



Advantages of Inline Dilution on LC-ICP-MS Based Applications

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Elemental Scientific, Inc. (ESI)



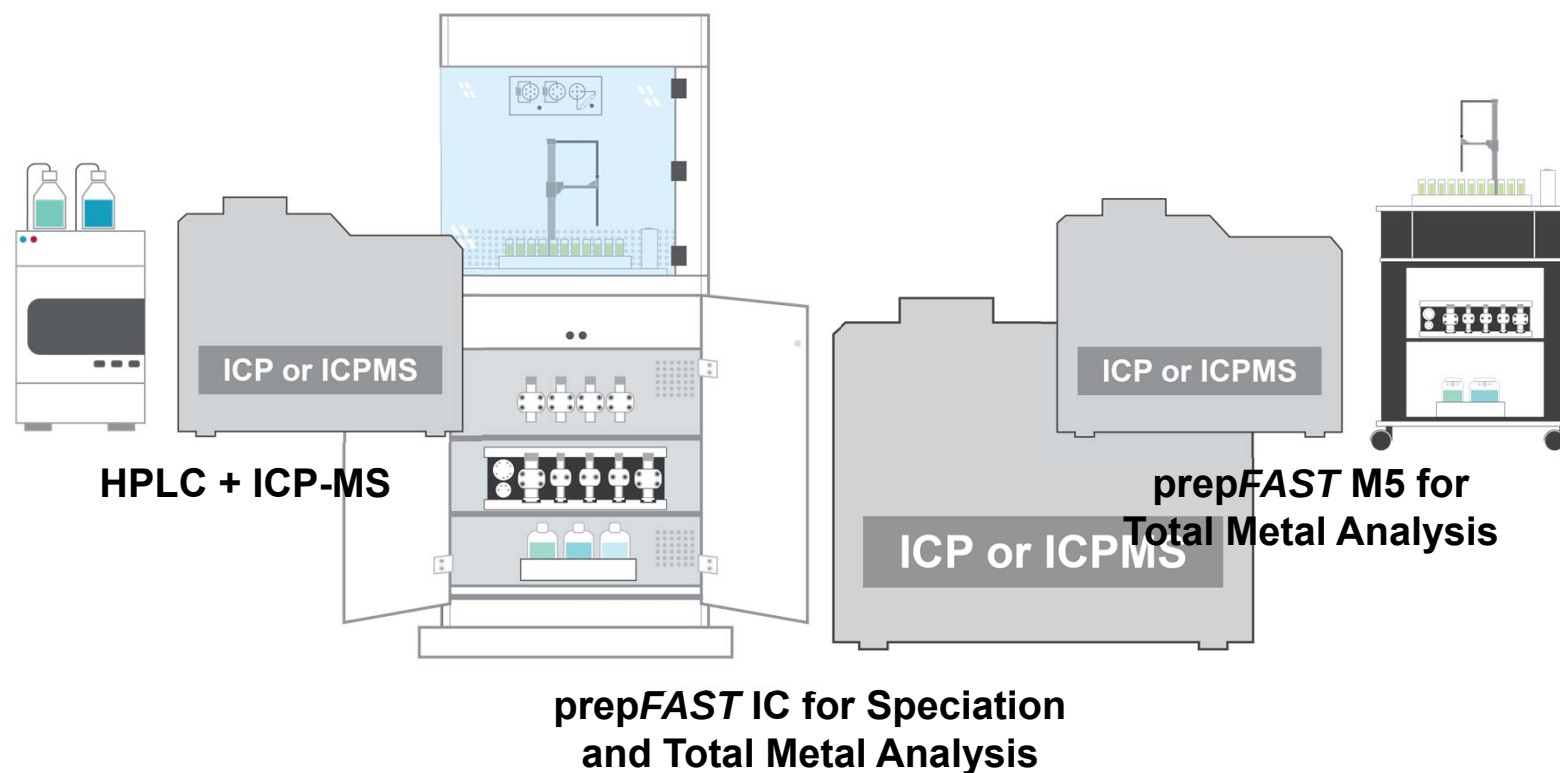
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Omaha, NE, USA



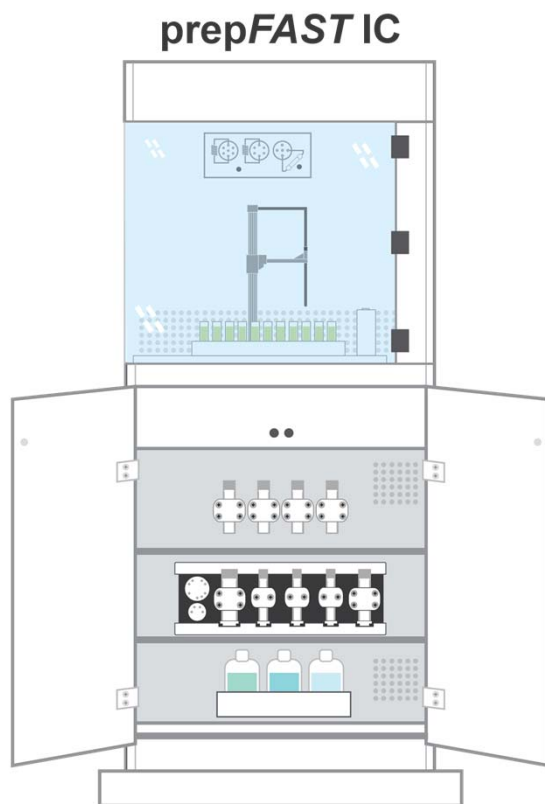
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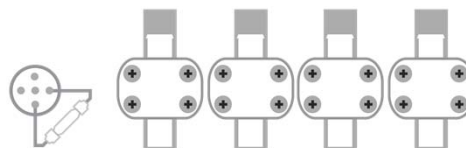
Instrumentation



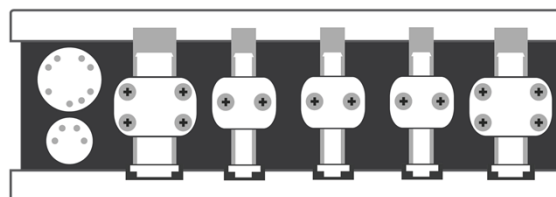
Key Components of prepFAST IC



prepFAST IC Speciation Module

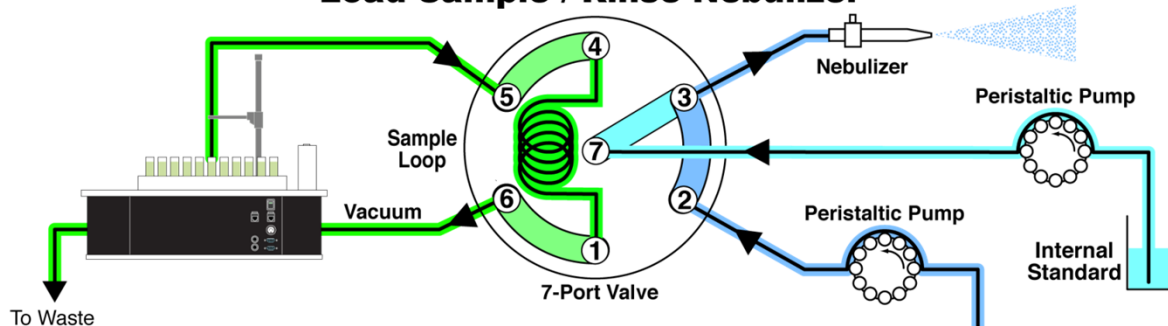


prepFAST M5

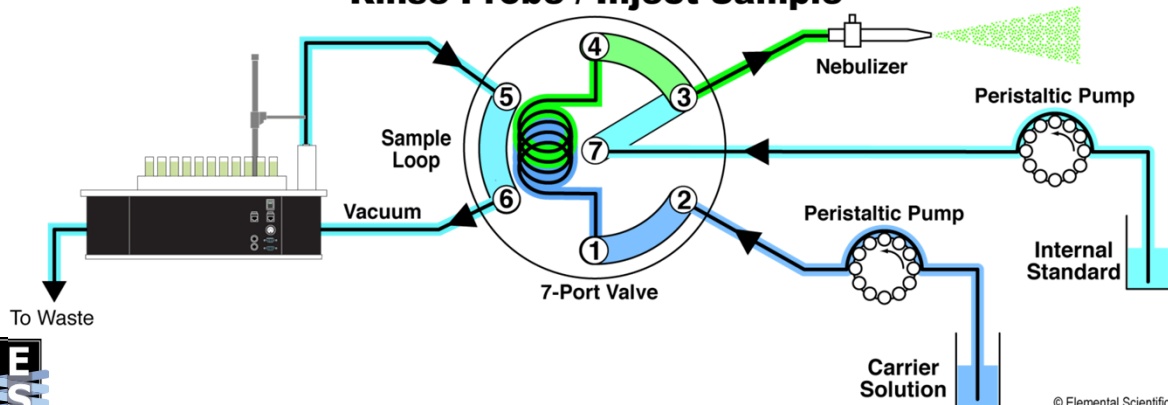


What is *FAST*?

