An interlaboratory comparison of elemental loadings on CSN $PM_{2.5}$ samples via energy-dispersive XRF and single quadrupole ICP-MS

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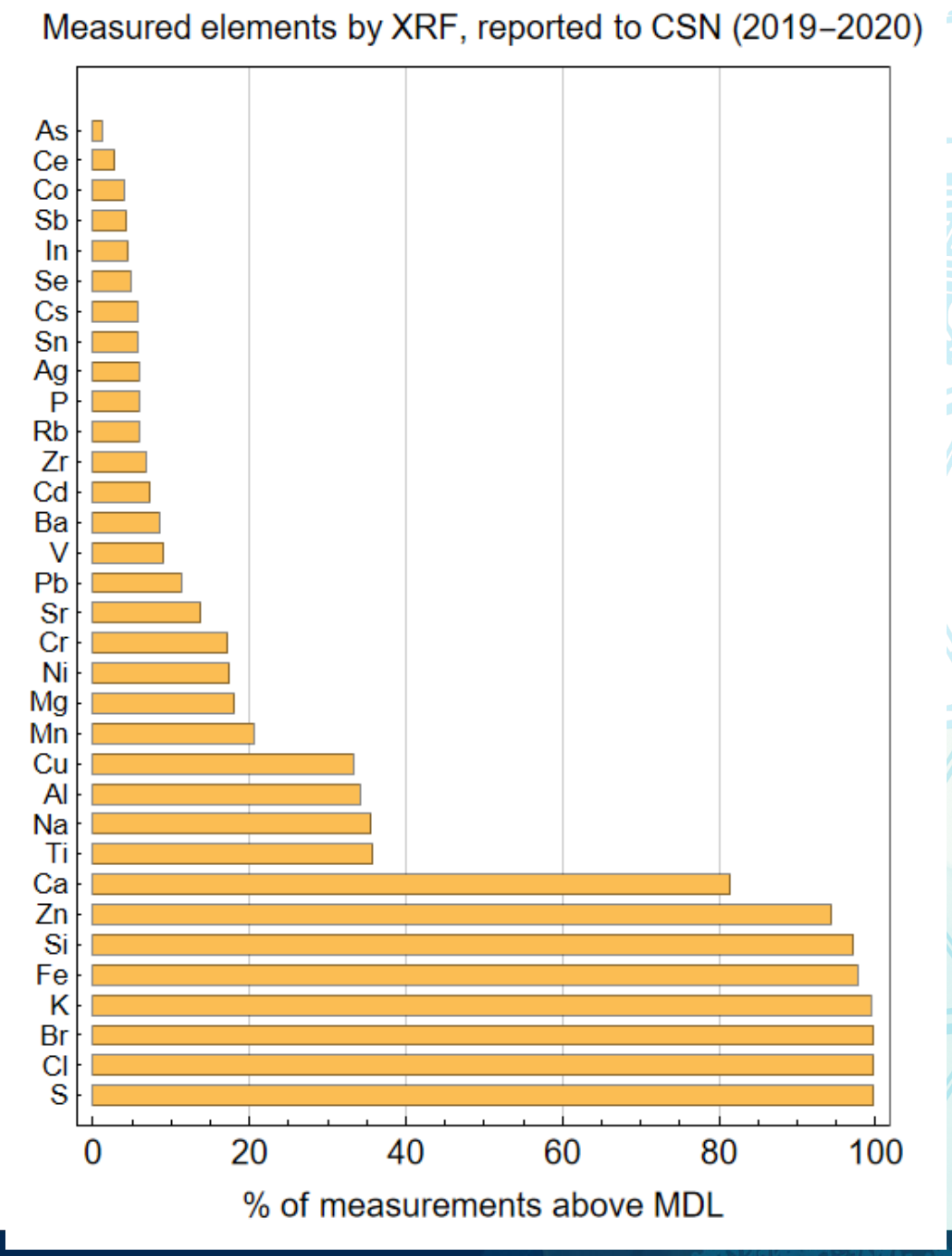
Motivation

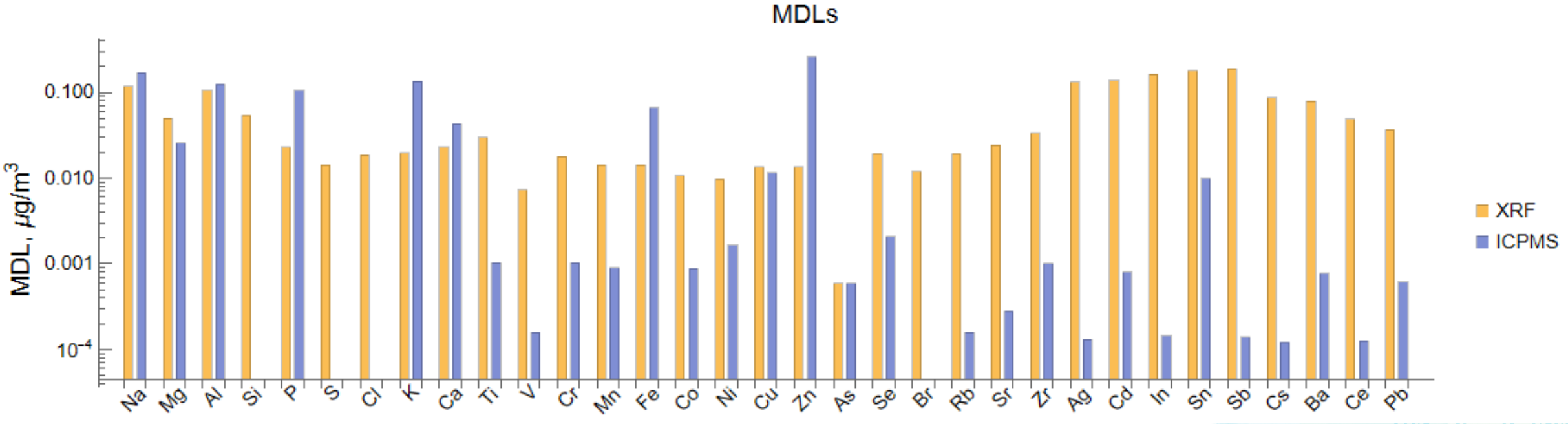
- Pollutant concentrations since inception of CSN have decreased

→Many elements are at/below the detection limits of current analytical techniques

→Can we use a low-cost ICPMS solution to achieve better detection of the elements?



MDLs



- 4 elements measured by XRF cannot be measured using the applied ICPMS protocol (Si, S, Cl, Br)
- All elements regularly measured below MDL by XRF can be measured via ICPMS
- Note: MDLs are calculated differently for XRF and ICPMS

XRF & ICPMS

Image from Thermo Fisher

	XRF	ICPMS
Sample Preparation	None	Acid digestion
Sample run time (multi-element)	~1 hour	10-15 minutes
Calibration Standards	Single or multi-element	Multi-elemental standard
Frequency of calibration	Yearly	Before every run
Sample Preservation	Nondestructive	Destructive

Sample Selection + Analyses

- **Archived CSN samples in UCD (analyzed via XRF): January 2019 – August 2020**

↓

- Batch 1 (N=209): 33 elements (10^{th}, 50^{th}, and 90^{th} percentile sample for each element)
- Batch 2 (N=146): Collocated samples from 3 sites
  - 18 from Rutgers, NJ; 38 from Dudley Square (Boston, MA); 20 from Rubidoux (Riverside, CA)
- Batch 3 (N=194) : Higher total elemental concentrations based on UCD XRF

