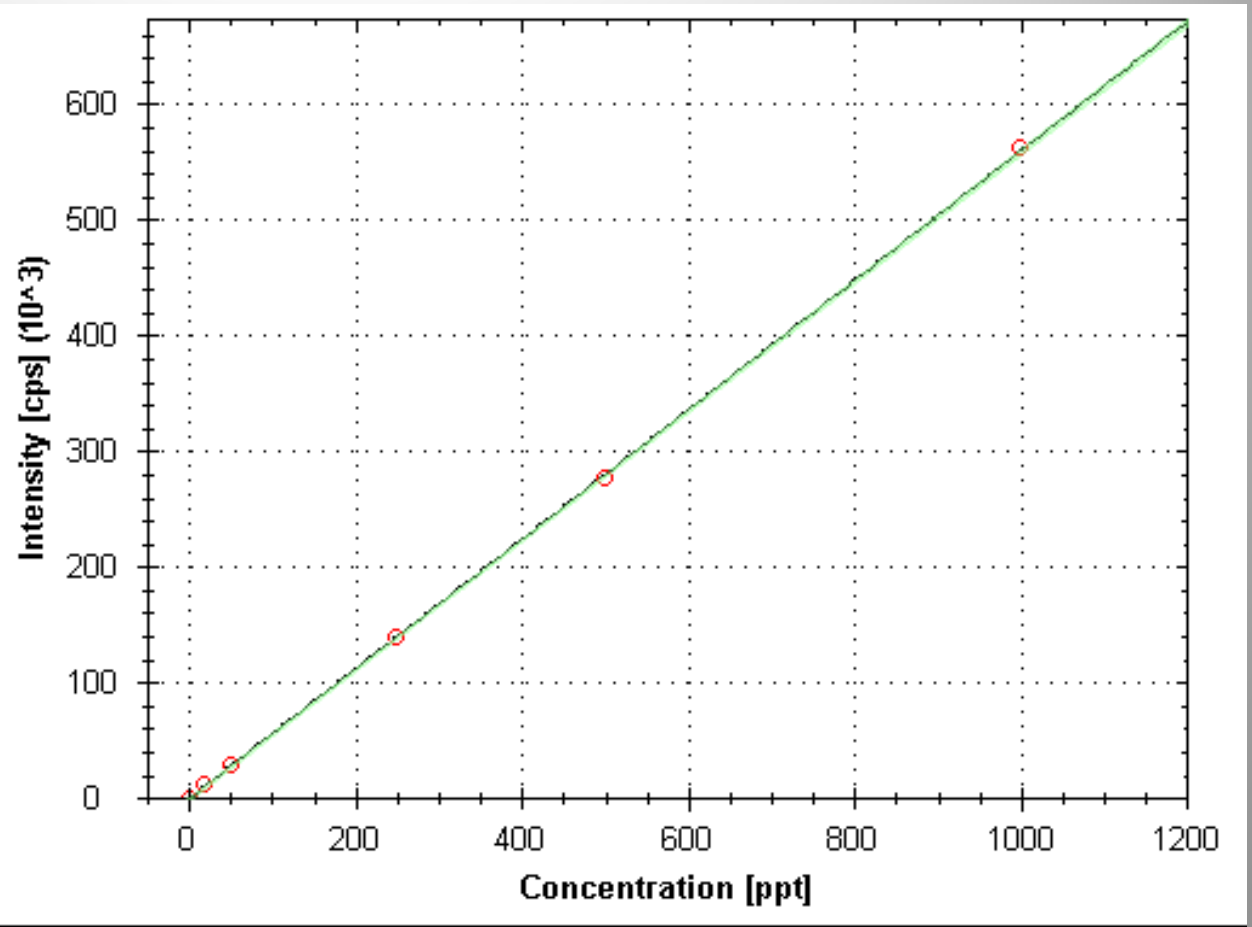
Sample prep:

0.1 M ammonium nitrate, pH = 4.0

Filtered (0.45 µm)

Gradient Linear Calibration

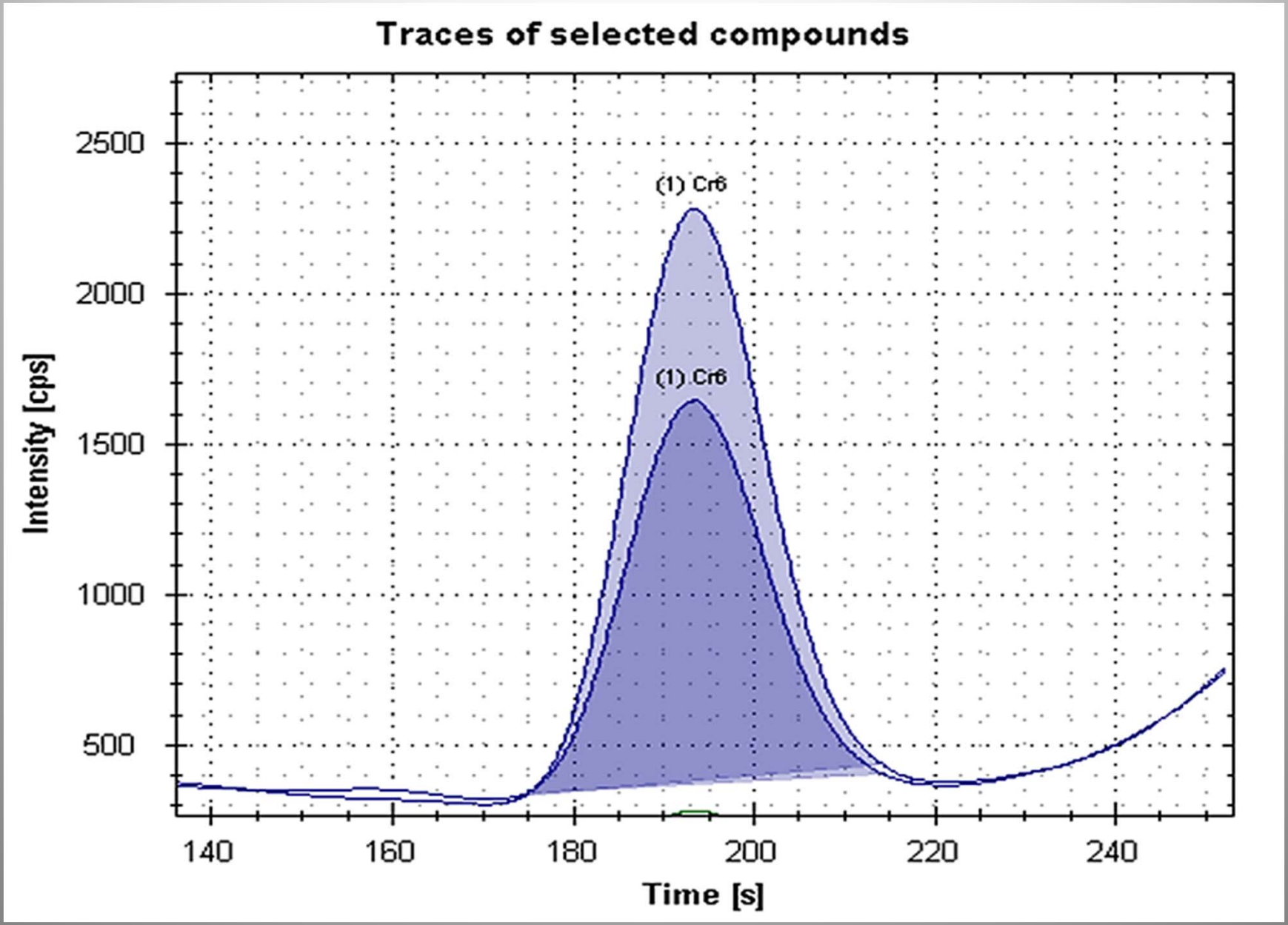
- 5 point calibration
  - 20 -1000 ppt
- $R^2 > 0.999$
- ~560 counts/ppt
- BEC range = [0.2 – 12 ppt]
- *BEC 1%-60% of low standard*