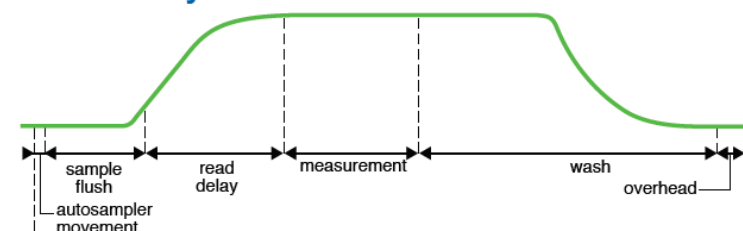
Load Sample / Rinse Nebulizer



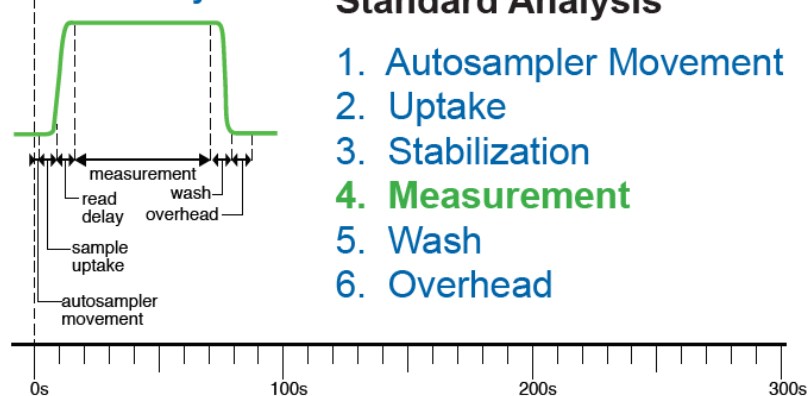
Rinse Probe / Inject Sample



Normal Analysis



FAST Analysis

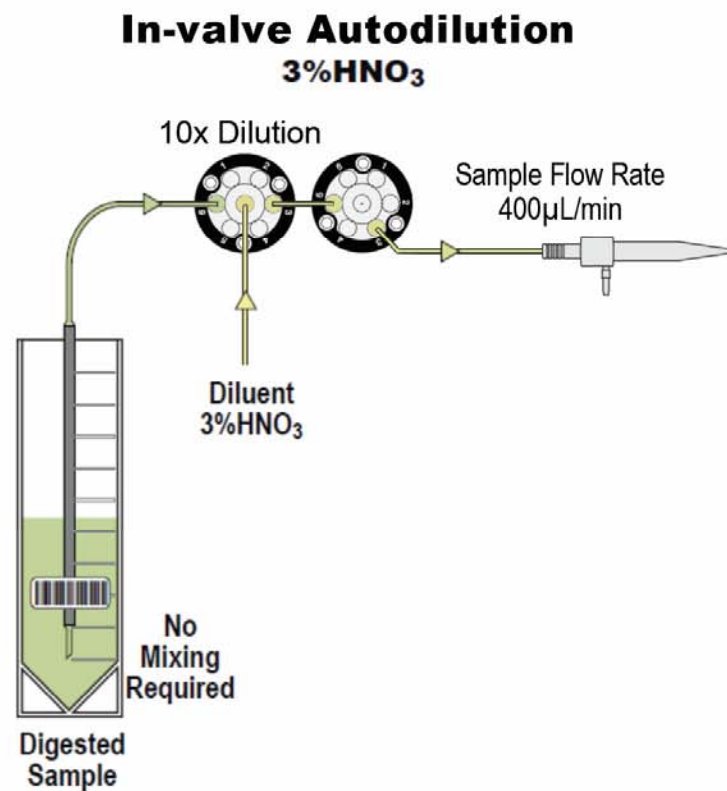
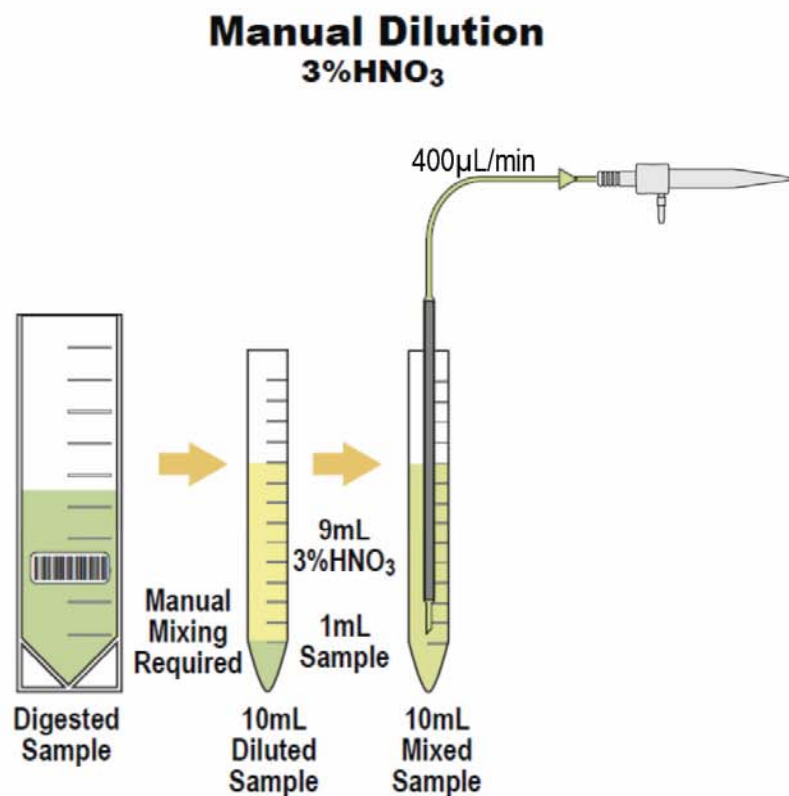


Six Steps in a Standard Analysis

1. Autosampler Movement
2. Uptake
3. Stabilization
4. Measurement
5. Wash
6. Overhead



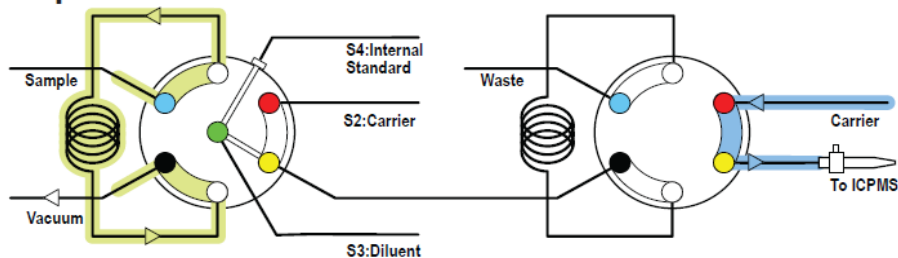
prepFAST M5 – Inline Dilution



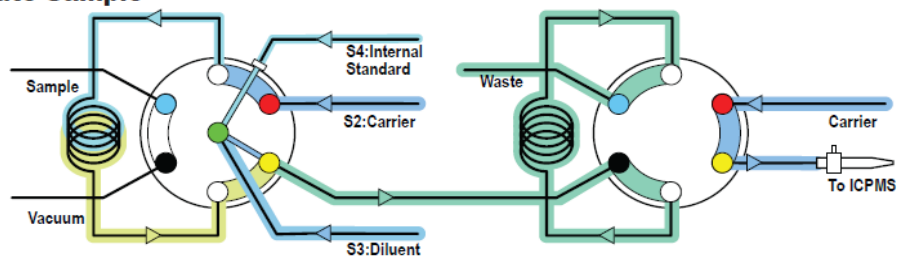
prepFAST M5 – Inline Dilution

prepFAST Analysis Steps

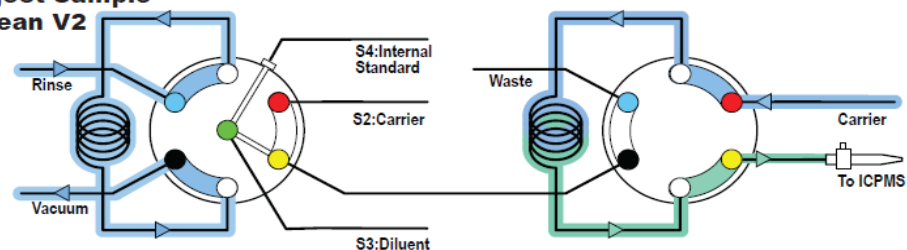
1. Fill Loop



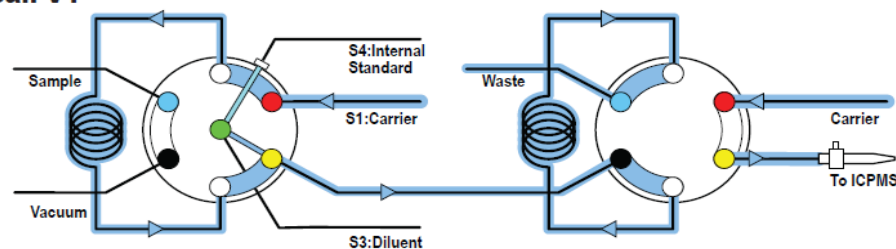
2. Dilute Sample



3. Inject Sample Clean V2



4. Clean V1

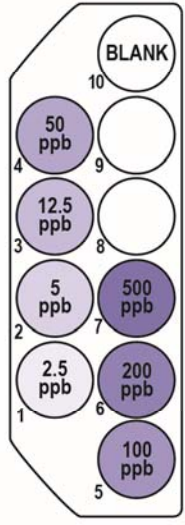


Conventional Calibration vs prepFAST Autocalibration

Conventional Calibration (seven points)

Offline Prep: 1 Blank + 7 Standards

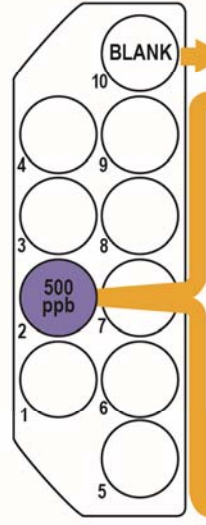
STD Position	Concentration
10	0
1	2.5
2	5
3	12.5
4	50
5	100
6	200
7	500



prepFAST Autocalibration (seven points)