↓

Sent to RTI

↓

XRF

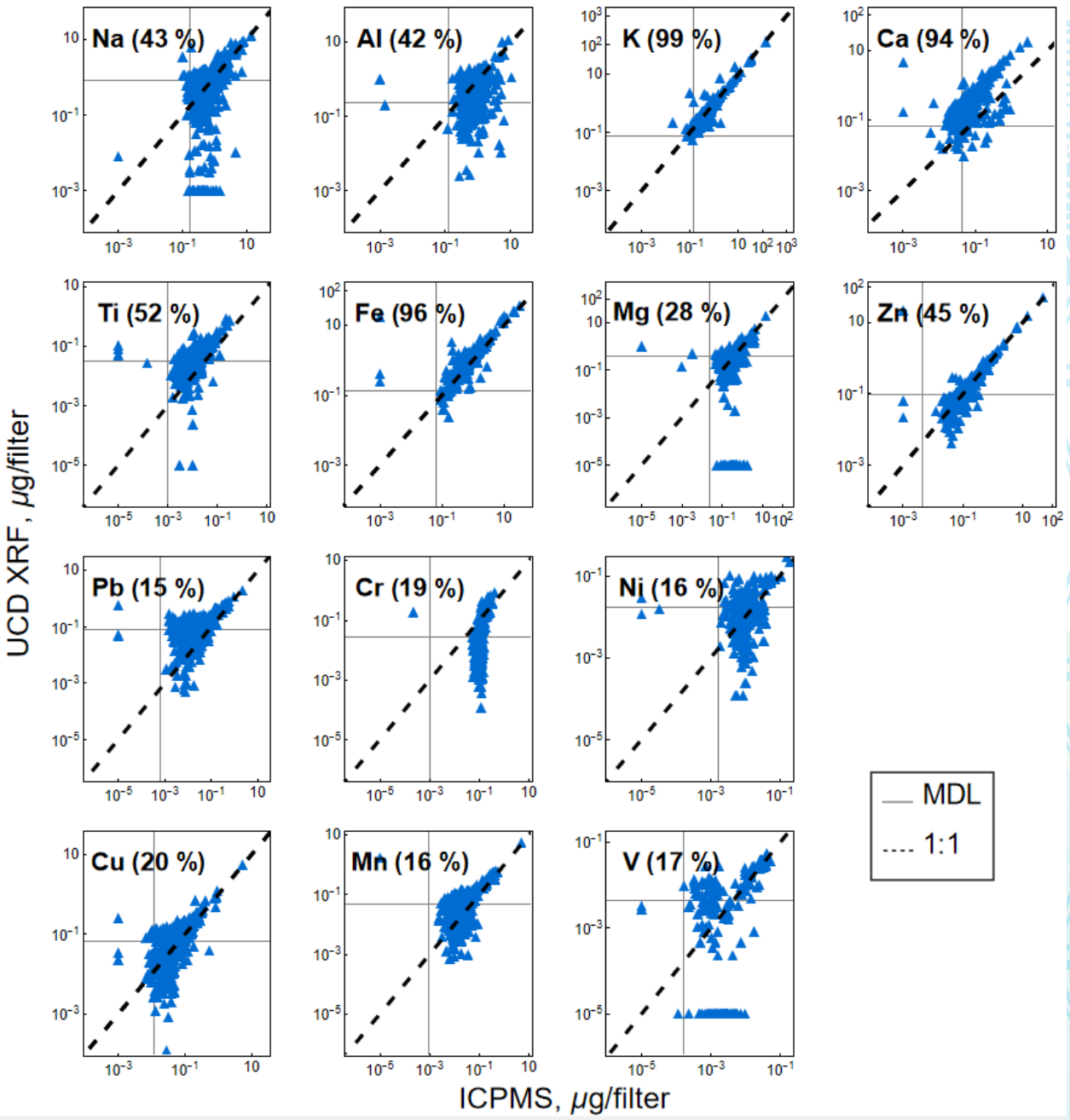
↓

ICPMS

UCD XRF - ICPMS

- Measurements compare well for elements measured above MDL >10% of the time.
  - Only 14 elements meet this criterion for XRF
- Ca, Cr and Ni agreement is poor even above MDL estimates

  → measurements not quantifiable by one or both methods or the extraction (leaching) is incomplete.



percentage = % of values above UCD XRF MDL

In these plots, values less than 10^{-3} (for Na, Al, K, Ca, Fe, Zn, and Mg) or 10^{-5} (for Ti, Cu, Pb, Cr, Ni, Mg, Mn, V) including negative values, were assigned a floor value of 10^{-3} or 10^{-5}, respectively.

Considerations:

- **Were the elements detected?**

  Intra-method: Method detection limits

- **Are the reported concentrations reliable?**

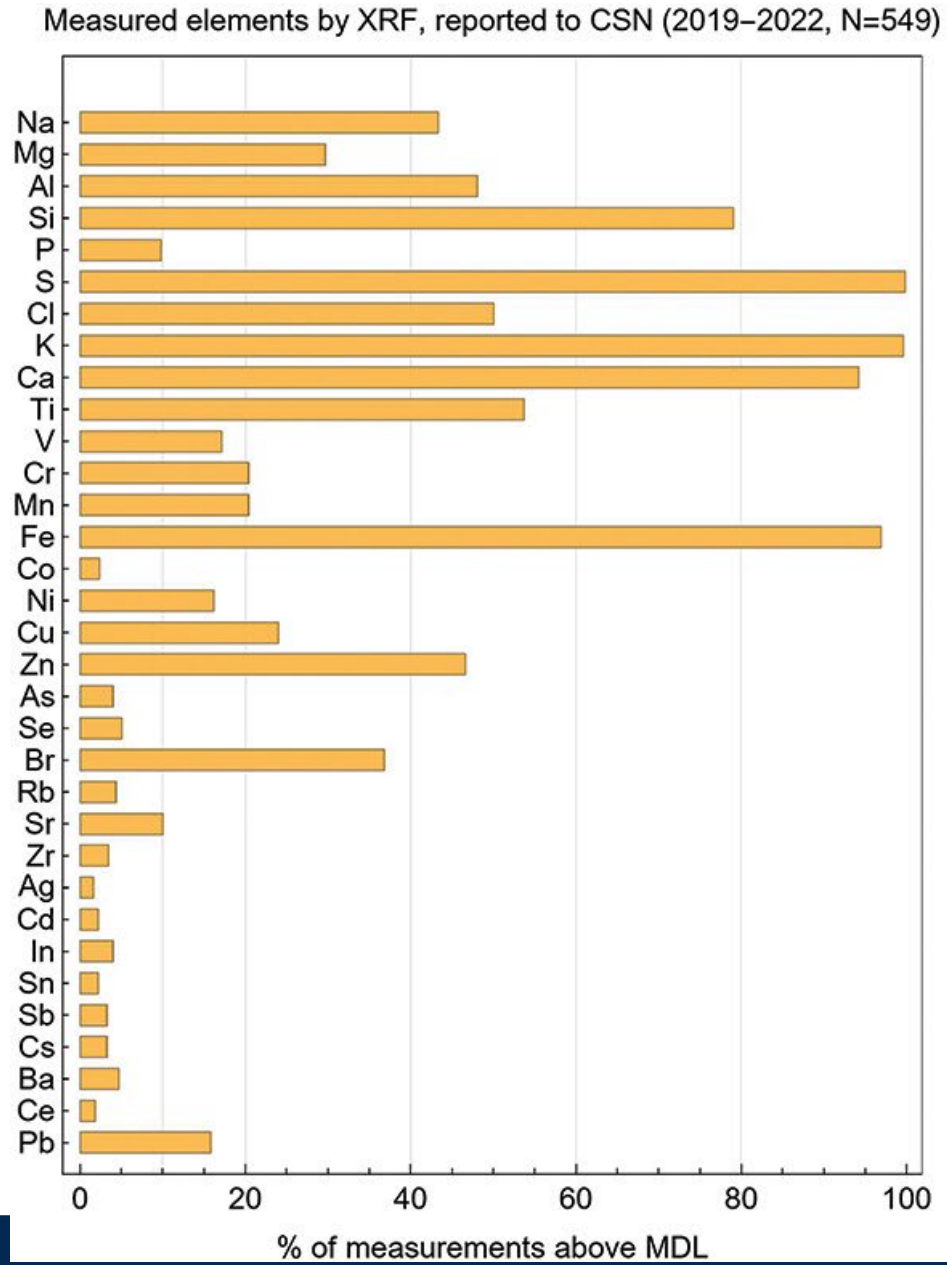
  Inter-method: XRF-ICPMS intercomparison

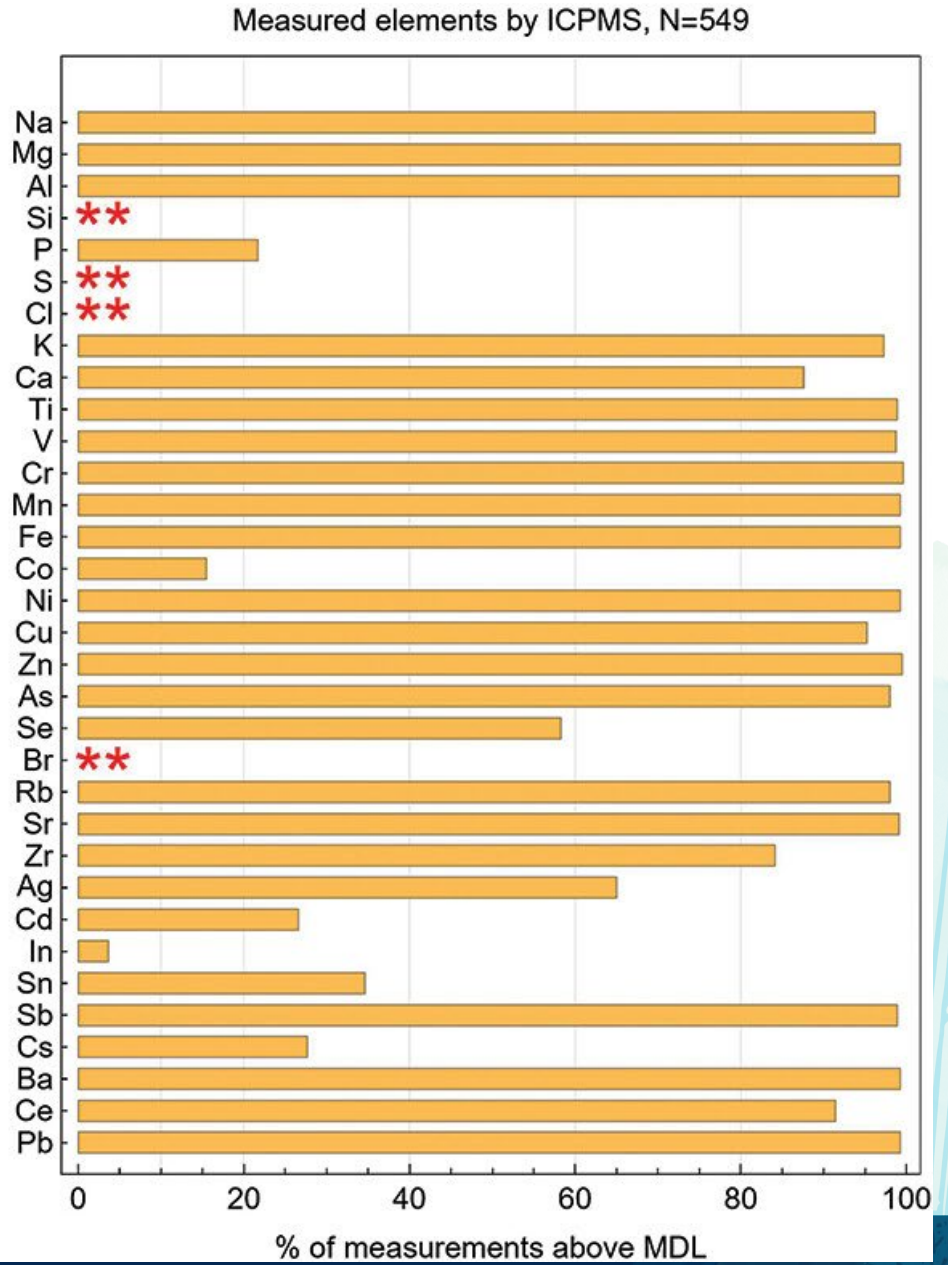
  Intra-method: inter-elemental comparison; collocated samples (precision)