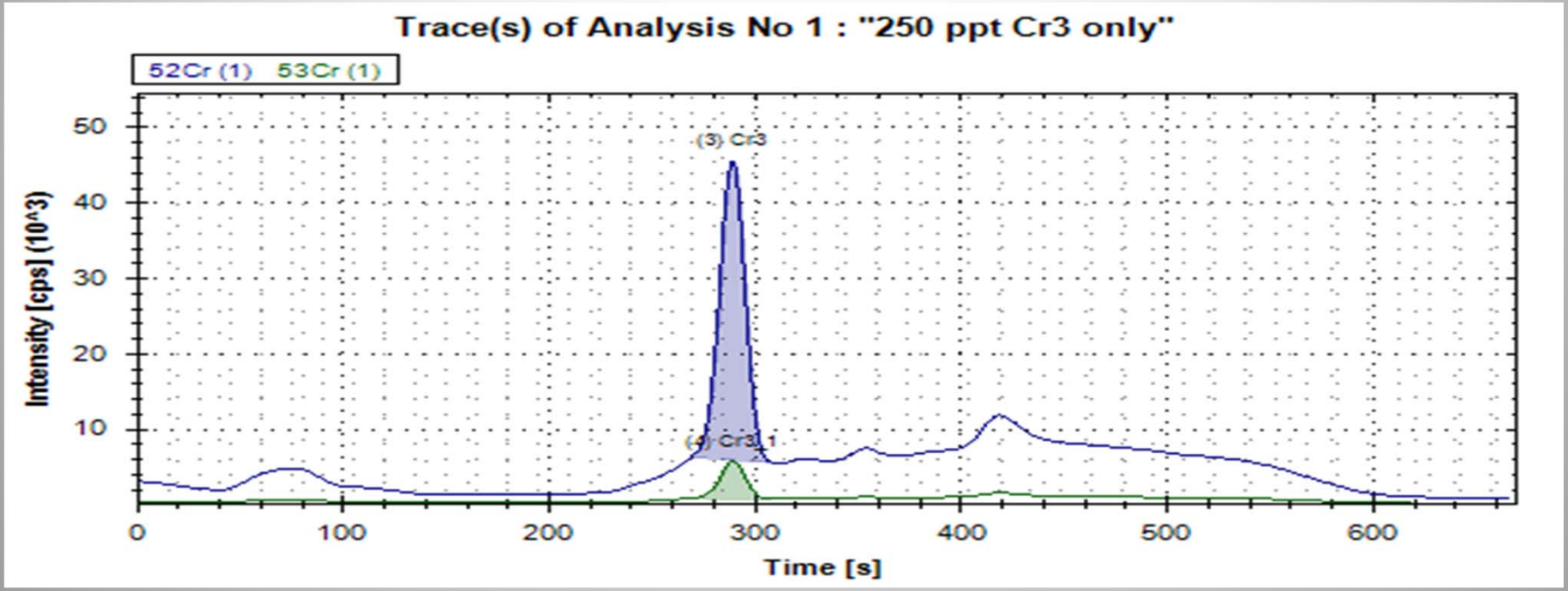
f(x) = b*x + a

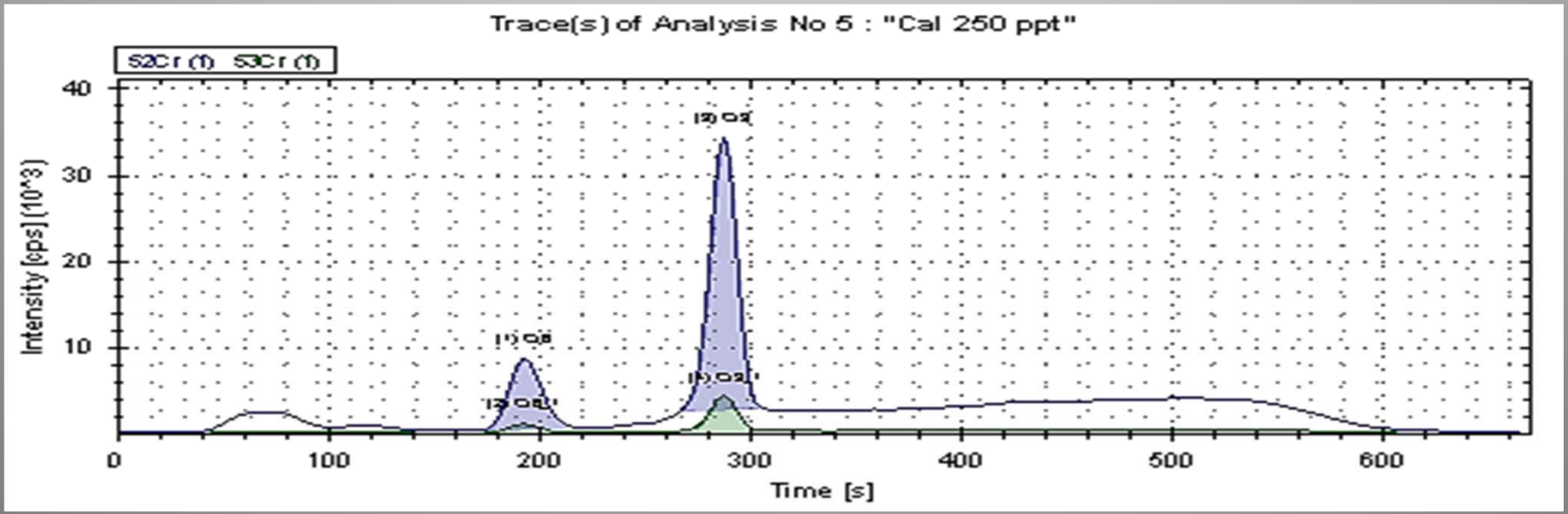
Parameter	Value	Confidence Delta at 90%	StdErr	Rel. StdErr [%]
b	560.017	+/-3.477	2.415	0.431
a	-130.966	+/-1,627.925	1,130.661	-863.326
R	0.99996282			
BEC	-0.234 ppt			