Inline Prep: 1 Blank + 1 Standard

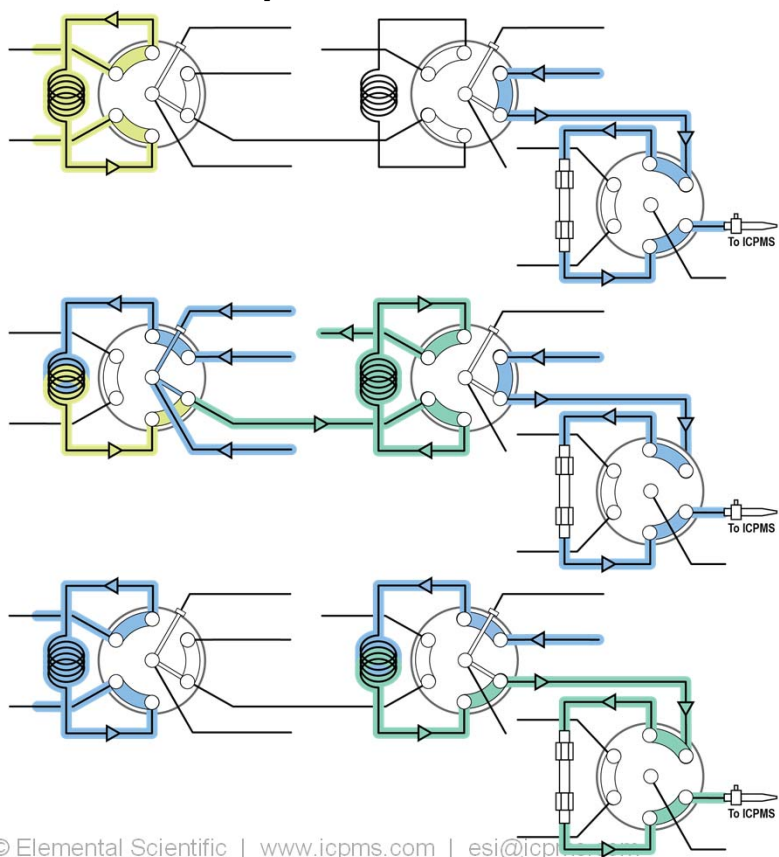
STD Position	Inline Dilution Factor	Dilution Rate			Concentration
		Std	Diluent	Total	
10	200x	50	9950	10000	0
2	200x	50	9950	10000	2.5
2	100x	100	9900	10000	5
2	40x	250	9750	10000	12.5
2	10x	1000	9000	10000	50
2	5x	2000	8000	10000	100
2	2.5x	4000	6000	10000	200
2	1x	10000	0	10000	500



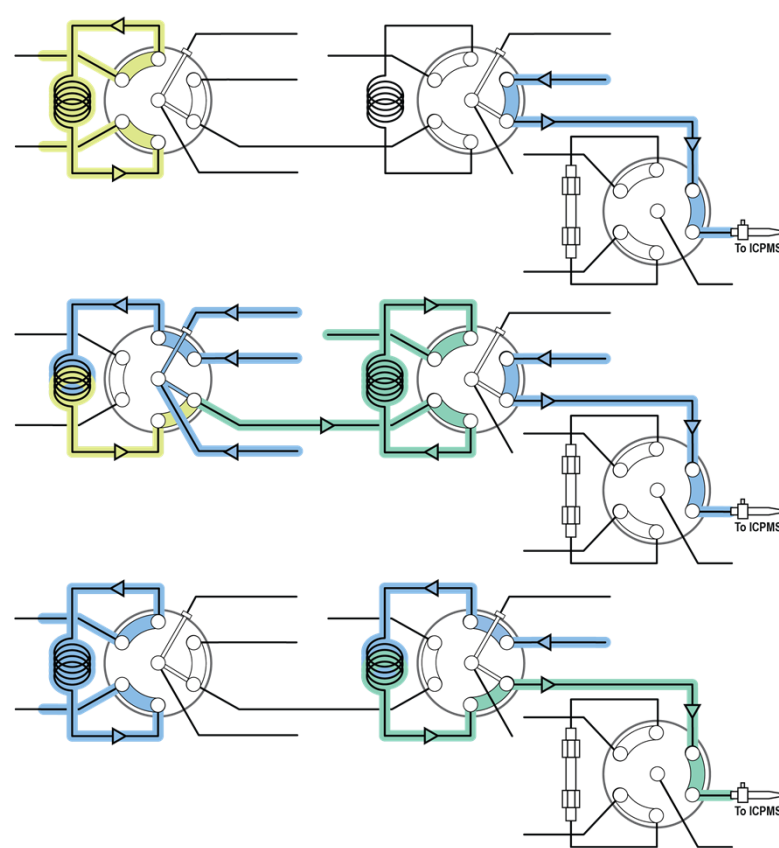
prepFAST Calibration: Blank can be analyzed diluted or undiluted.

prepFAST IC – Speciation or Total Metals

Speciation Mode

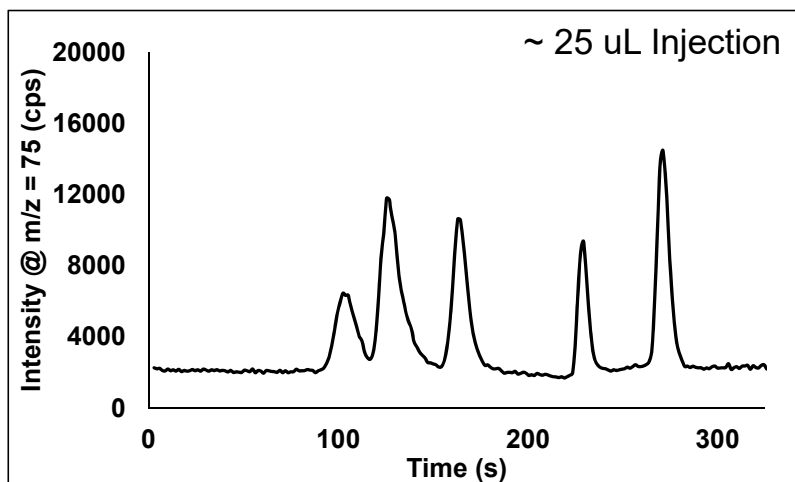
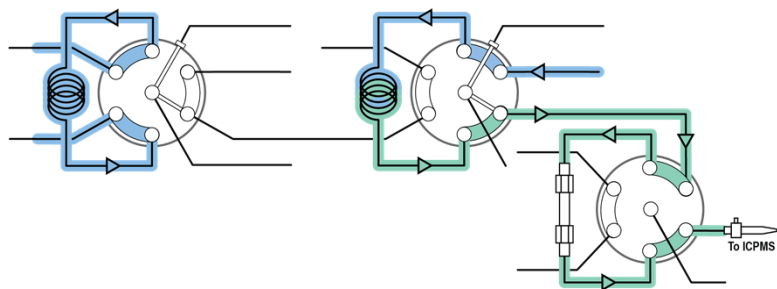


Total Metals Mode

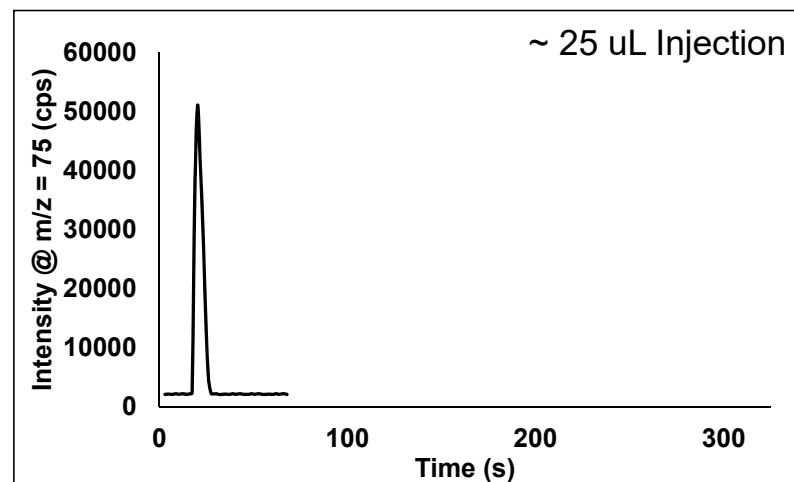
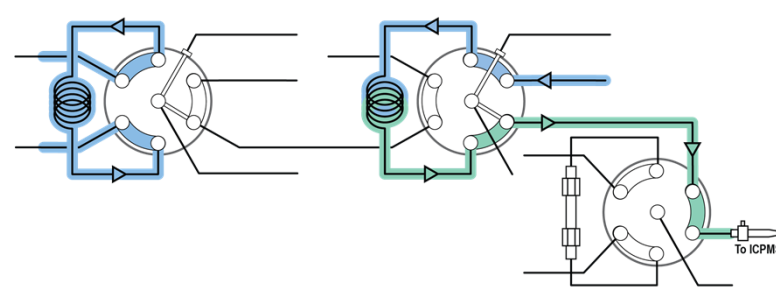