- **Was the ICPMS extraction complete?**

  Evaluated using reference materials (NIST SRM 1648a, 1633)

Detection Rates in this Study





Considerations:

- **Were the elements detected?**

  Intra-method: Method detection limits

- **Are the reported concentrations reliable?**

  Inter-method: XRF-ICPMS intercomparison

  Intra-method: inter-elemental comparison; collocated samples (precision)

- **Was the ICPMS extraction complete?**

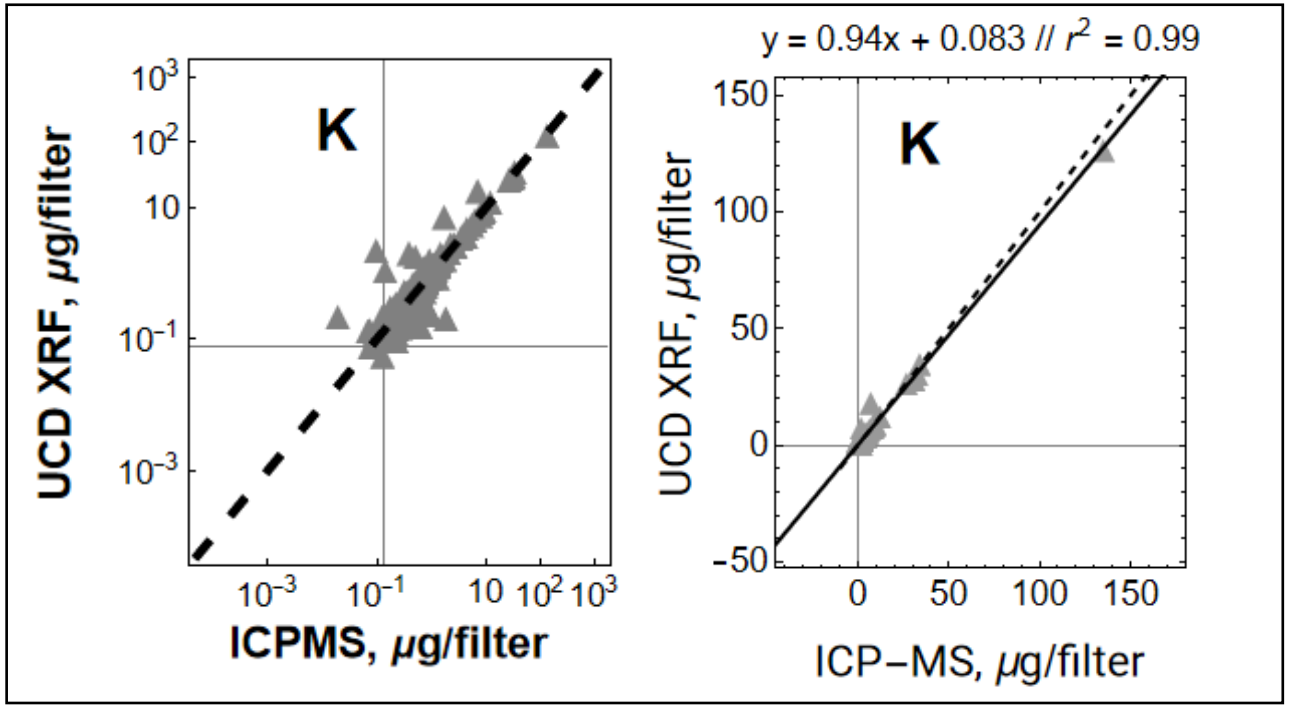
  Evaluated using reference materials (NIST SRM 1648a, 1633)

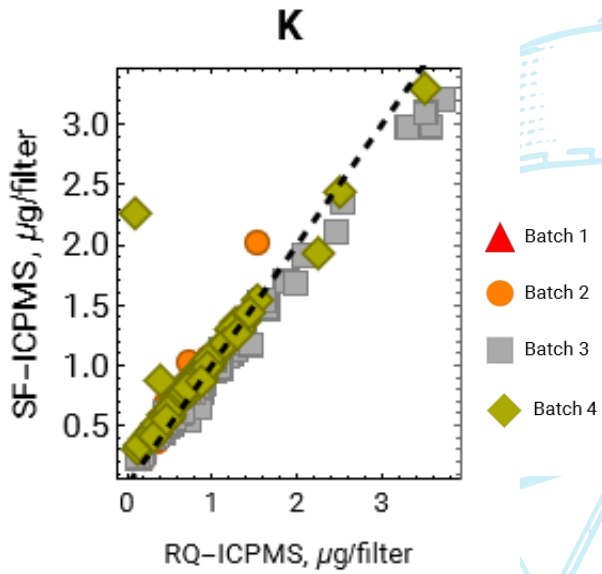
✓ **XRF**
✓ **RQ ICPMS**

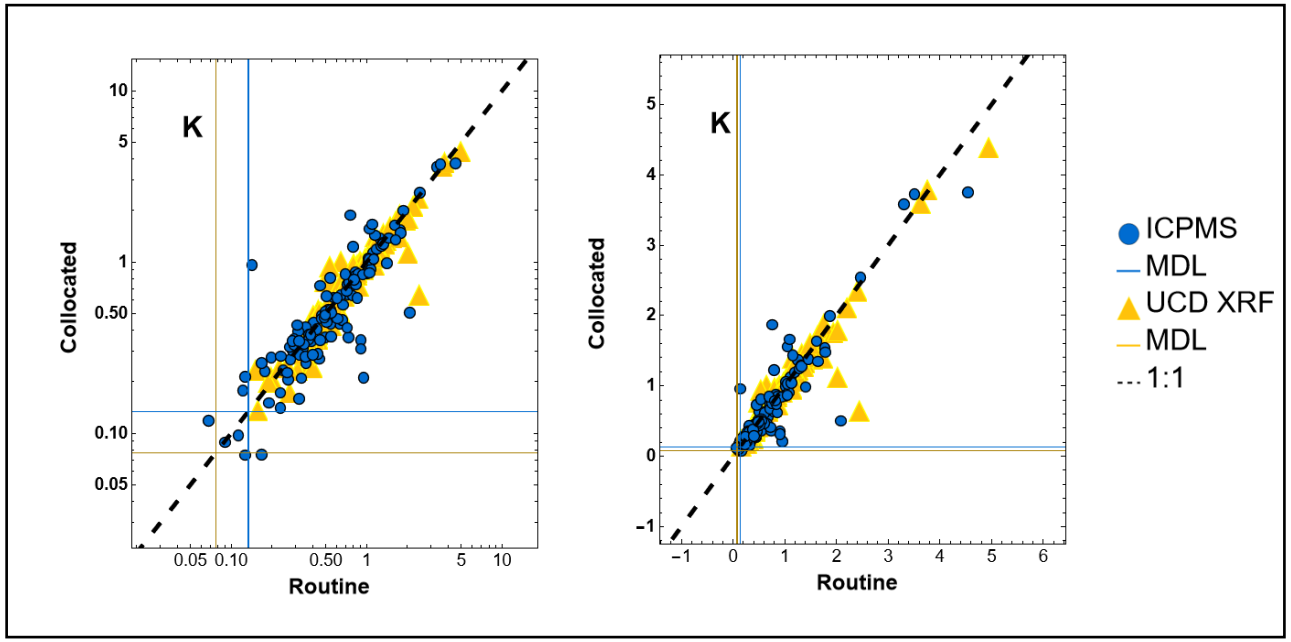
- Lighter elements show good collocated-routine agreement for both ICP-MS and XRF (K, Zn, Fe)

K

XRF > 10% MDL	YES
% above MDL	99%
RQ ICPMS >10% MDL	YES
% above MDL	97%
RQ ICPMS 1648a recovery acceptable? (5% HNO3 + 2 hour hot block digestion)	NO
Which MDL is lower	UCD XRF
Other notes	•OK MDL •OK XRF-ICPMS inter-method