Tap Water with 20 ppt Cr^{+6} Spike



Sample Preservation





Gradient Method Detection Limit

1	2	3	4	5	6	7	8	Avg	SD	MDL
17.2	16.6	16.5	18.2	16.9	15.5	16.4	16.3	16.7	0.786	2.36

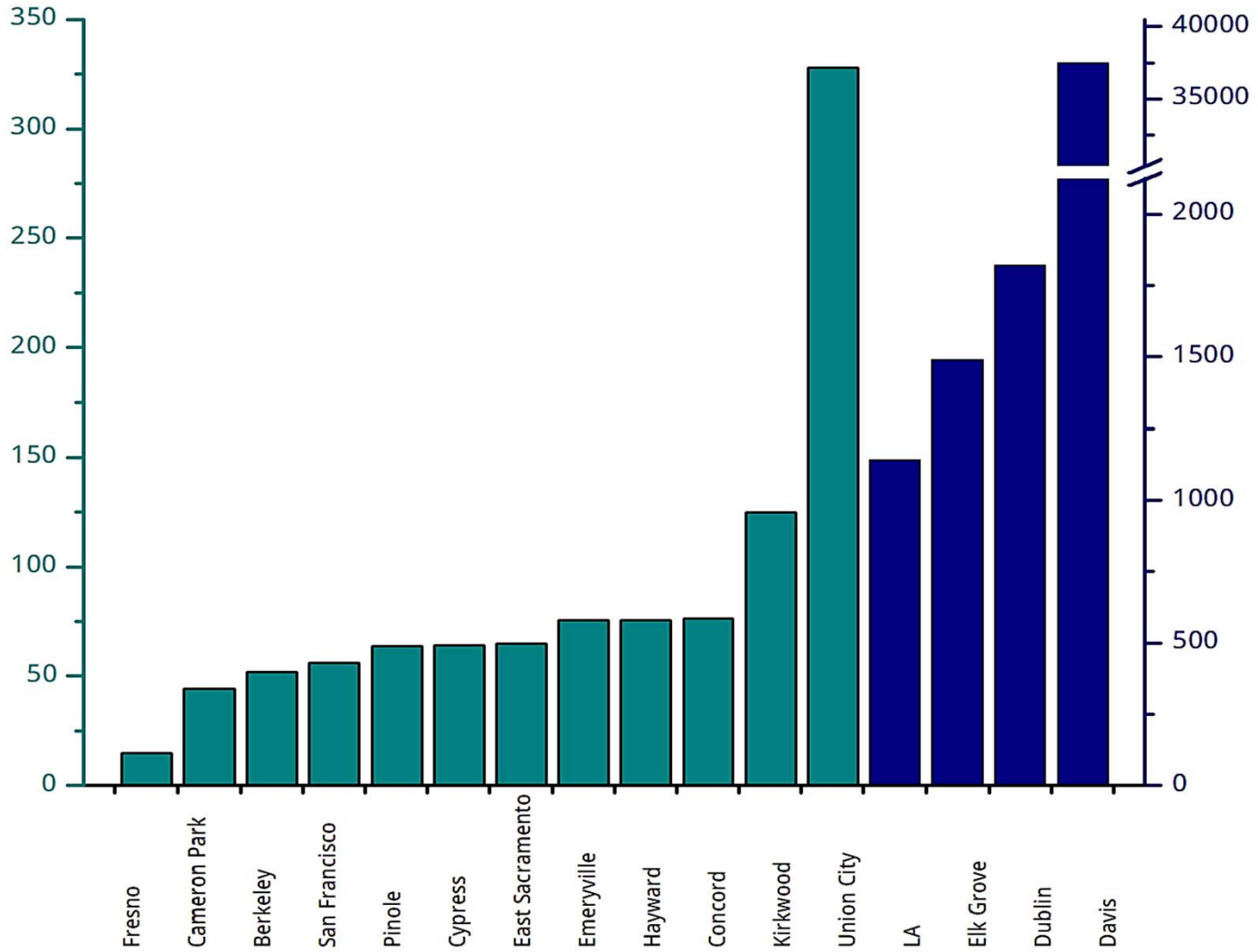
MDL determination using DI spiked with 20 ppt Cr^{+6}, t=2.998

Gradient Method, Accuracy and Precision

Sample	Spike	Result	Average recovery	RSD
52.1 ppt Cr^{+6}	20 ppt Cr^{+6}	73.0	105%	0.9%
	250 ppt Cr^{+6}	326	110%	1.0%
	750 ppt Cr^{+6}	891	112%	2.2%

Tap water spiked at various concentrations (n=7)

Hexavalent Chromium Concentrations in Drinking Water (ppt)