prepFAST IC – Speciation or Total Metals

Speciation Mode



Total Metals Mode

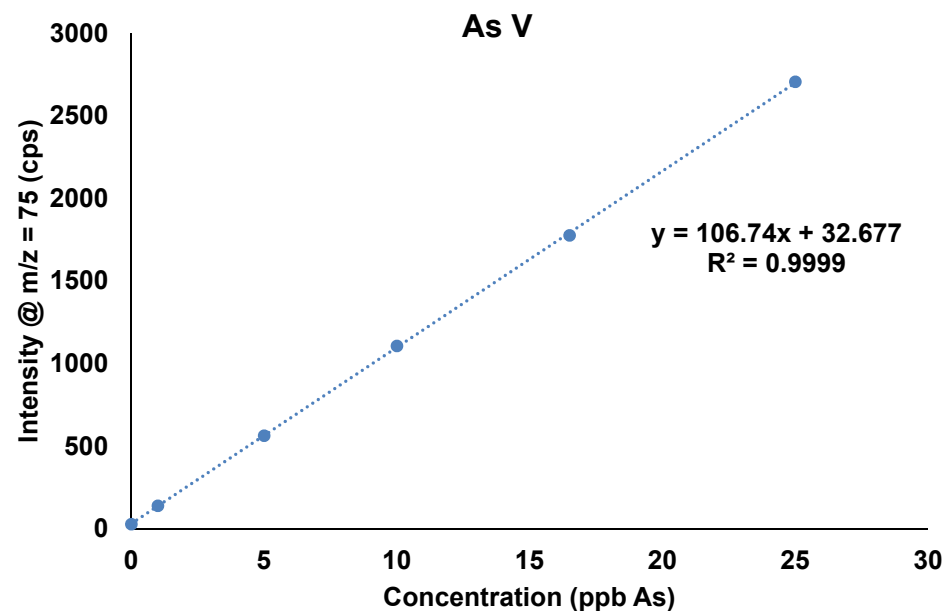
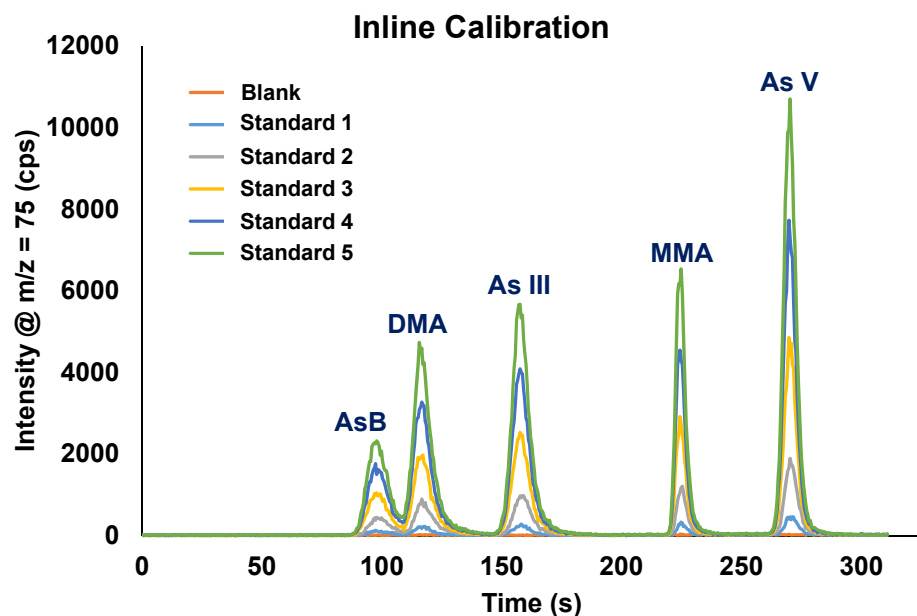


Clinical Application: Analysis of Arsenic in Urine

prepFAST IC + Perkin Elmer NexION 350 ICP-MS



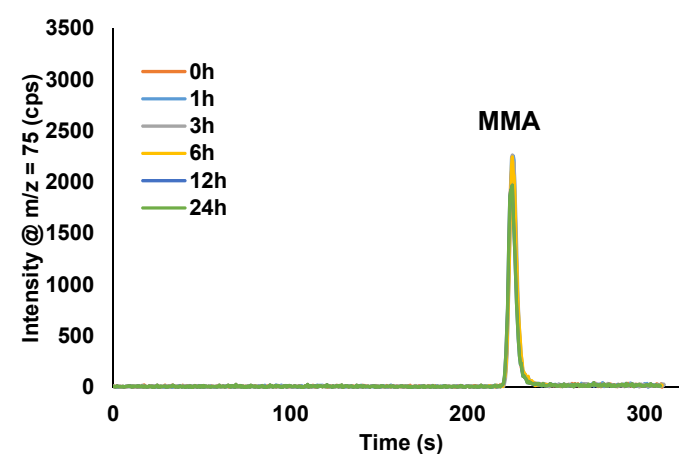
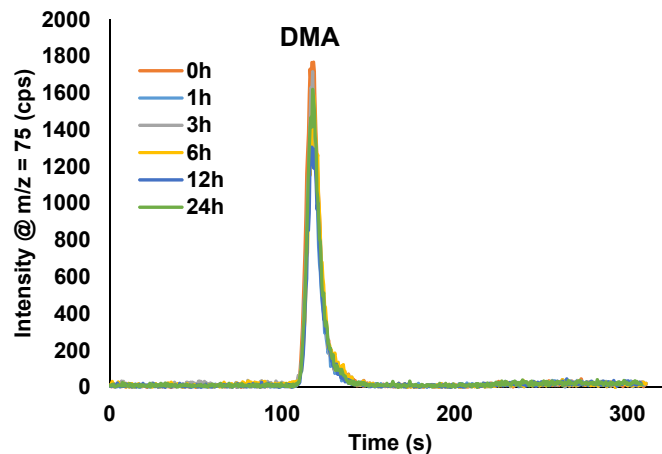
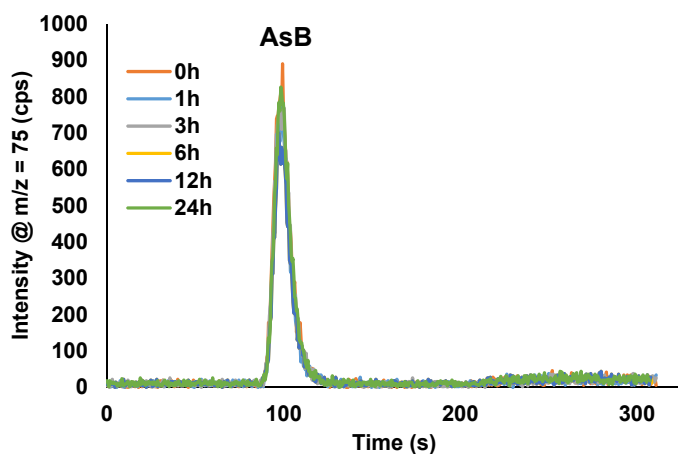
Inline Calibration – Arsenic in Urine



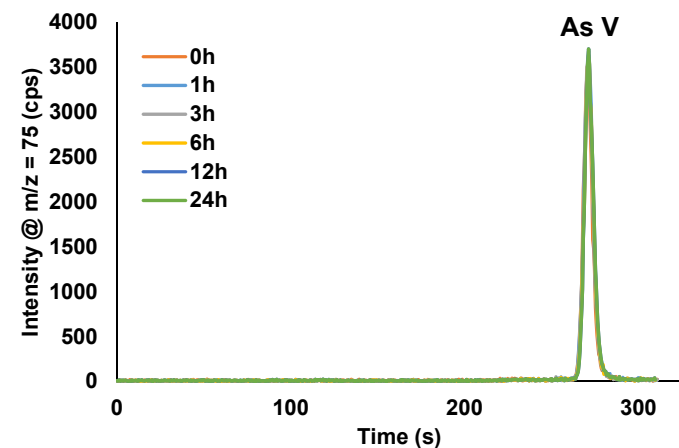
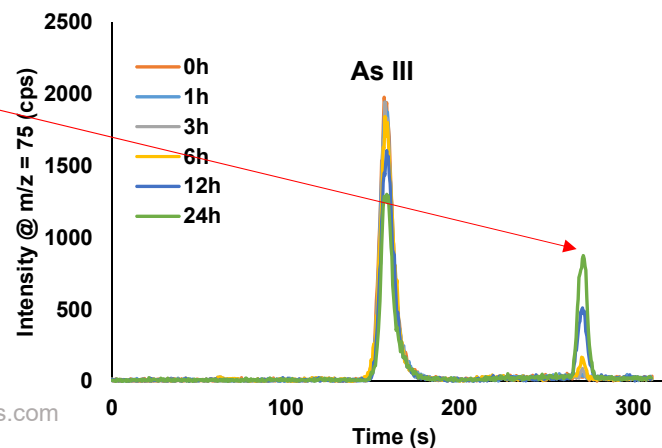
	LOD (ppt)				
	AsB	DMA	As III	MMA	As V
LOD (ppt)	1.7	0.7	0.6	1.0	0.3
LOQ (ppt)	5.8	2.5	1.9	3.2	1.0