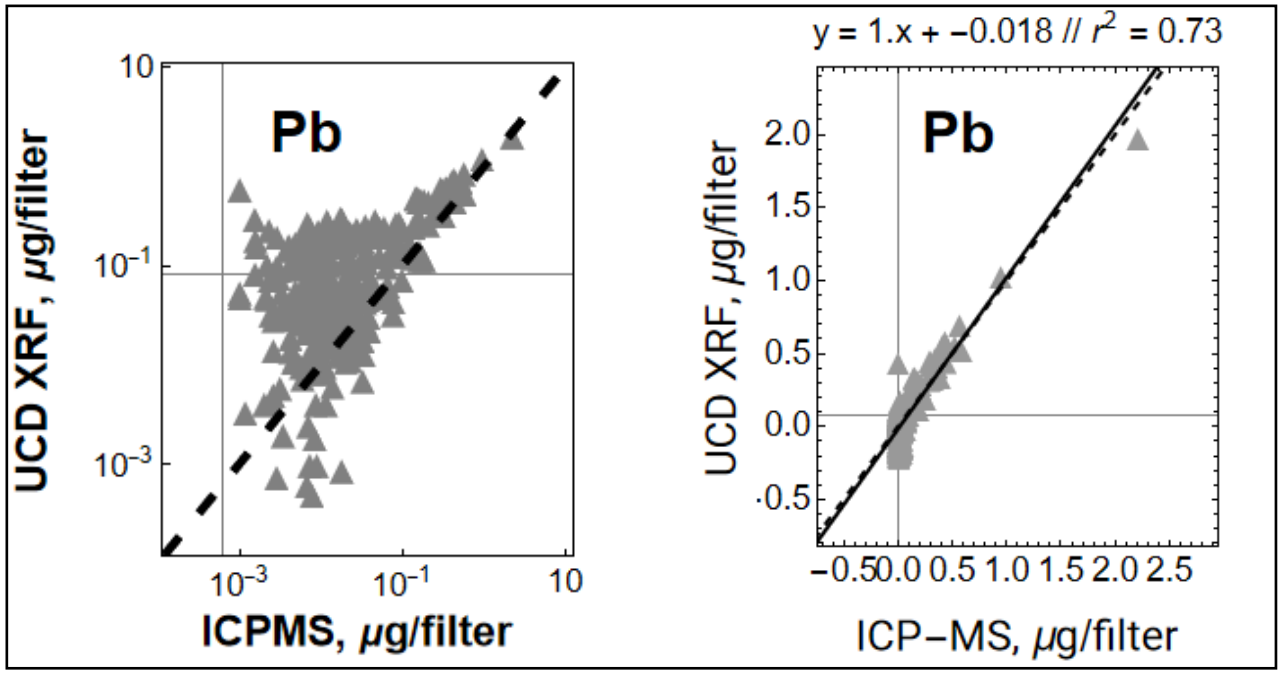


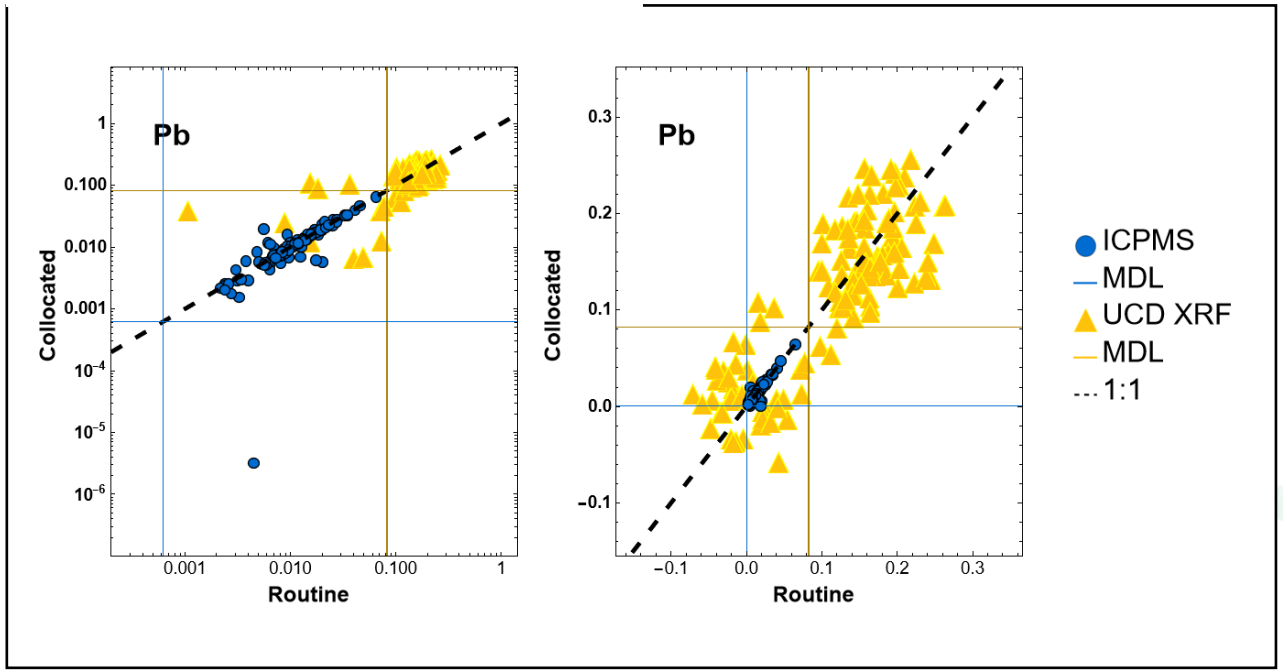
✓ XRF
✓ RQ ICPMS

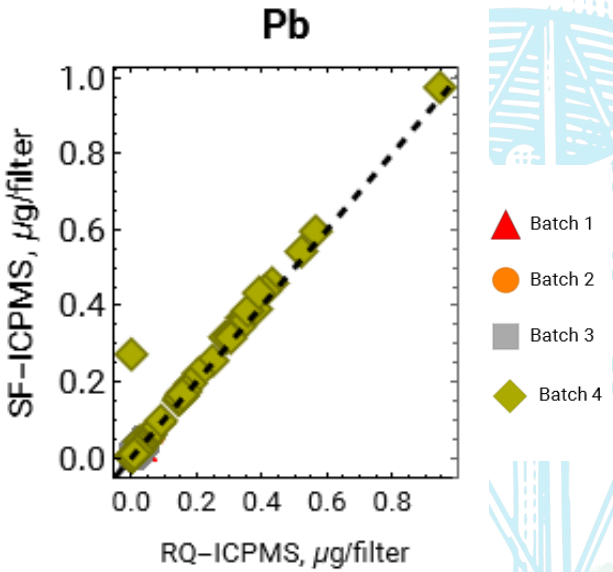
- Lighter elements show good collocated-routine agreement for both ICP-MS and XRF (K, Zn, Fe)

Pb

XRF > 10% MDL	YES
% above MDL	15%
RQ ICPMS > 10% MDL	YES
% above MDL	99%
RQ ICPMS 1648a recovery acceptable? (5% HNO3 + 2 hour hot block digestion)	YES
Which MDL is lower	ICPMS
Other notes	Pb is "noise" above MDL in XRF - ICPMS intercomparison







✓ XRF
✓ RQ ICPMS

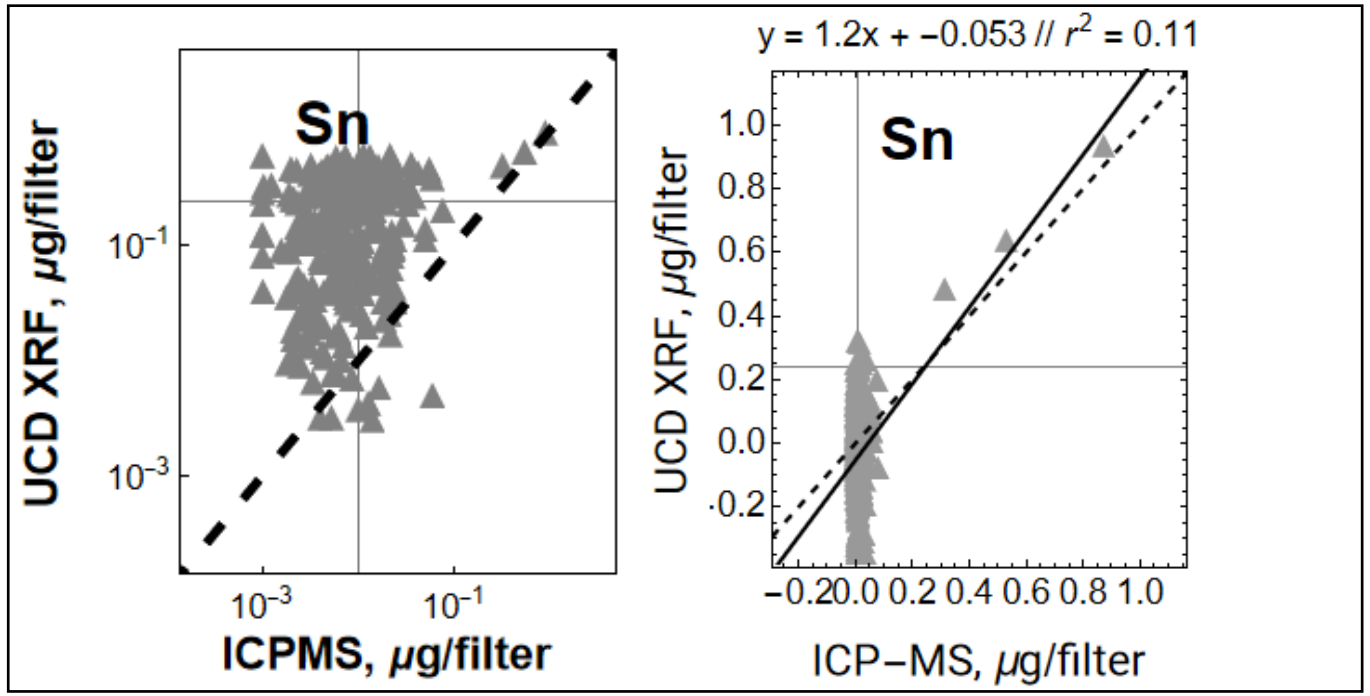
- Lighter elements show good collocated-routine agreement for both ICP-MS and XRF (K, Zn, Fe)