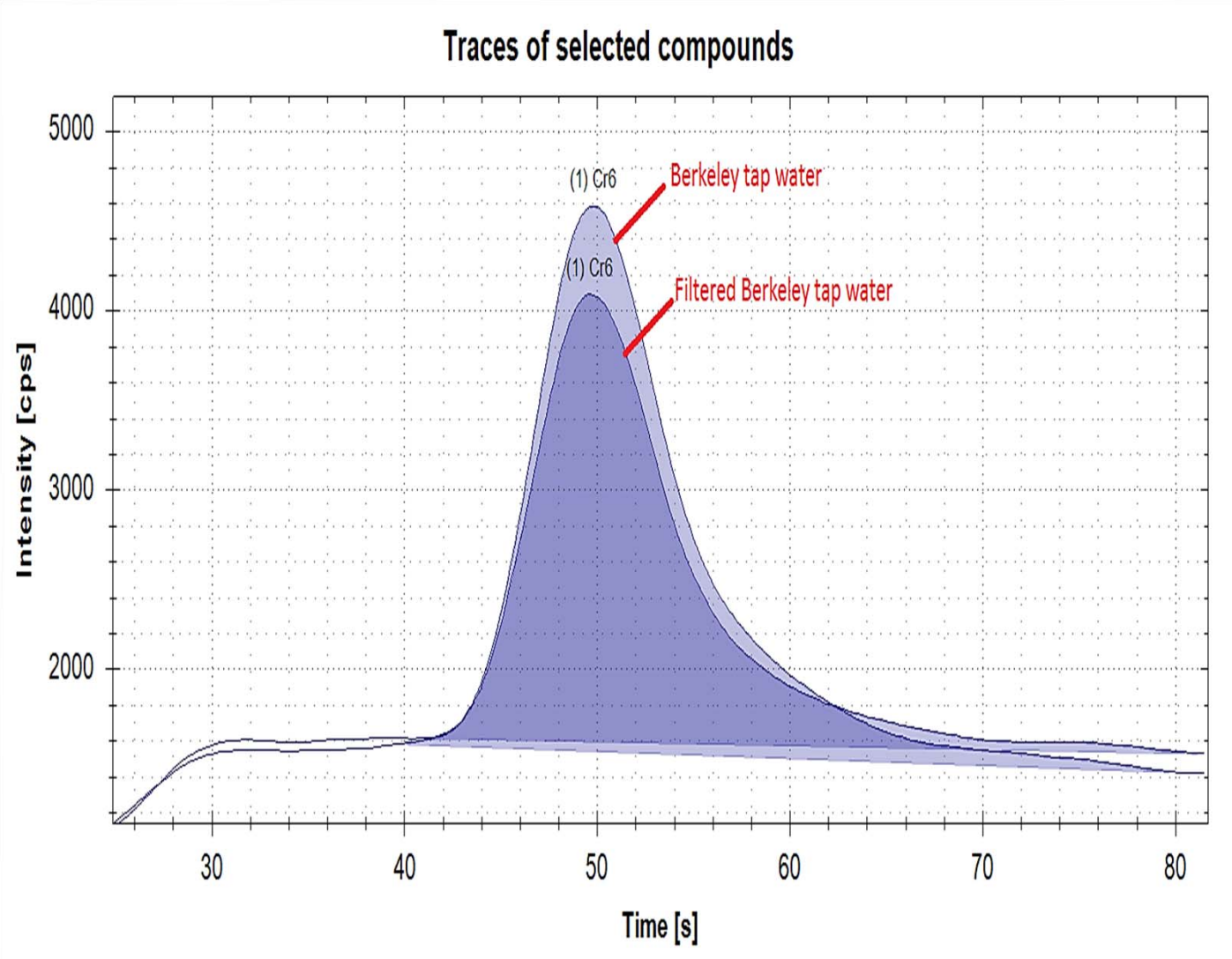


Hexavalent Chromium Concentrations in Drinking Water

Sample ID	Replicates	Average result (ppt)	Result range
Fresno	6	<20	<20 - <20
Cameron Park	2	44.5	43.7 - 45.2
Berkeley	7	52.2	39.6 - 74.3
San Francisco	1	56.4	56.4 - 56.4
Pinole	2	63.8	33.5 - 94.1
Cypress	6	64.2	48.1 - 78.5
East Sacramento	2	65.2	63.0 - 67.4
Emeryville	2	75.9	75.9 - 75.9
Hayward	1	75.9	75.9 - 75.9
Concord	11	76.5	53.3 - 132
Kirkwood	2	125	113 - 137
Union City	1	328	328 - 328
LA	3	1140	1050 - 1260
Elk Grove	4	1490	197 - 4840
Dublin	4	1820	896 - 3190
Davis	7	37500	648 - 52700

Point of Use Filtration

(Activated Carbon and ION Exchange Resin)