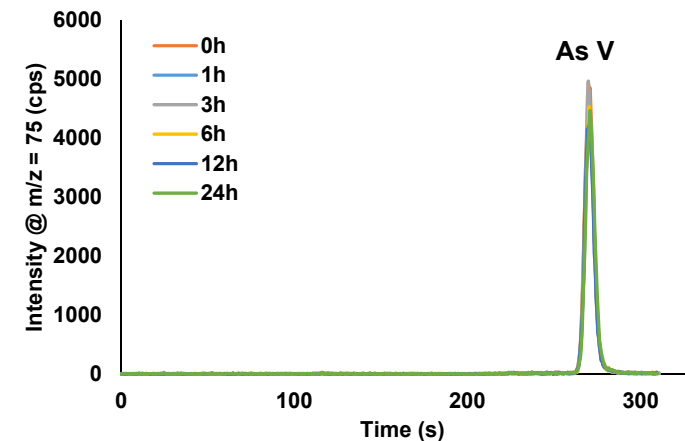
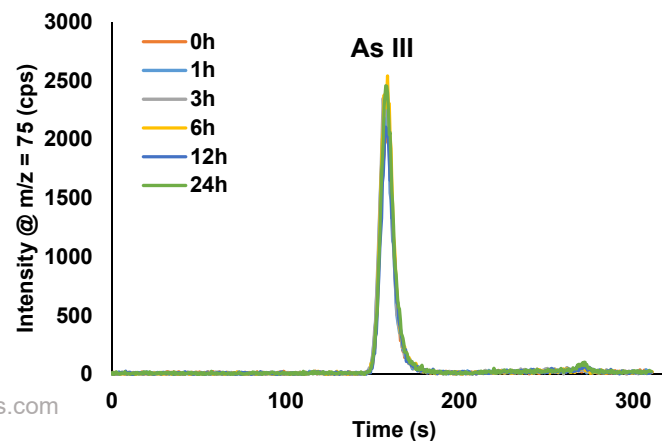
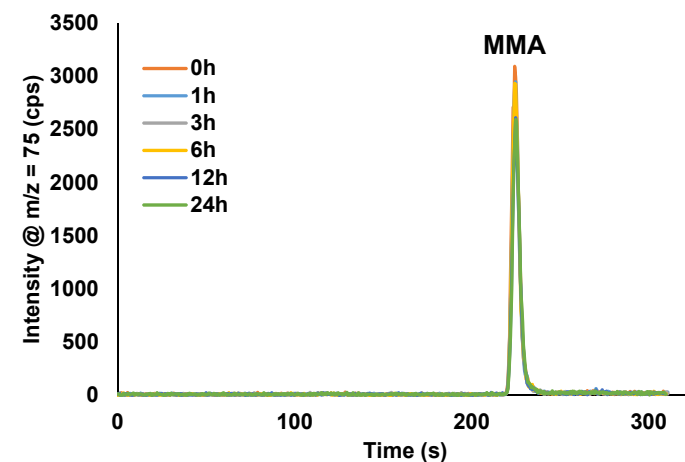
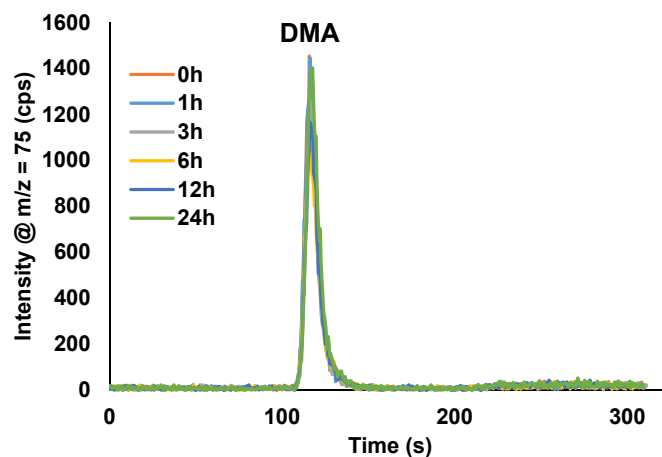
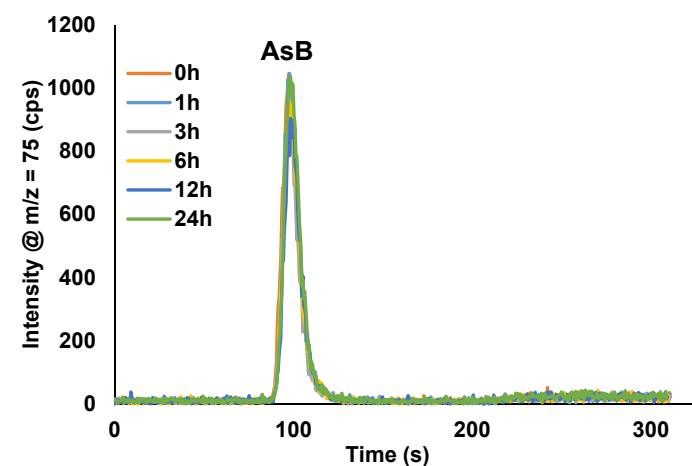
Manual Dilution Study – Urine Spiked with 10 ppb As



As V interconversion



Inline Dilution Study – Urine Spiked with 10 ppb As



Manual Dilution vs Inline Dilution - Summary

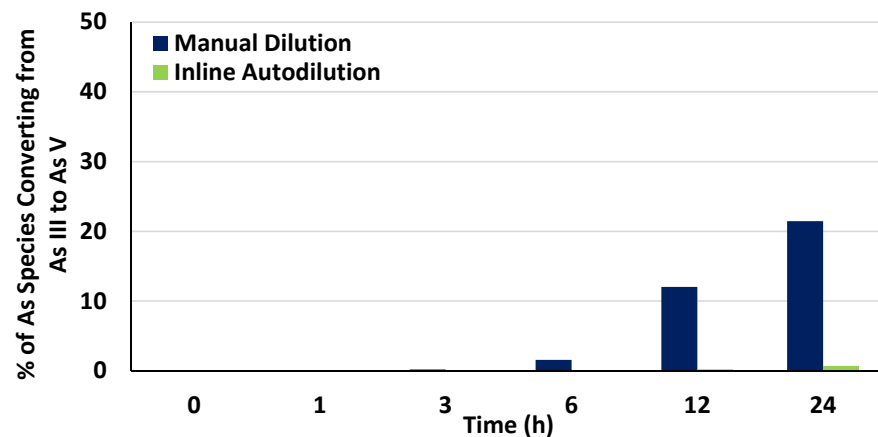
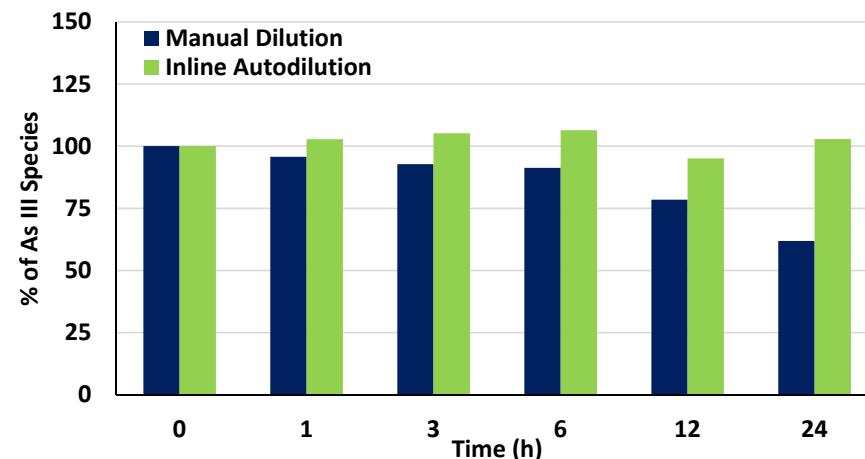
<i>Manual Dilution</i>	Time (h)	10 ppb As III Spiked Urine Samples		
		As III %	As V %	As III + As V
	0	100.0	0.0	100.0
	1	95.7	0.0	95.7
	3	92.8	0.2	93.0
	6	91.3	1.6	92.9
	12	78.5	12.0	90.6
	24	61.9	21.4	83.4

<i>Inline Autodilution</i>	Time (h)	10 ppb As III Spiked Urine Samples		
		As III %	As V %	As III + As V
	0	100.0	0.0	100.0
	1	102.8	0.0	102.8
	3	105.2	0.0	105.2
	6	106.4	0.0	106.4
	12	95.1	0.5	95.6
	24	102.9	1.3	104.2

As III % = (x h As III / 0 h As III) * 100

As V % = (x h As V / 0 h As III) * 100

As III + As V = As III % + As V %



Accuracy to NIST SRM 2669

	NIST Level I Certified Value (ppb)	All Methods Reported (ppb)		Measured Values (ppb)
		Min	Max	Avg $\pm$ 1 SD
AsB	12.4 $\pm$ 1.9	10.48	14.68	12.3 $\pm$ 1.0
DMA	3.47 $\pm$ 0.41	2.98	4.09	3.39 $\pm$ 0.35
As III	1.47 $\pm$ 0.10	1.14	1.86	1.34 $\pm$ 0.37
MMA	1.87 $\pm$ 0.39	1.5	2.55	1.54 $\pm$ 0.17
As V	2.41 $\pm$ 0.30	1.9	2.88	2.57 $\pm$ 0.53
Total	22.2 $\pm$ 4.8	18	26.06	20.85

	NIST Level II Certified Value (ppb)	All Methods Reported (ppb)		Measured Values (ppb)
		Min	Max	Avg $\pm$ 1 SD
AsB	1.43 $\pm$ 0.08	1.26	1.84	2.45 $\pm$ 0.54 [^]
DMA	25.3 $\pm$ 0.7	24.1	27.1	26.0 $\pm$ 3.6
As III	5.03 $\pm$ 0.31	4	6.2	5.58 $\pm$ 0.24
MMA	7.18 $\pm$ 0.56	6.51	8.24	6.96 $\pm$ 0.79
As V	6.16 $\pm$ 0.95	4.99	7.48	6.68 $\pm$ 0.85
AC	3.74 $\pm$ 0.35	3.14	4.27	n/a
TMAO	1.94 $\pm$ 0.27	1.18	3.02	n/a
Total	50.7 $\pm$ 6.3	45.18	58.15	47.62

[^] AsB (1.43) + TMAO (1.94) = 3.37 ppb (2.44 ppb (min.) – 4.86 ppb (max.))