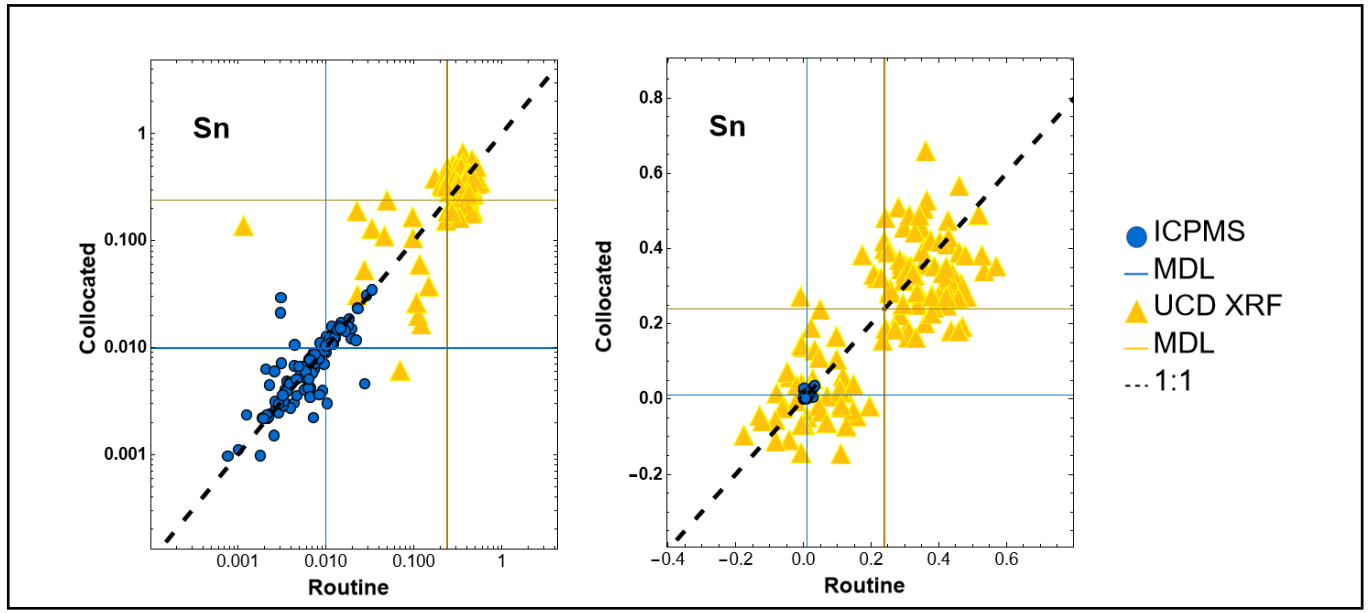
× XRF
✓ RQ ICPMS

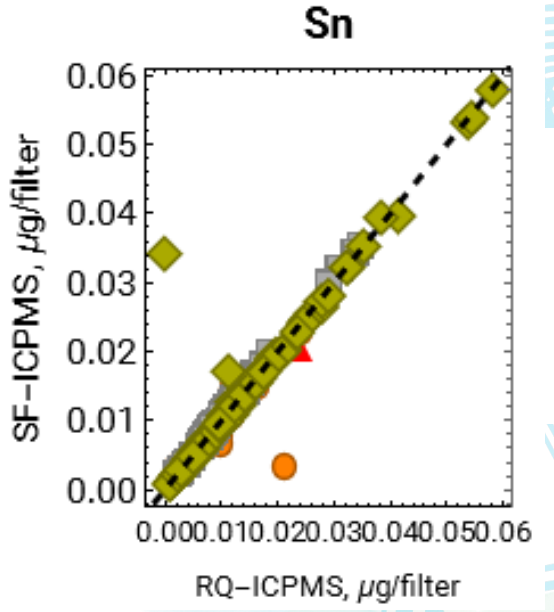
- Lower ICP-MS MDL are obvious
- Collocated measurements agreeing down to much lower concentrations for ICP-MS than XRF (As, Cd, Sb, Pb, Zr, Rb, Sr)

Sn

XRF > 10% MDL	NO
% above MDL	2%
RQ ICPMS > 10% MDL	YES
% above MDL	35%
RQ ICPMS 1648a recovery acceptable ? (5% HNO3 + 2 hour hot block digestion)	Not evaluated
Which MDL is lower	ICPMS







✓ XRF
✓ RQ ICPMS

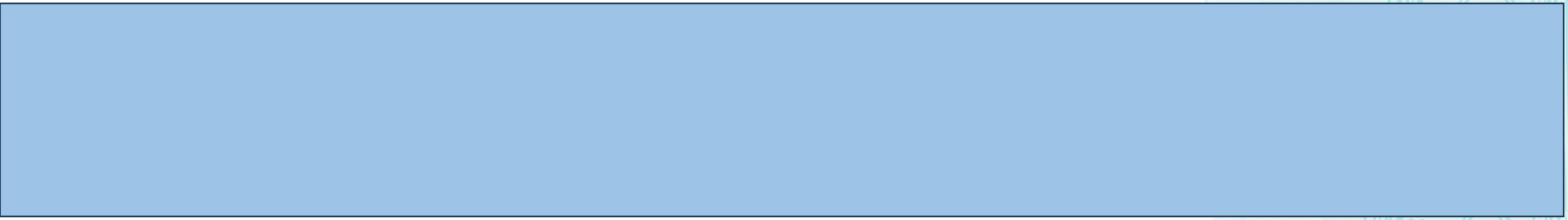
- Lighter elements show good collocated-routine agreement for both ICP-MS and XRF (K, Zn, Fe)

× XRF
✓ RQ ICPMS

- Lower ICP-MS MDL are obvious
- Collocated measurements agreeing down to much lower concentrations for ICP-MS than XRF (As, Cd, Sb, Pb, Zr, Rb, Sr)