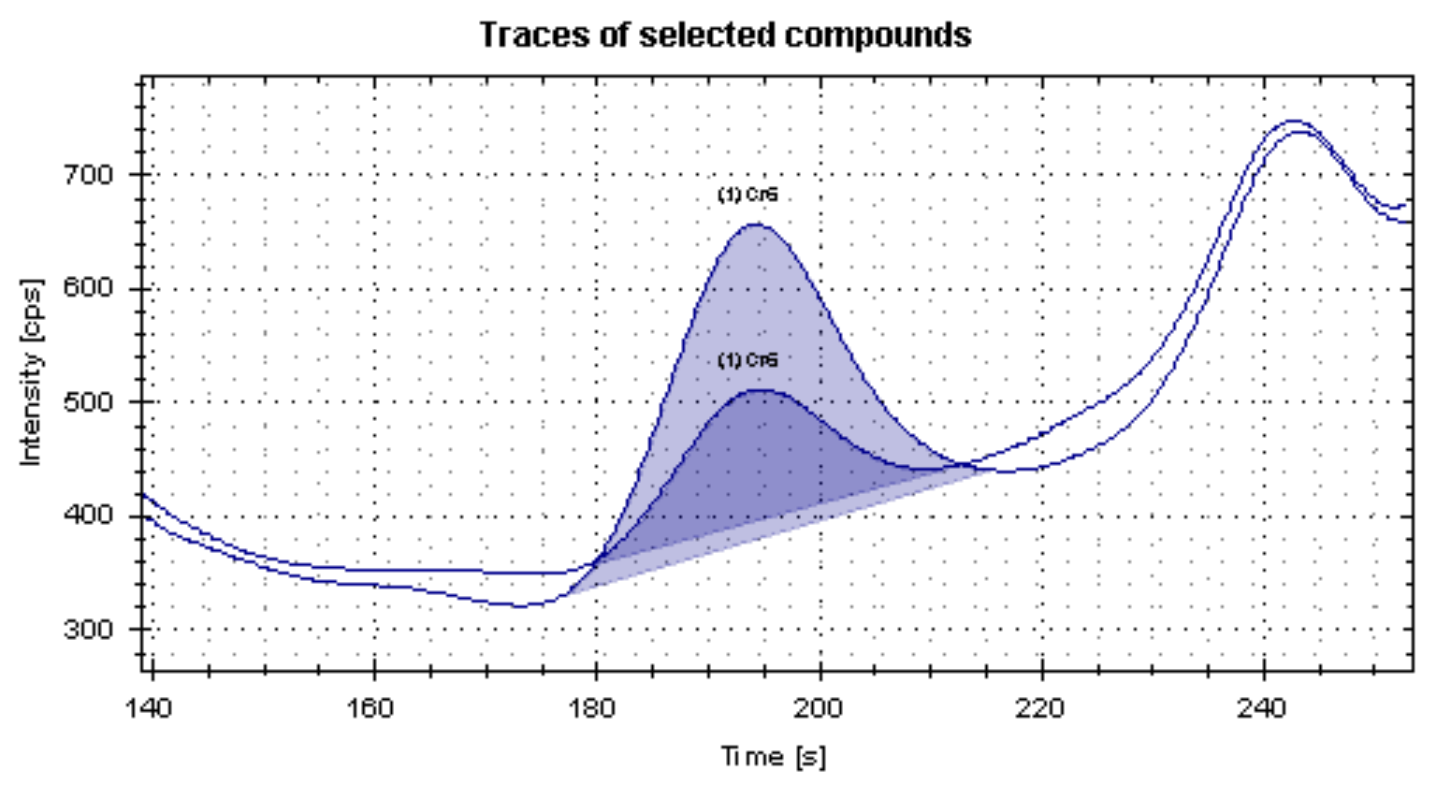
<u>Average of 3 replicates:</u>

Unfiltered = 55 ppt

Filtered = 40 ppt

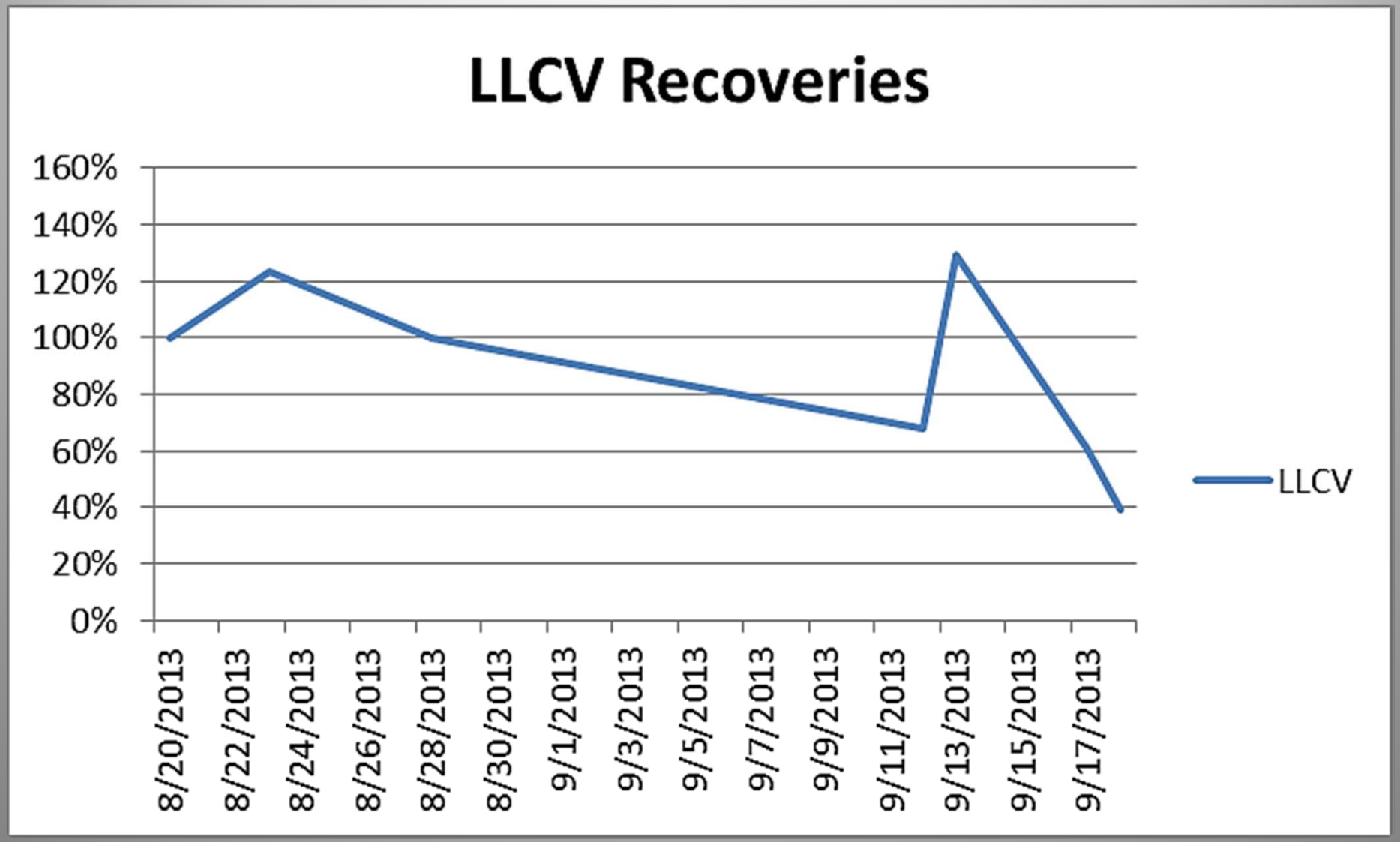
27 % reduction

Limit of Detection



DI spiked with 5 and 10 ppt Cr^{+6}

BEC Effect on LLCV Recoveries



Method of Standard Additions (MSA)
(EPA Method 7000B, Section 9.10)

- Add known amounts of standard to one or more aliquots of sample
- Mitigates additive and destructive matrix interferences
- Resulting calibration curve must be linear
  - $R^2 \geq 0.995$
  - Interference effect should not vary as the analyte/sample matrix ratio changes