Automated Aqua Regia & Cr Speciation Method

prepFAST IC + Agilent 7900 ICP-MS

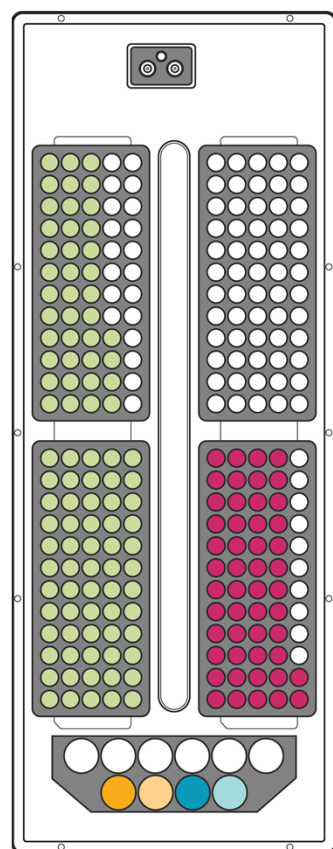


Scope

- Update older HPLC + ICP-MS method that has been used for testing Cr VI in drinking water, waste water, and soil
- Implement a new automated LC system from Elemental Scientific that incorporates inline dilutions and the ability to switch between speciation and total metals
 - Develop and validate Cr speciation method using the prepFAST IC + Agilent 7900 ICP-MS
 - Transfer Aqua Regia digest method for total metals (63 elements) onto the prepFAST IC platform



prepFAST IC –Total Metals and Speciation



- Samples of Total Metals
- Samples of Speciation
- Speciation Stock Standard
- Speciation Blank
- Total Metals Stock Standard
- Total Metals Blank

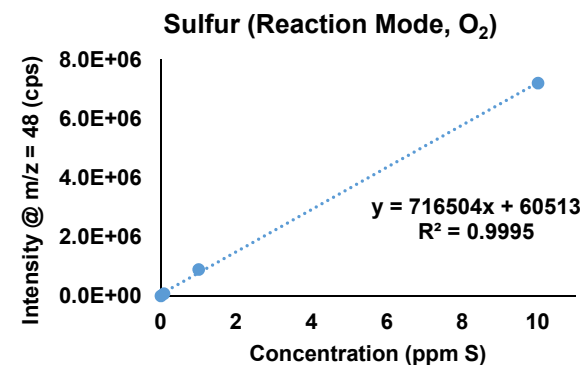
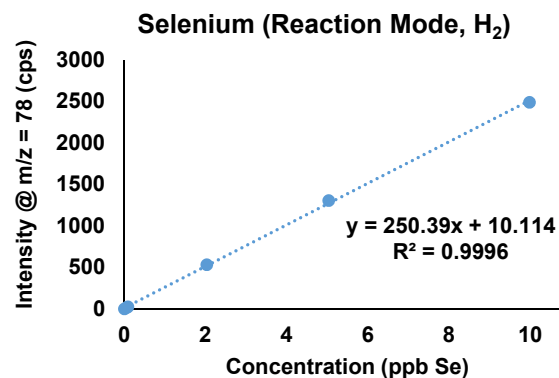
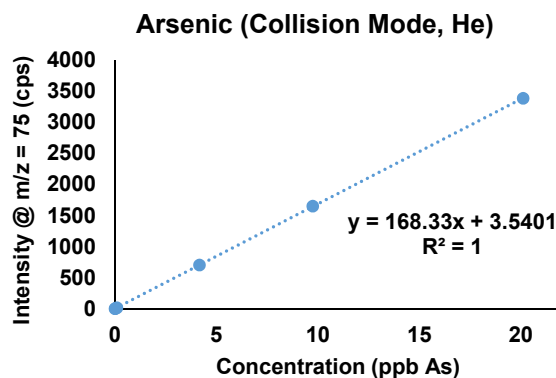
Autosampler Location	Dilution Factor	Sample	Action
1	1	Blank - Total Metals	Total Metals
2	50	Standard 1	Total Metals
2	25	Standard 2	Total Metals
2	10	Standard 3	Total Metals
2	5	Standard 4	Total Metals
2	1	Standard 5	Total Metals
101	10	Sample 1	Total Metals
↓	↓	↓	Total Metals
240	10	Sample 100	Total Metals
10	1	Dummy Sample	Prime for Speciation Method
3	1	Blank - Speciation	Speciation
4	100	Standard 1	Speciation
4	20	Standard 2	Speciation
4	10	Standard 3	Speciation
4	5	Standard 4	Speciation
4	2	Standard 5	Speciation
301	10	Sample 1	Speciation
↓	↓	↓	Speciation
350	10	Sample 50	Speciation
9	1	Dummy Sample	Prime for Total Metals

Aqua Regia Method (Total Metals)

prep*FAST* IC + Agilent 7900 ICP-MS



prepFAST IC for Total Metals

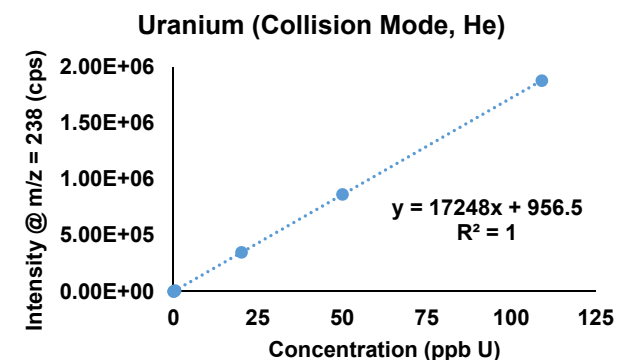
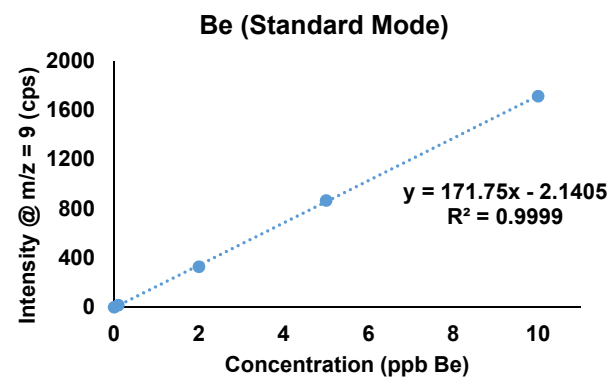


Total Metals Method:

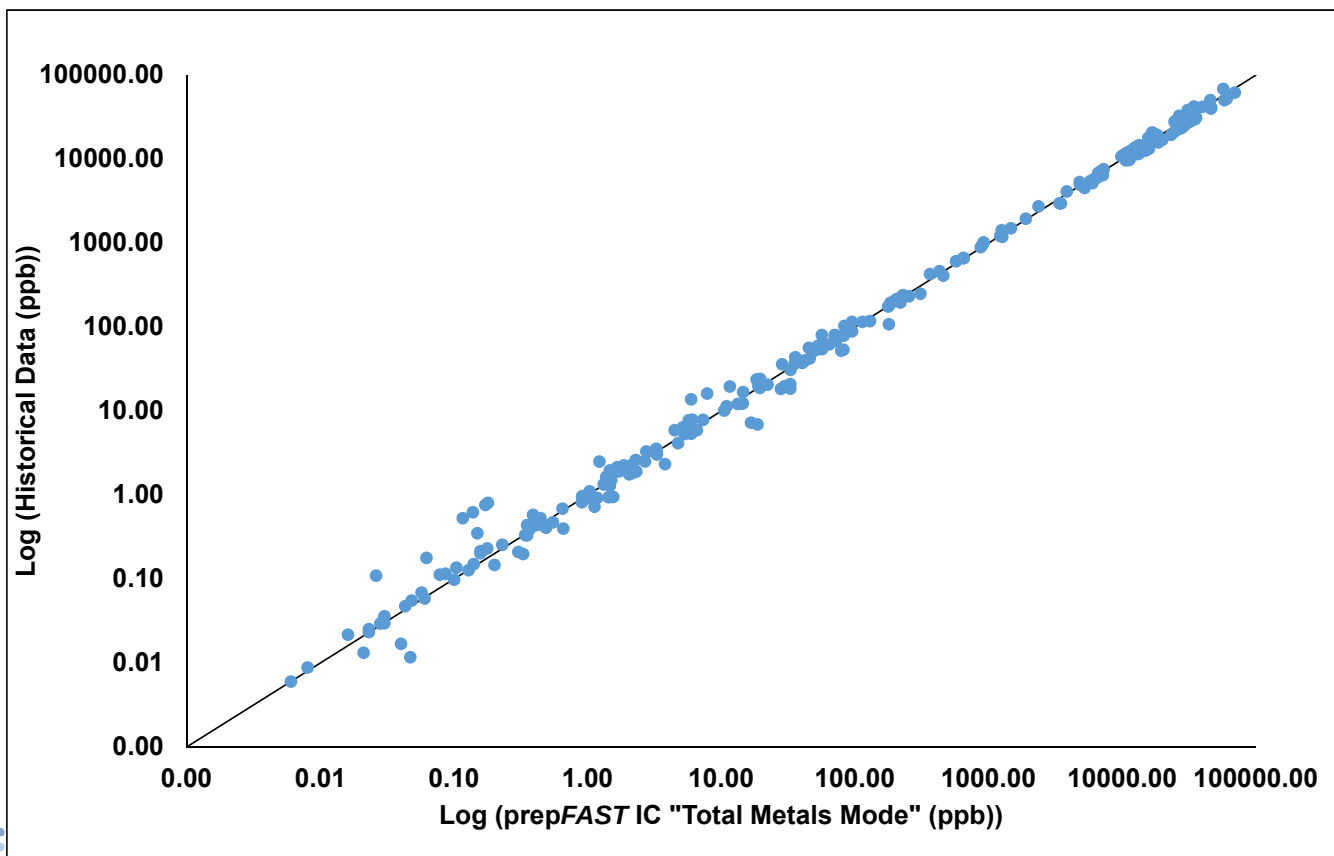
63 elements

Aqua regia matrix

4 different modes



Total Metals - Comparison to Historical Data



Average %BIAS = 1.1%

-2.23% Difference in Methods

$(0.9777 - 1.0)/1.0 \times 100 = -2.23\%$

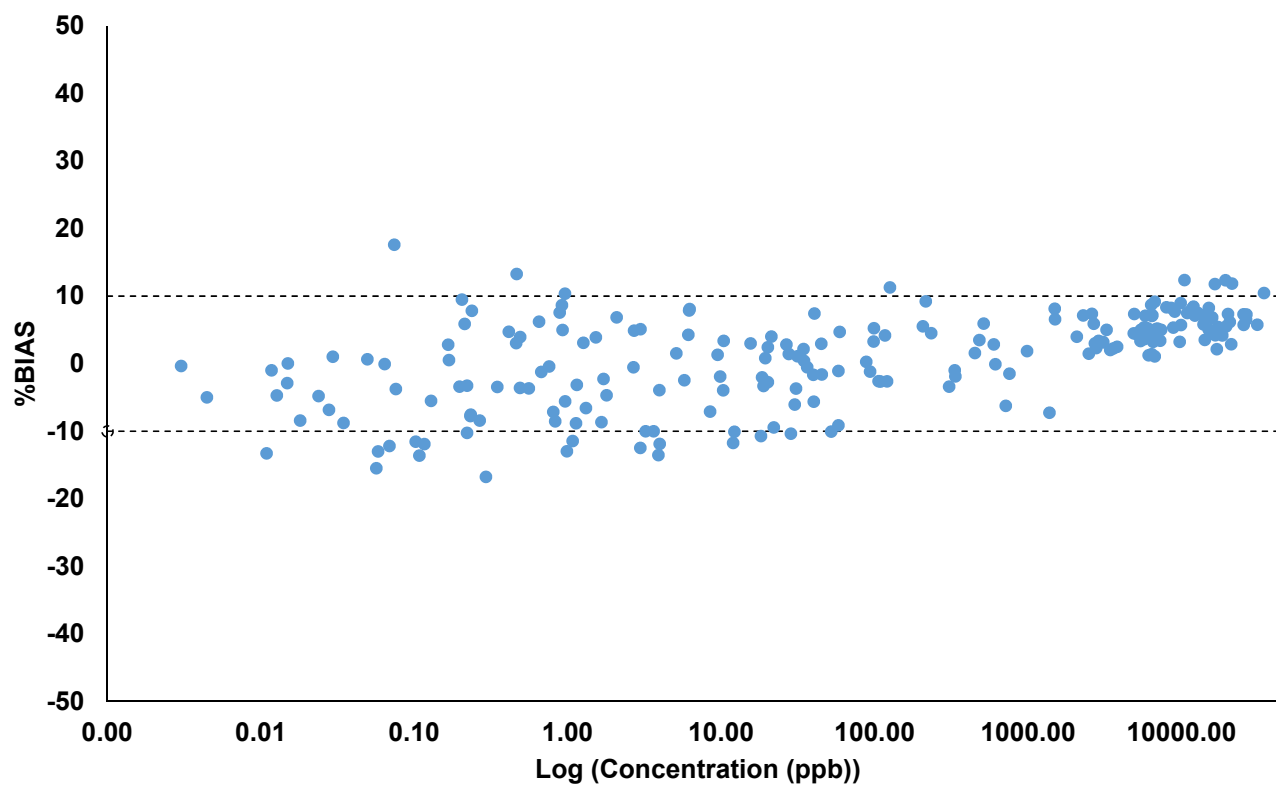
Samples:

Historical and prepFAST IC data all collected on same type of ICP-MS

Summary of 63 element method across 15 samples analyzed.



Comparison to Historical Data



Average %BIAS = 1.1%

Absolute Value %BIAS = 5.6%

Samples:

Historical and prepFAST IC data all collected on Agilent 7900 ICP-MS



Cr Speciation

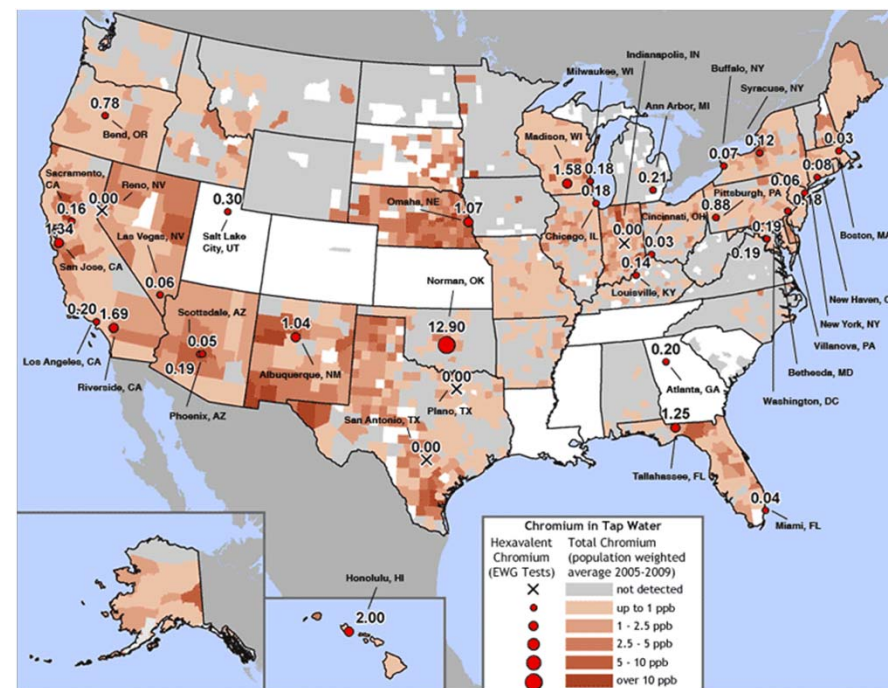
prep*FAST* IC + Agilent 7900 ICP-MS



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Chromium

- Cr (VI) is toxic where Cr (III) is an essential element in carbohydrate metabolism.
- Cr (VI) is easily transported across cell membranes, and is linked to lung cancer and stomach ulcers.
- Cr exposure:**
 - fruit, meat, vegetables, supplements, Industrial exposure (leather tanning, stainless steel welding, alloy production).
 - Degradation of metal-on-metal implants.
 - Contamination coming from utility companies producing Cr (VI) that is released into river or streams.
- Drinking Water Regulations**
 - US EPA – 100 ppb Cr (100 ppb Cr VI, assumed total Cr)
 - California pushing for 10 ppb Cr VI
 - European Union – 50 ppb Cr
 - WHO – 50 ppb Cr



HPLC and prepFAST IC Methods

HPLC + Agilent 7900 ICP-MS

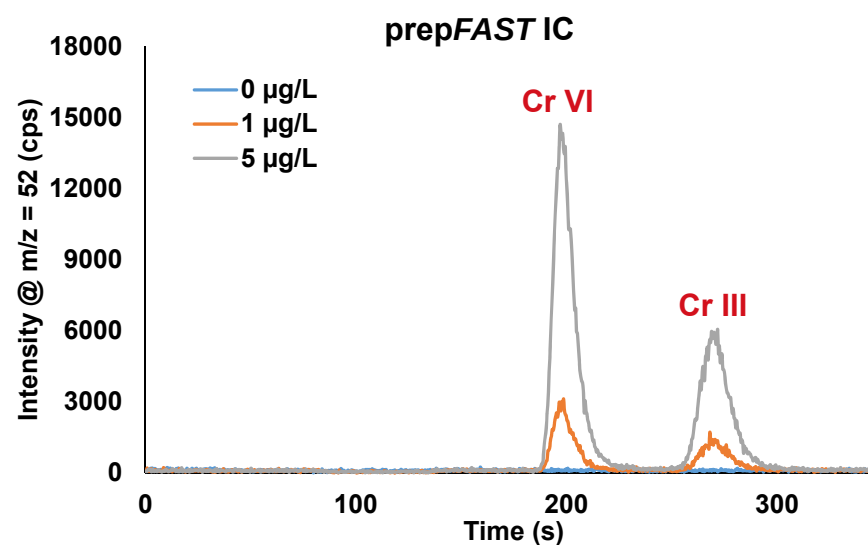
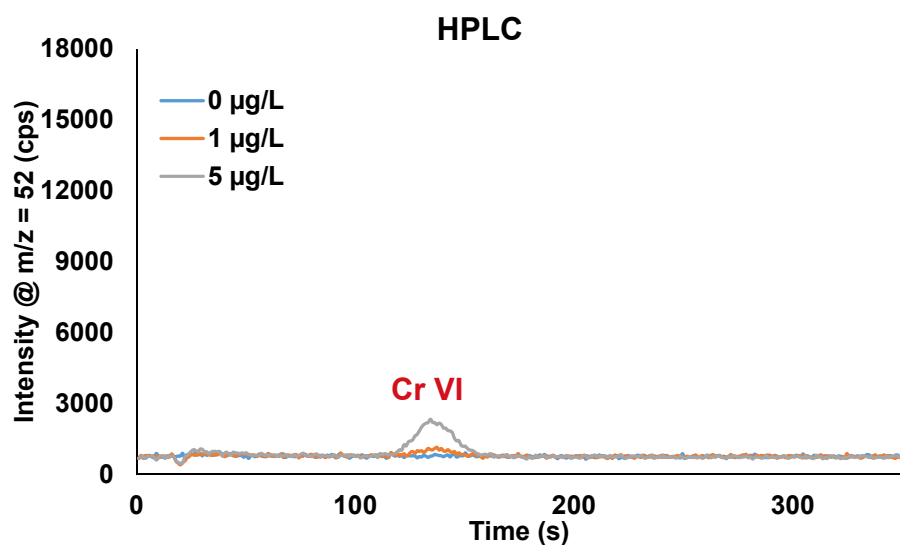
- Anion Exchange Column, 30 x 4.6 mm
- Eluent: 5 mM EDTA, 5 mM NaH₂PO₄, 15 mM Na₂SO₄, pH = 7
- Flow Rate = 1.2 mL/min
- Injection Volume = 100 µL
- Dwell Time = 500 ms
- Cell gas = 2 mL/min He

prepFAST IC + Agilent 7900 ICP-MS

- Anion Exchange Column, 50 x 4 mm
- Eluent: 10 ppm Tm, ~500 mM NH₄NO₃, pH = 1.9
- Flow Rate = 0.3 mL/min
- Injection Volume = 300 µL
- Dwell Time = 100 ms
- Cell gas = 2 mL/min He