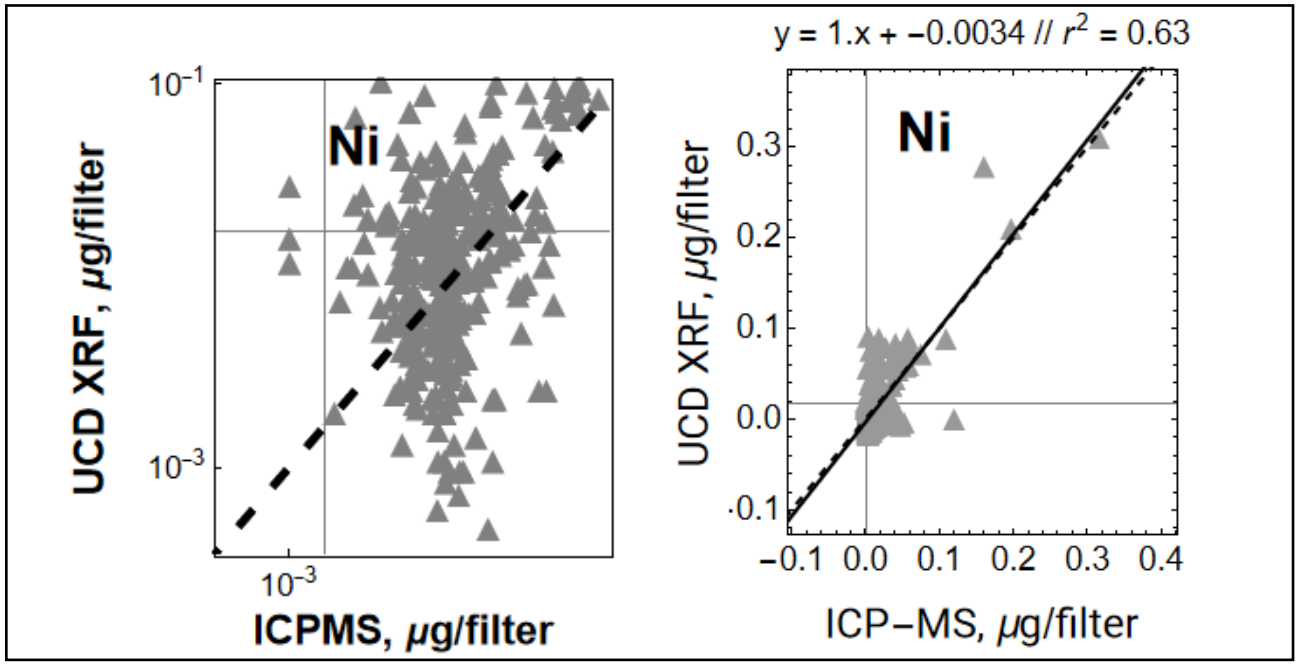
× XRF
? RQ ICPMS

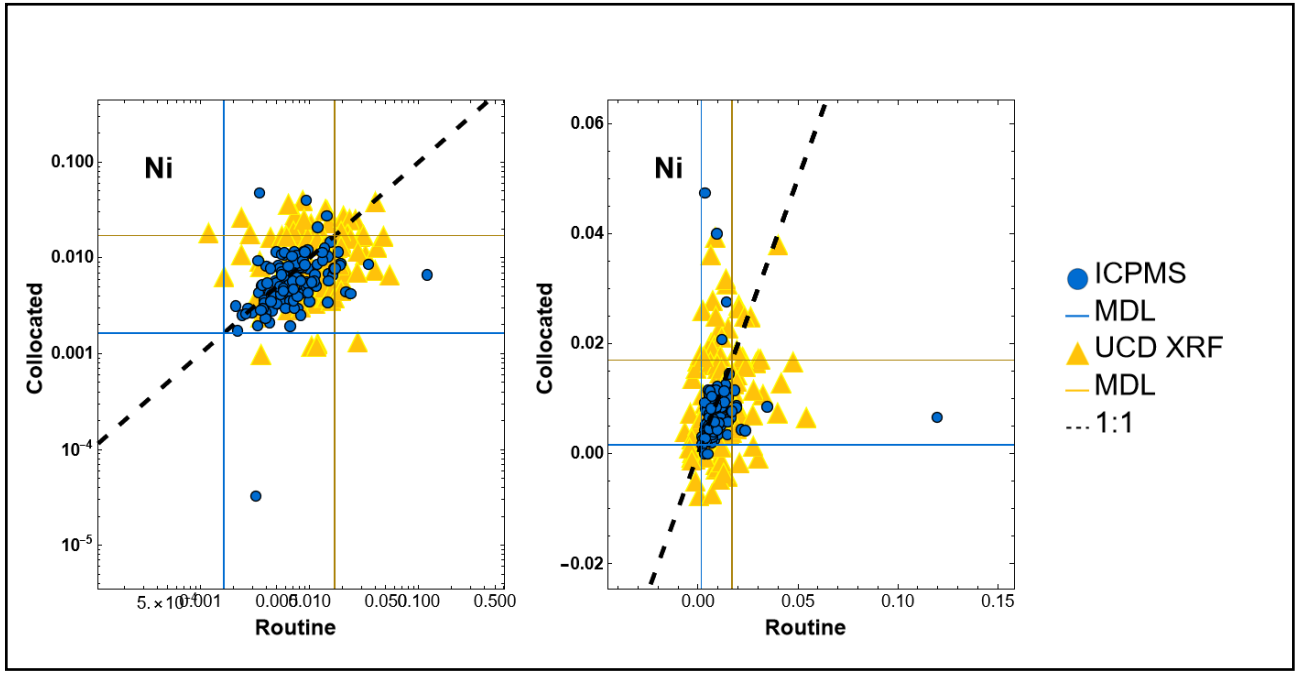
- ICPMS measurements are greater than the MDL more than 10% but less than 50% of the time (Cr, Cs)
- Recovery not acceptable or not evaluated (Ba, P, Sn, Ce)

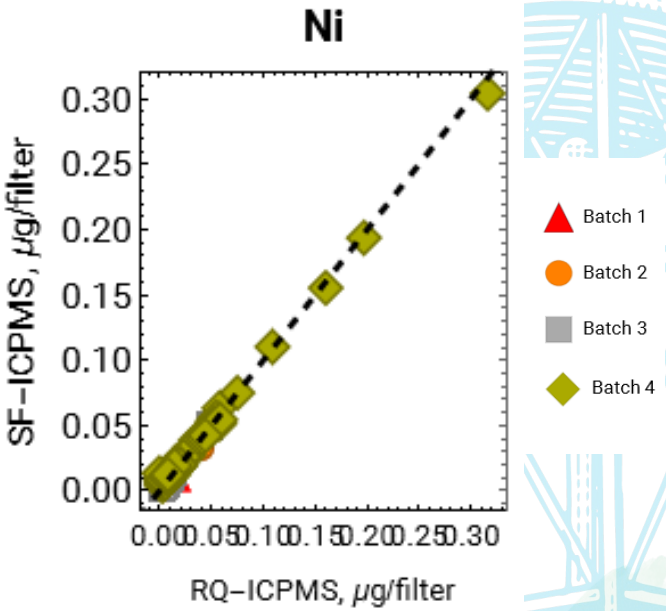


Ni

XRF > 10% MDL	YES
% above MDL	16%
RQ ICPMS > 10% MDL	YES
% above MDL	99%
RQ ICPMS 1648a recovery acceptable? (5% HNO3 + 2 hour hot block digestion)	NO
Which MDL is lower	ICPMS
Other Notes	Ni is known to be better extracted with HF (+ microwave digestion?)

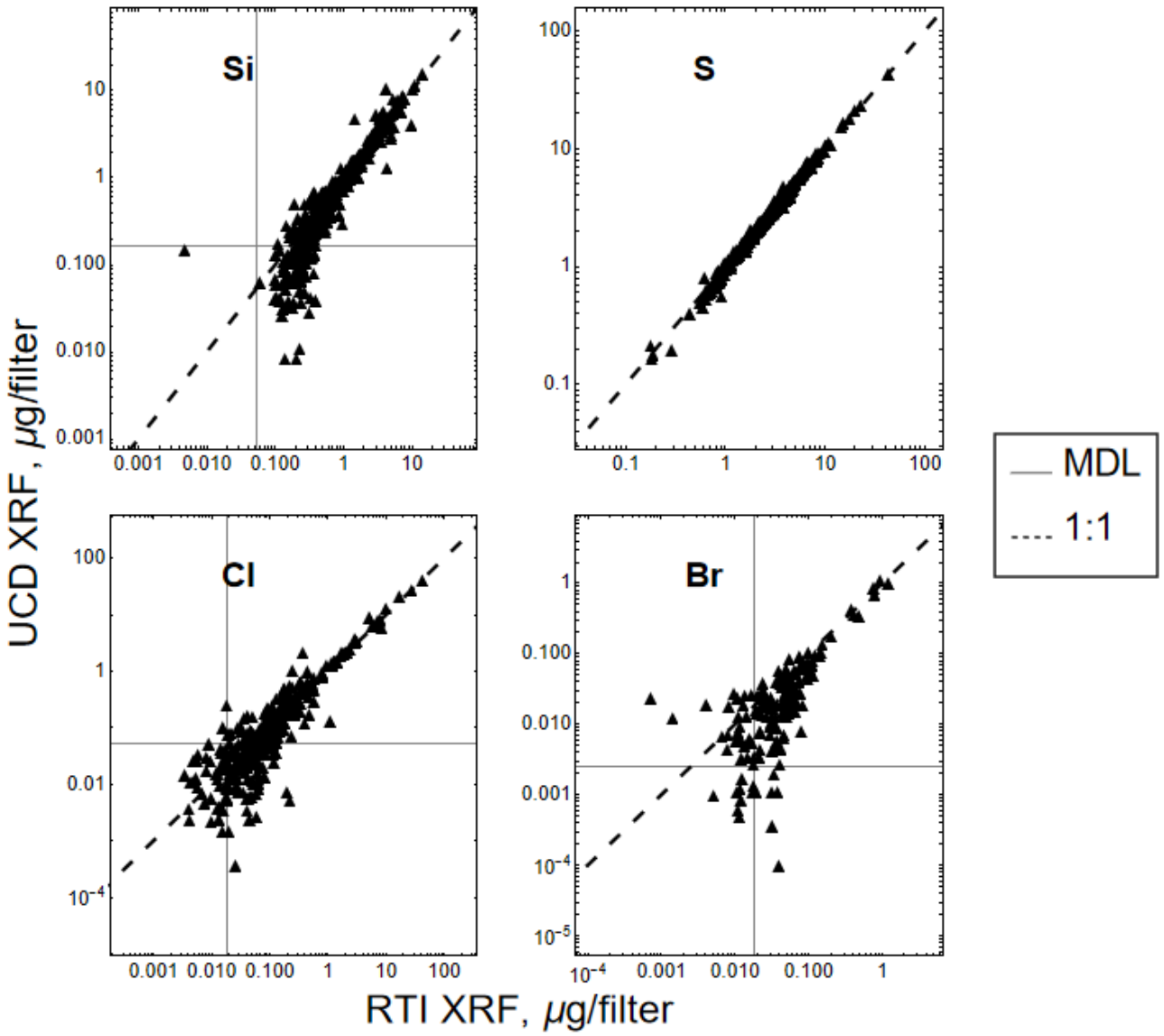






✓ XRF

- Polyatomic interferences (S, Si) and detector limitations (S, Br, Cl) make these elements difficult to measure via ICP-MS.
- Since these filters are reanalyzed with RTI XRF, Br and Cl may be 15-20 % different than the original reported UCD XRF concentration due to Br and Cl lost in the vacuum of the XRF.