Method of Standard Addition Plot

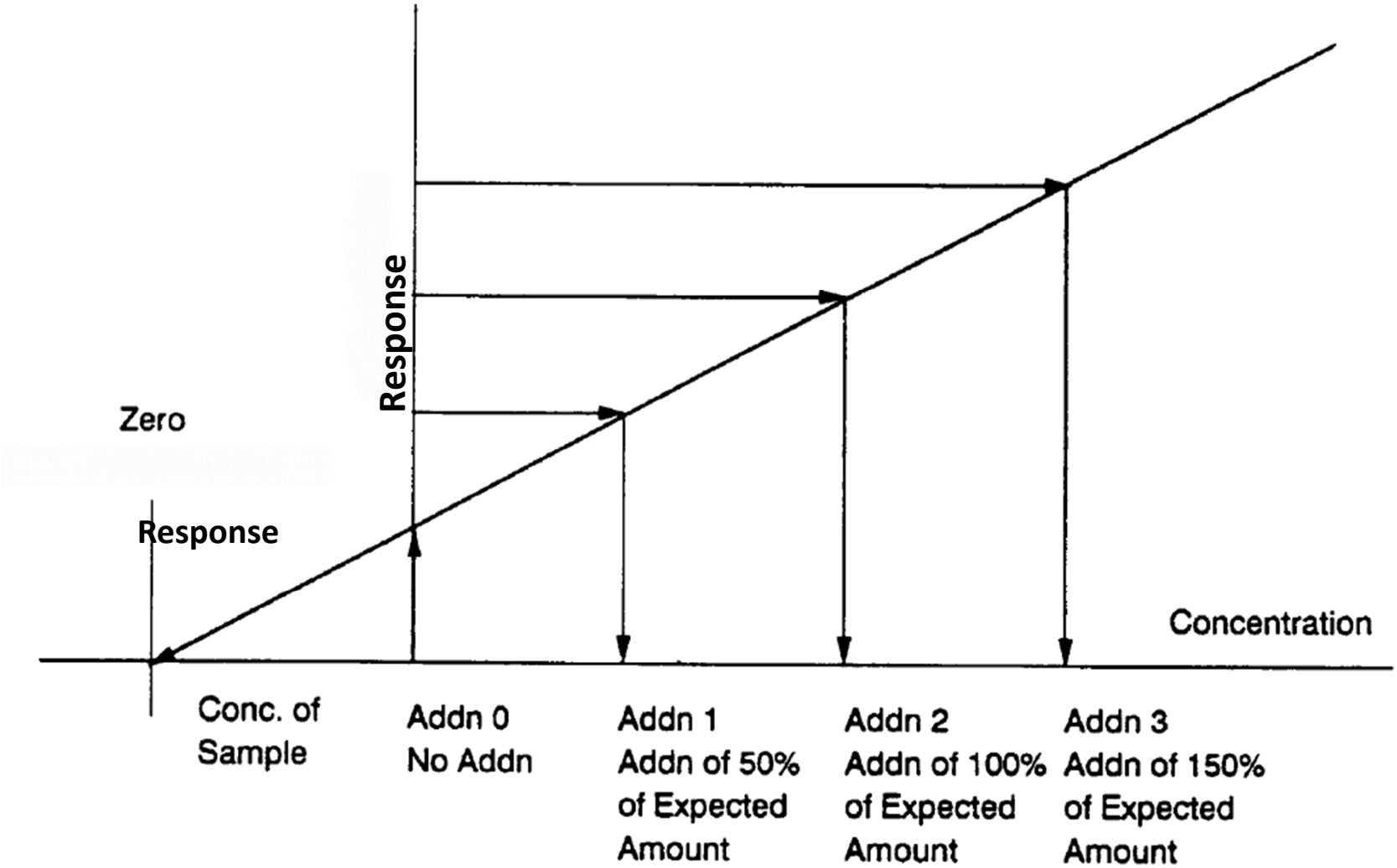
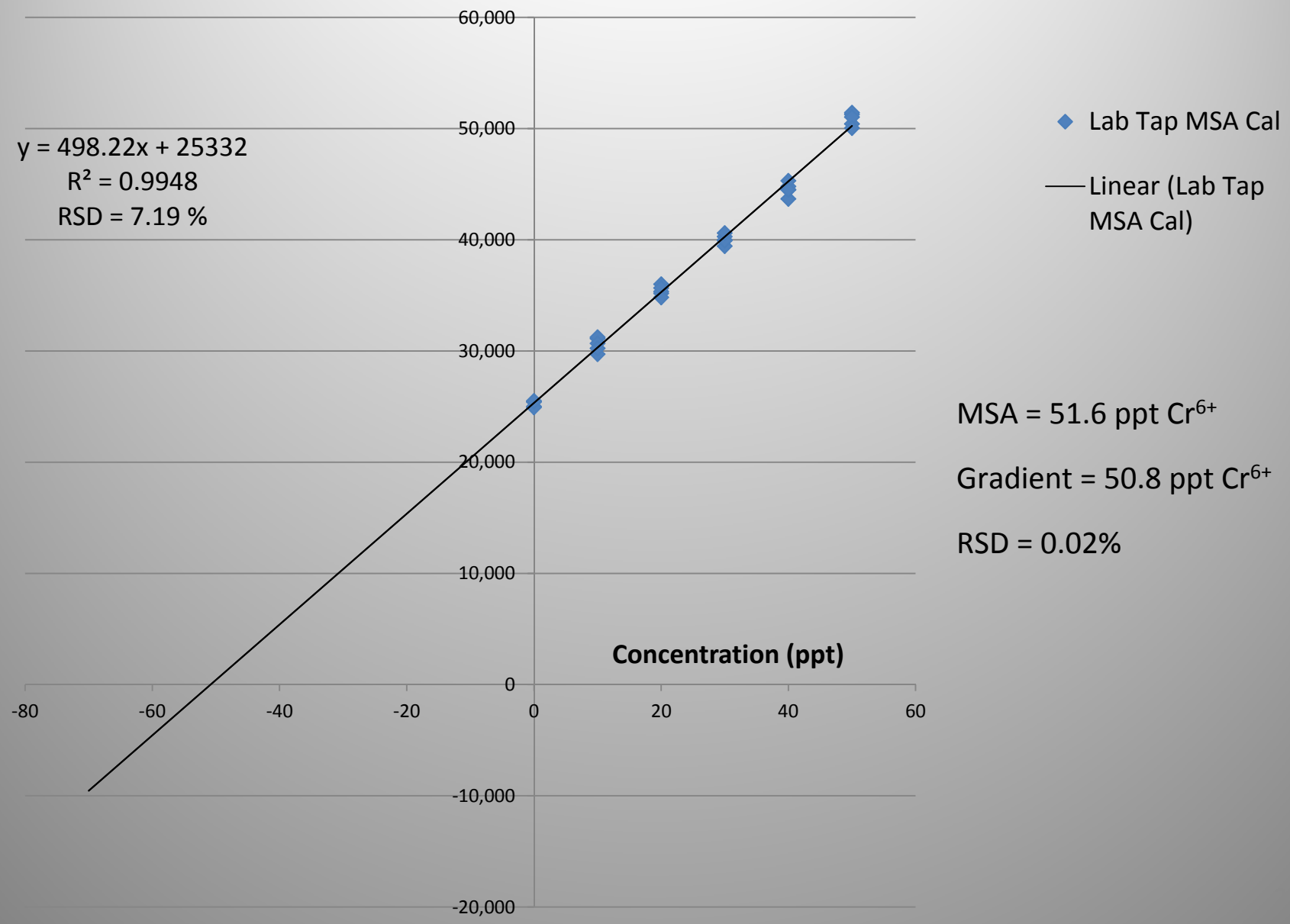