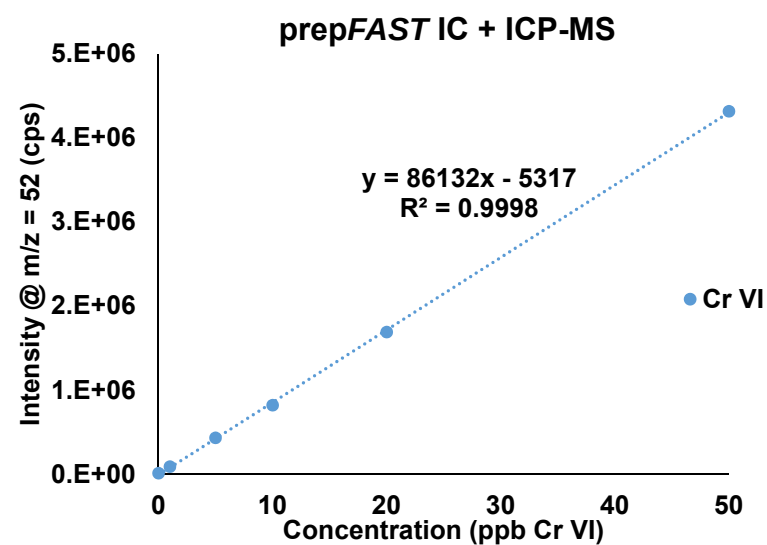
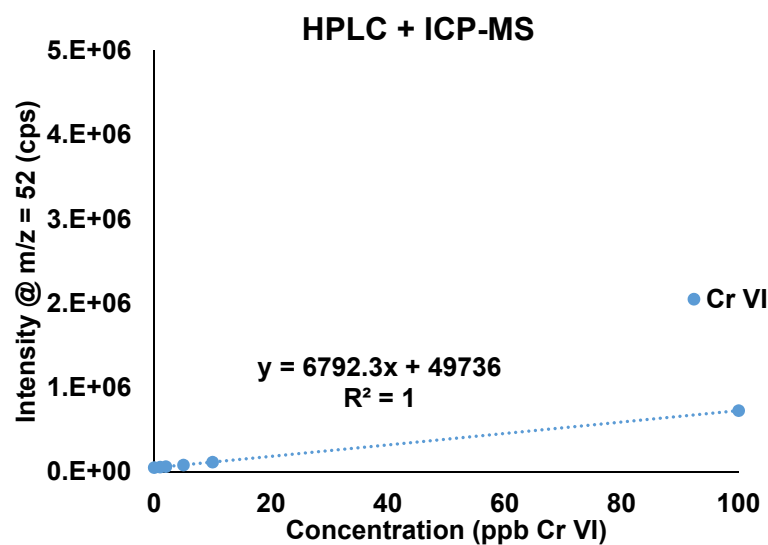
Comparison to HPLC



* Same type of ICP-MS used for both methods.



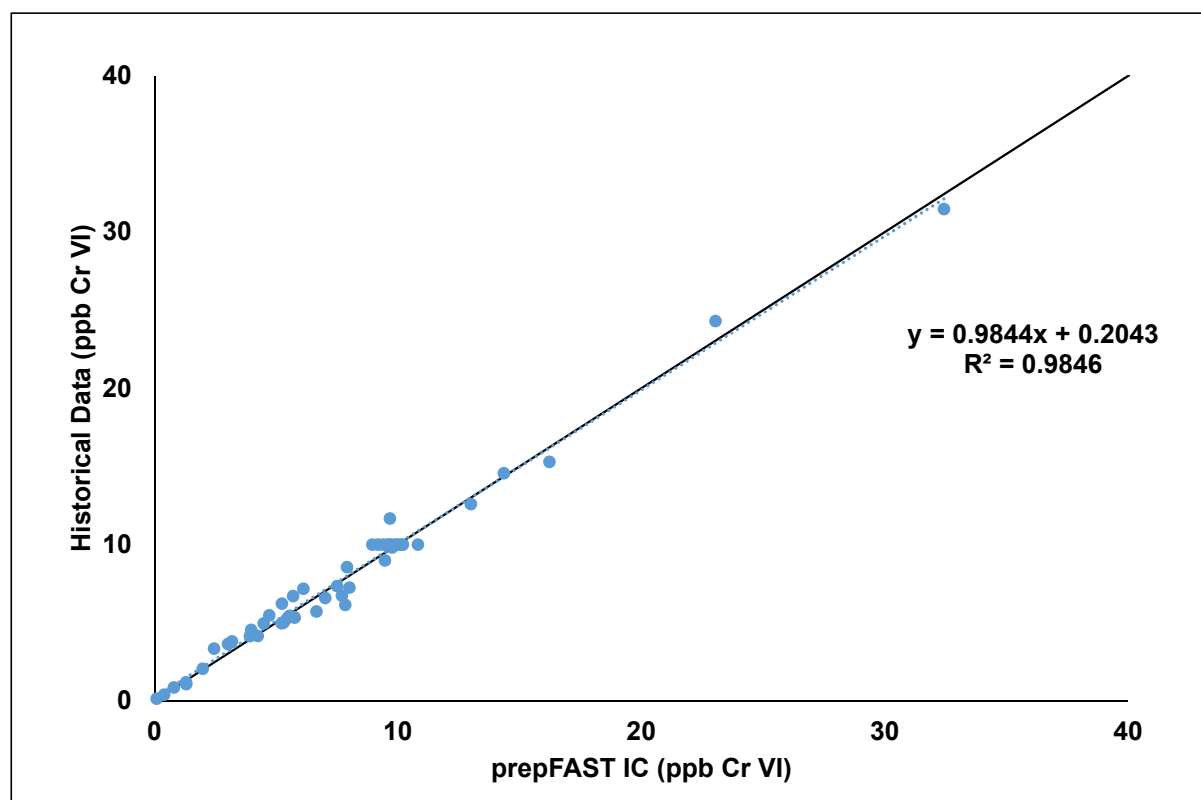
Comparison to HPLC



* Same type of ICP-MS used for both methods.



Cr Speciation - Comparison to Historical Data



Average %BIAS = -1.9%

-1.56% Difference in Methods

$(0.9844 - 1.0)/1.0 \times 100 = -1.56\%$

Samples:

Historical Data = HPLC

HPLC – No Dilution Factor

prepFAST IC – 10X Inline Dilution



Figures of Merit

	Cr VI	
	LOD	LOQ
HPLC + Agilent 7900 ICP-MS	0.3 µg/L	1.0 µg/L
prepFAST IC + Agilent 7900 ICP-MS	0.007 µg/L	0.023 µg/L

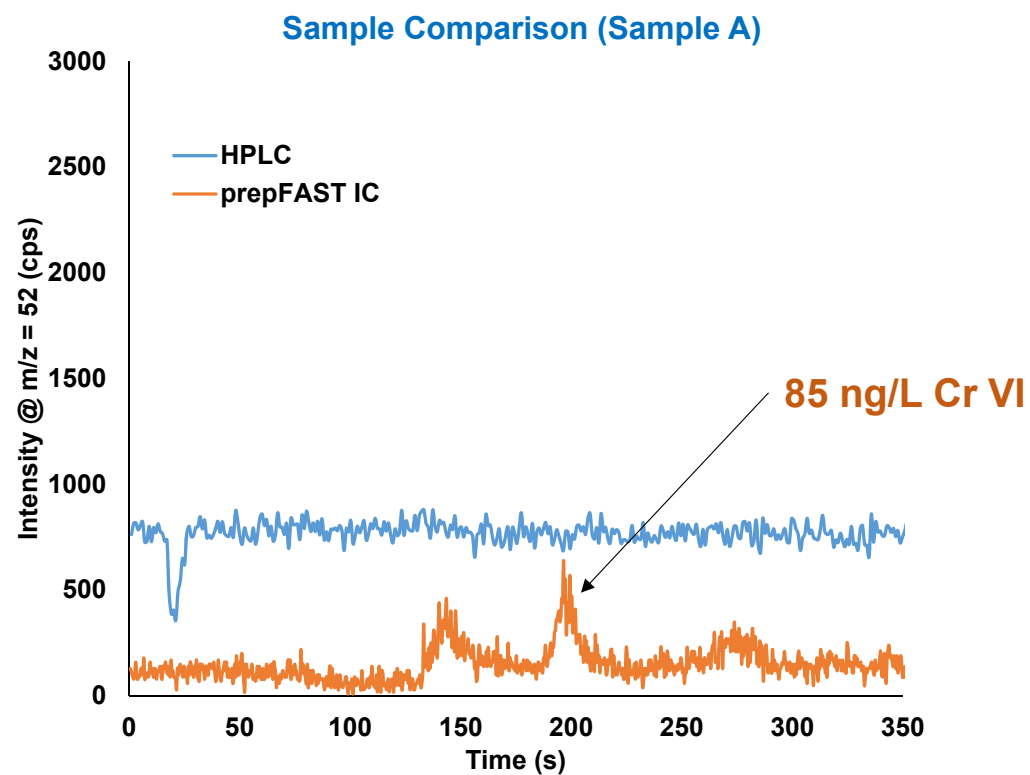
	HPLC + Agilent 7900 ICP-MS	prepFAST IC + Agilent 7900 ICP-MS
QC Target (µg/L)	10.00	10.00
Measured Value (µg/L)	9.91 ± 0.67	9.85 ± 0.46
Min - Max Value (µg/L)	8.34 - 11.44	9.18 - 10.82
%BIAS	-0.88%	-1.52%

Sensitivity Check	Response for 1 ppb Cr (cps)
ICP-MS used for HPLC measurements	7091 ± 860
ICP-MS used for prepFAST IC measurements	6813 ± 344

1 ppb Cr solution analyzed as daily performance check solution. n = 3.



Improvements in Low Level Detection



prepFAST IC Method provides a ~ 43X improvement in LOD/LOQ as compared to the older method



Acknowledgements

Elemental Scientific, Omaha, NE, USA

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Sandra Pettersson

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PerkinElmer Technical Center, John's Creek, GA, USA

John Leone



THANK YOU



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