Considerations:

- **Were the elements detected?**

  Intra-method: Method detection limits

- **Are the reported concentrations reliable?**

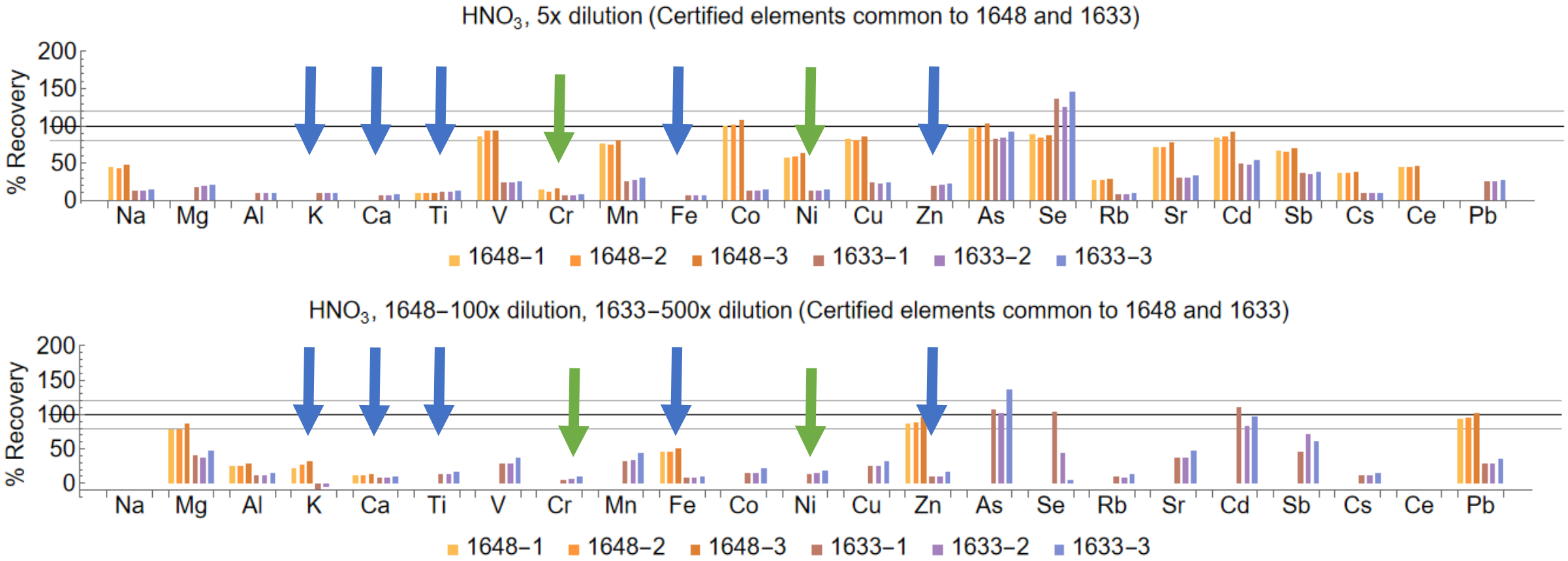
  Intra-method: inter-elemental comparison; collocated samples (precision)

  Inter-method: XRF-ICPMS intercomparison

- **Was the ICPMS extraction complete?**

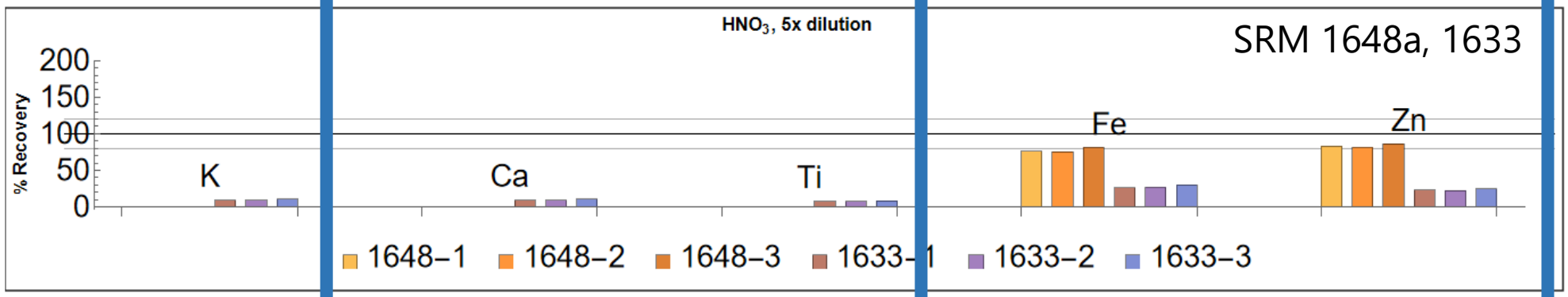
  Evaluated using reference materials (NIST SRM 1648a, 1633)

SRM Recoveries - ICPMS

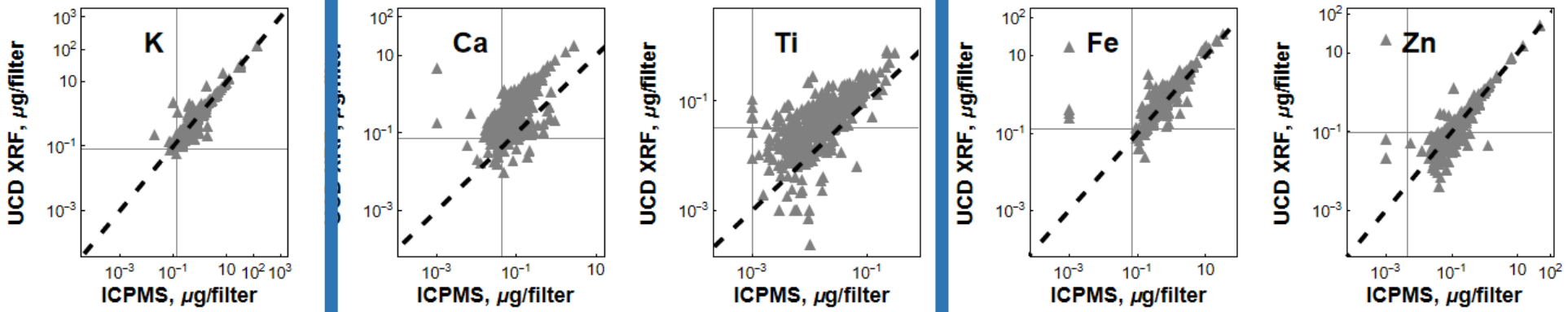


- Some elements cannot be extracted with only HNO_3
- **Some elements did not have good recoveries, but XRF –ICPMS intercomparison is good/acceptable**
  - may just need longer than 2 hours for extraction or comparable loadings for SRM and sample
  - sample mean mass: ~100 ug, max ~500 ug vs 10-20 mg of SRM (homogeneity issues)

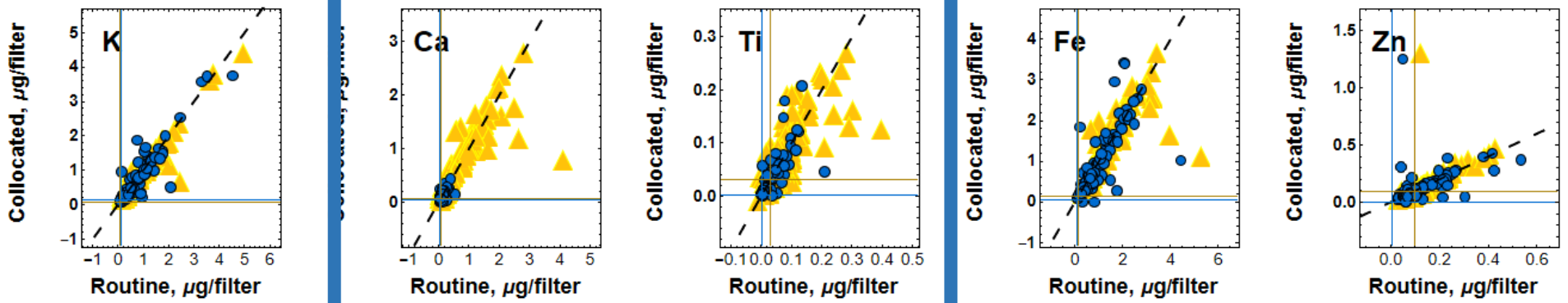
Some elements: Good inter & intra-method comparison, but bad recovery