Image from SW-846, Third Edition

LAB Tap MSA Calibration

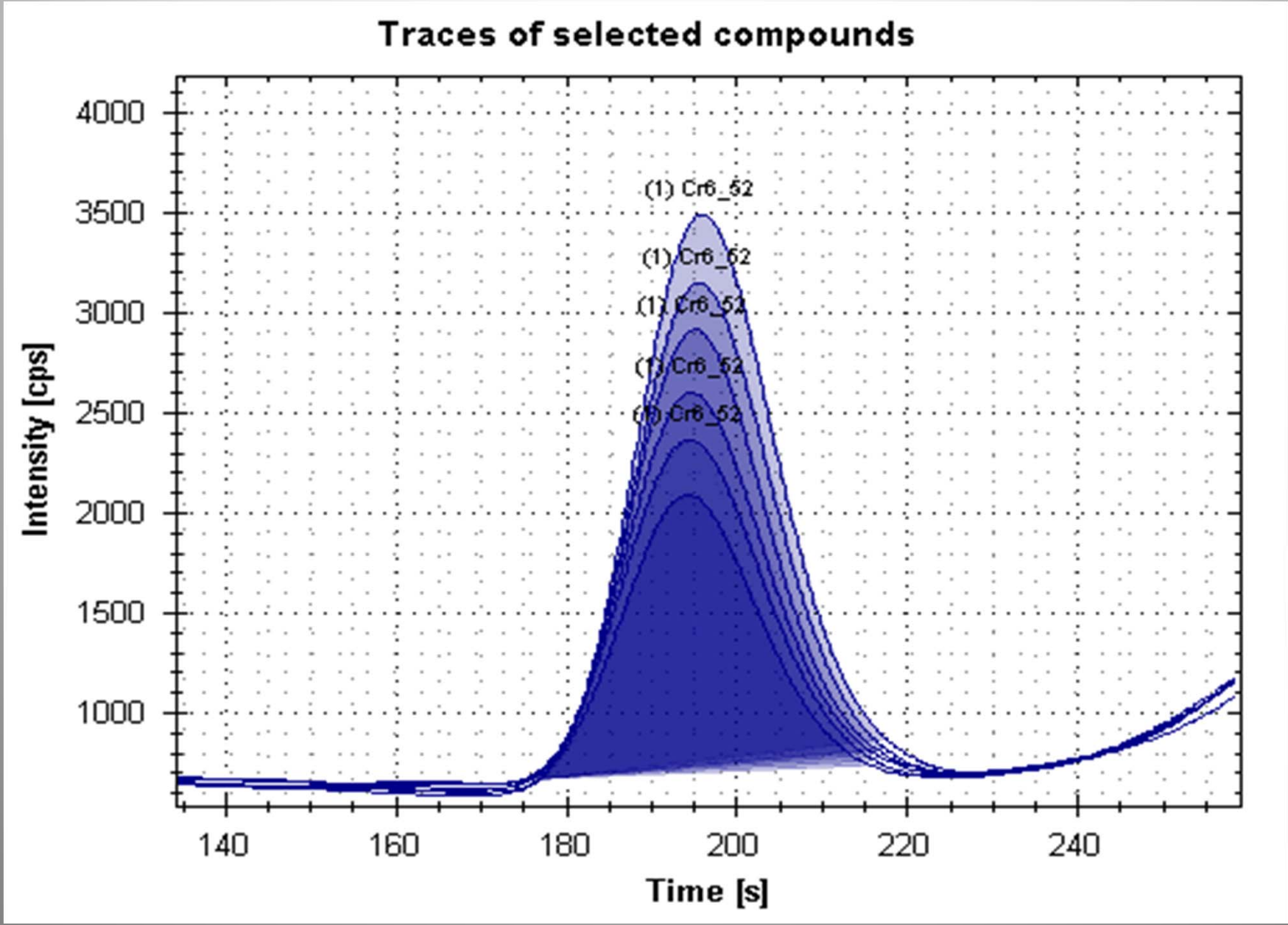


MSA = 51.6 ppt Cr^{6+}

Gradient = 50.8 ppt Cr^{6+}

RSD = 0.02%

Tap Water Spiked at 10, 20, 30, 40 & 50 ppt



MSA Method, Accuracy and Precision

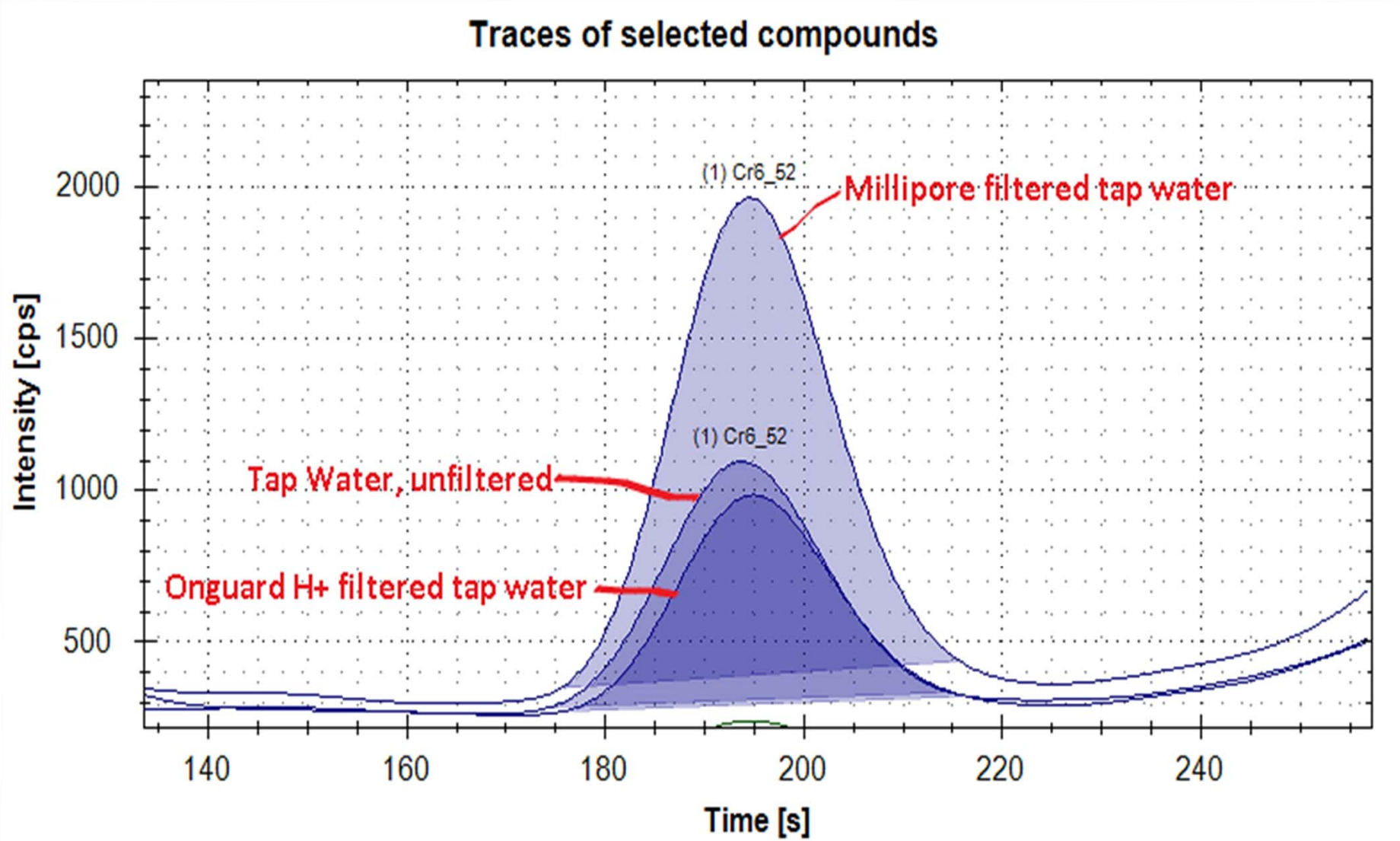
Sample	Spike	Average recovery	RSD
51.6 ppt Cr^{+6}	10 ppt Cr^{6+}	136%	7.0%
	20 ppt Cr^{+6}	75%	3.6%
	30 ppt Cr^{+6}	76%	4.0%
	50 ppt Cr^{+6}	86%	5.9%

Tap water spiked at various concentrations (n=5)

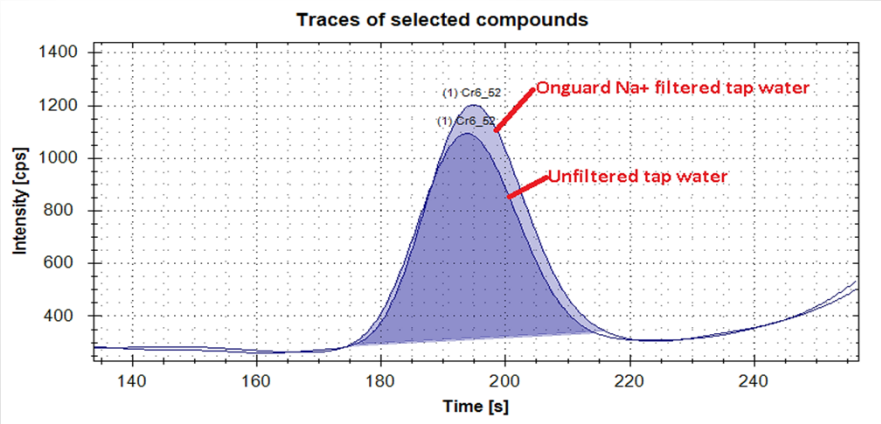
Sample Preparation

- Examined 5 different filter options
  - Millipore 0.45 µm glass fibre/ Polyvinylidene fluoride (PVDF)
  - Whatman 0.45 µm Polysulfone
  - Nalgene 0.45 µm Polytetrafluoroethylene (PTFE)
  - OnGuard: styrene-based, sulfonic acid resin
    - Thermo Dionex OnGuard II H ion exchange filter
    - Thermo Dionex OnGuard II Na ion exchange filter
      - remove high levels of alkaline earth and transition metals

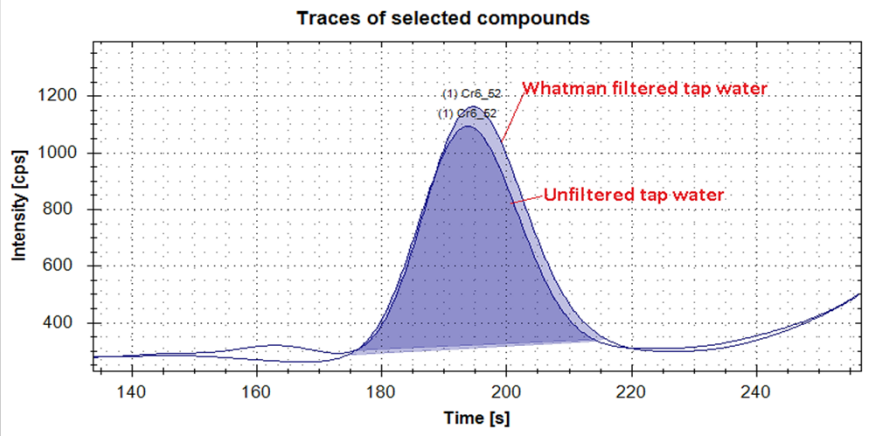
Millipore and OnGuard II H



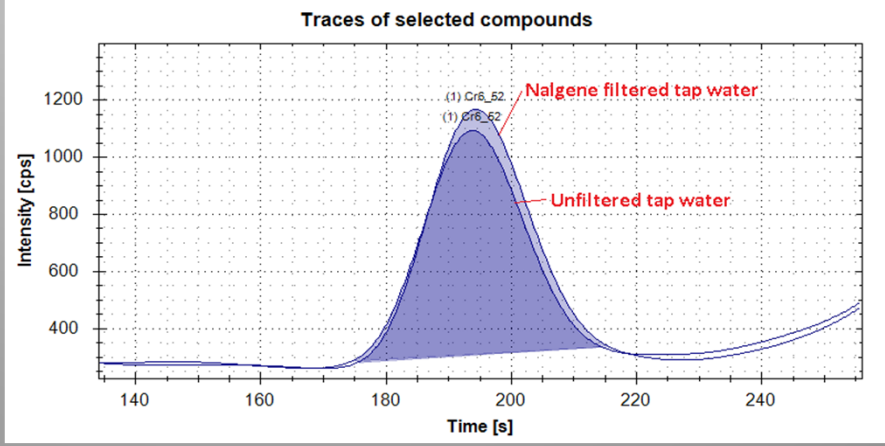
OnGuard II Na



Whatman



Nalgene



Filter Comparisons

Sample	Response	Response Relative to Unfiltered Tap Water
Unfiltered tap water	14,533	-
Thermo Dionex Onguard II H	12,519	-14%
Whatman - Polysulfone	15,673	+8%
Nalgene - PTFE	16,030	+10%
Thermo Dionex Onguard II Na	16,296	+12%
Millipore – glass fibre/PVDF	29,237	+101%

Discussion

- Accuracy is questionable below 50 ppt
  - Large BEC relative to 20 ppt reporting limit
- MSA/Gradient method
  - 20 – 1000 ppt
- Sample preparation
  - PVDF contamination
  - Polysulfone or PTFE preferred
- OTC filtration – 30% reduction

Conclusions

- Hexavalent chromium present at trace levels in drinking water
- Chromatographic separation is optimized
- Matrix issues resolved
- Avoid PVDF-based filters
- Utilize MSA for low-level analysis
- Future studies
  - Develop trivalent chromium calibration
  - Continued analysis of drinking water samples
    - Comparison of Gradient vs MSA for low level samples
  - Comparison of raw vs treated waters
  - Correlation of redox conditions and Cr^{6+} concentrations
  - SID-ICP-MS

Acknowledgments

- ✓ Dr. John Quinn
- ✓ Dr. Sayaka Takaku-Pugh
- ✓ Carol Wortham
- ✓ Eric Lytle
- ✓ Dr. Aleksander Soin
- ✓ CA-DTSC-ECL