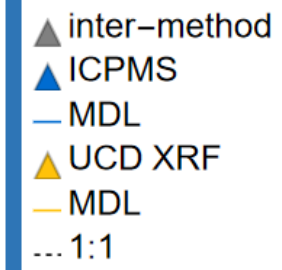


Inter-method

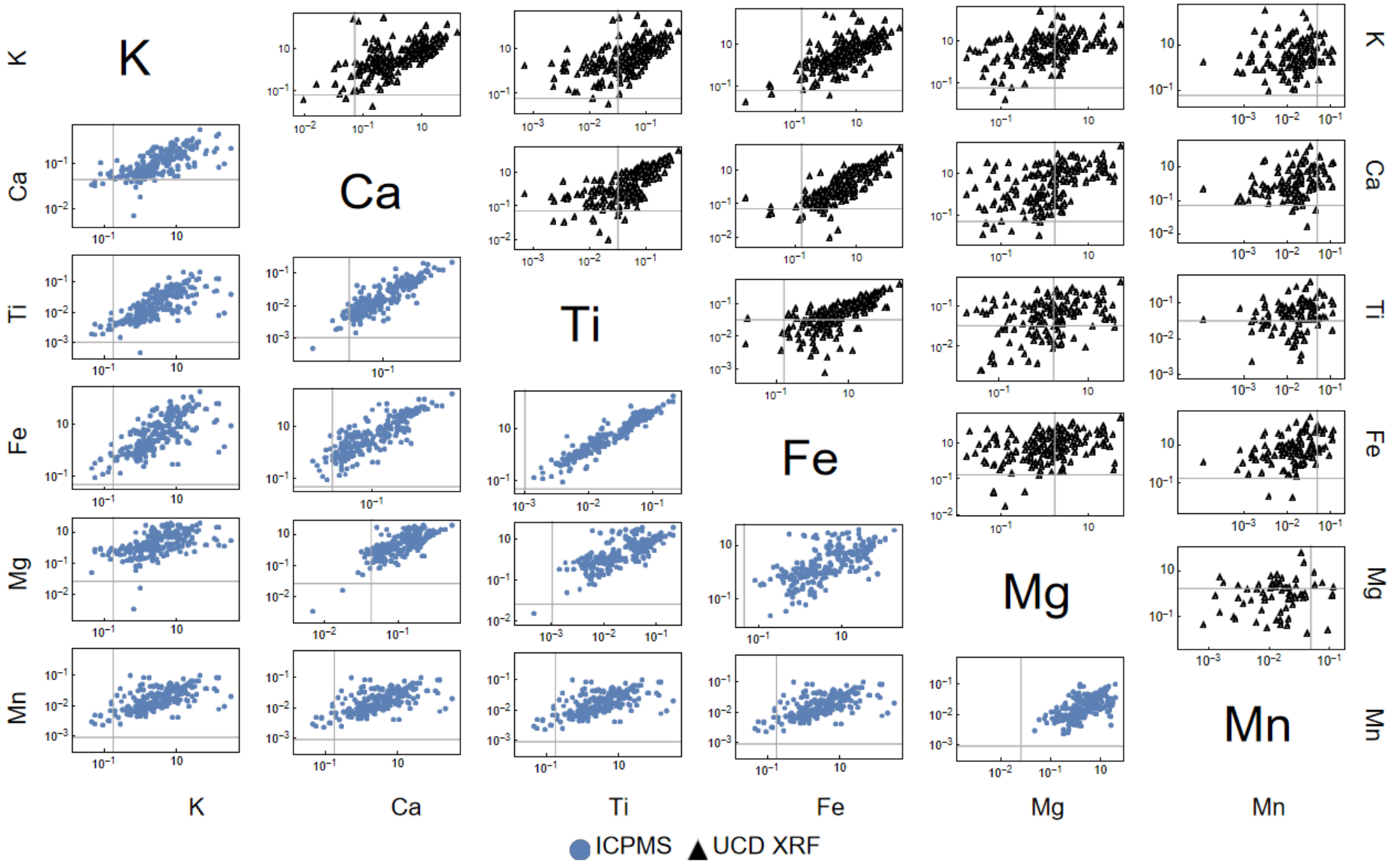


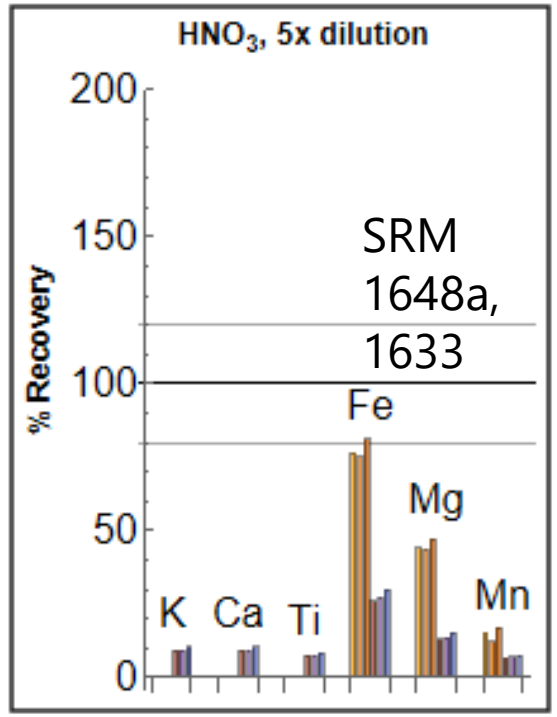
Intra-method (collocated)





Some elements: Good inter-elemental comparison, but bad recovery





Next steps

1. Evaluating extraction efficiency

- Troubleshoot: element recoveries for SRM that don't align with inter- and intra-method agreement on CSN samples
  - Smaller amount of SRM (1-2mg) for extraction
  - Test out different digestion method for the SRM (5% HNO_3 + small % of HF)
  - Developing reference materials at ambient loadings to test the extraction

2. ICP-MS analysis on nylon filters

3. Quantitative comparison of the data

4. Evaluate the current list of elements being measured

- Additional heavier elements can be measured by ICP-MS

Guide to the plots

In all plots, dashed line is 1:1
Solid lines are fits

- Were the measurements above the **UCD XRF MDL at least 10 %** of the time?
- Out of N=594, what % of were measurements above the stated **UCD XRF MDL**?
- Were the measurements above the **ICPMS MDL** at least 10 % of the time?
- Out of N=594, what % of were measurements above the stated **ICPMS MDL**?

- Did the element have an **acceptable recovery** based on the digestion of **SRM 1648a**?

- Which of the MDL for this element is lower, **UCD XRF MDL or ICPMS MDL?**

***Inter*-method:** XRF on y, ICPMS on x
or vice versa

***Intra*-method:** XRF on both y and x
or ICPMS on both y and x

Excludes S, Si, Br, Cl

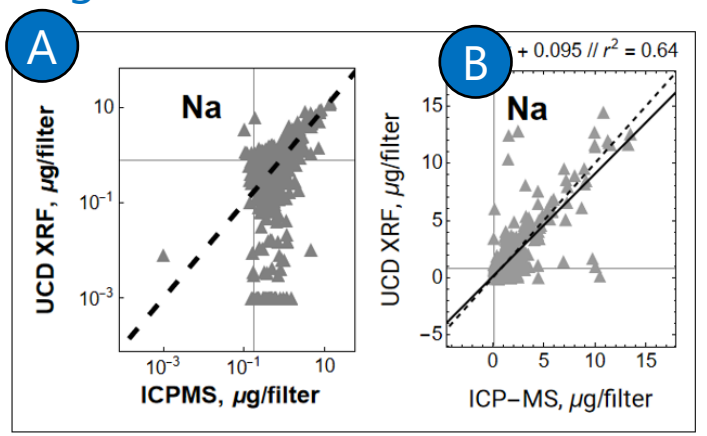
Inter-method comparison (N=594*)

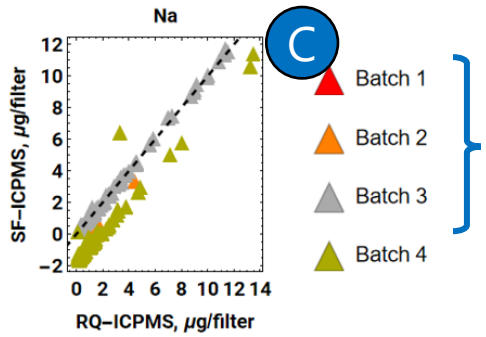
log scale linear scale

SF-RQ ICPMS comparison (N=94)

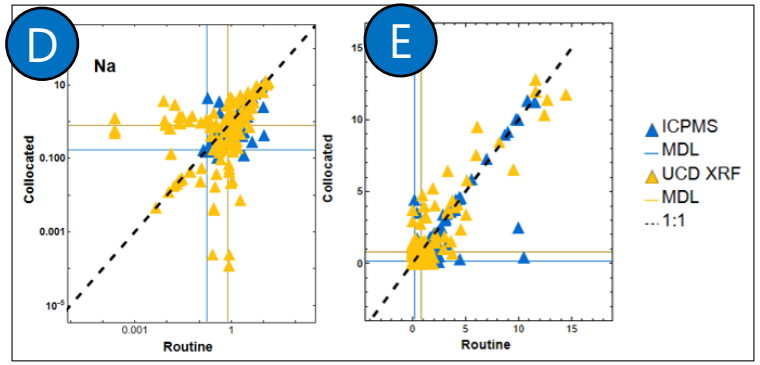
Na

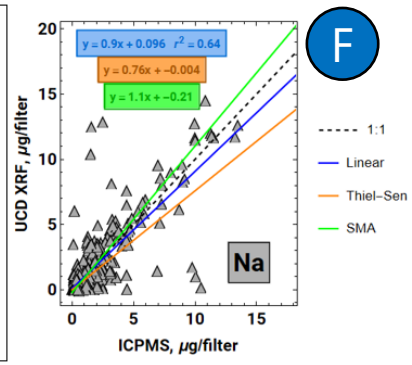
XRF > 10% MDL	YES
% above MDL	43%
RQ ICPMS >10% MDL	YES
% above MDL	96%
RQ ICPMS 1648a recovery acceptable? (5% HNO3 + 2 hour hot block digestion)	NO
Which MDL is lower	ICPMS





Batches based on when sent to RTI





log scale linear scale

Collocated, intra-method (N= 248*)

Various fits for inter-method comparison (N= 594*)

A more detailed version of plot B

* N will be less for log scale plots, as they don't show negative or zero values

Preliminary conclusions

- Based on the current leaching method, of the 14 elements evaluated:
  - Na, Mg, Al, **K**, Ca, Ti, V, Cr, Mn, **Fe**, Ni, Cu, **Zn**, and Pb have >10% samples above UCD XRF MDL
  - Mg, V, Mn, Cu, Zn, and Pb are recommended to be analyzed with ICP-MS with a dilute acid digestion (5% HNO_3 + hot block) as described (based on recovery).

- Of the remaining 19 elements not evaluated, we recommend measuring
  - S, Si, Cl, and Br using XRF.
  - Co, As, Se, and Cd with ICP-MS based on both acceptable recovery and frequency of detection above MDL.
  - P, Rb, Sr, Zr, Ag, Sn, Sb, Cs, Ba, and Ce using ICP-MS based on frequency of detection above MDL only.

- In total

  $18/33$ elements with XRF $20/33$ elements with ICP-MS $6/33$ elements with either XRF or ICP-MS

- Performing ICP-MS in addition to XRF will decrease number of non-detects for elements where ICPMS has lower MDL.

UCD XRF

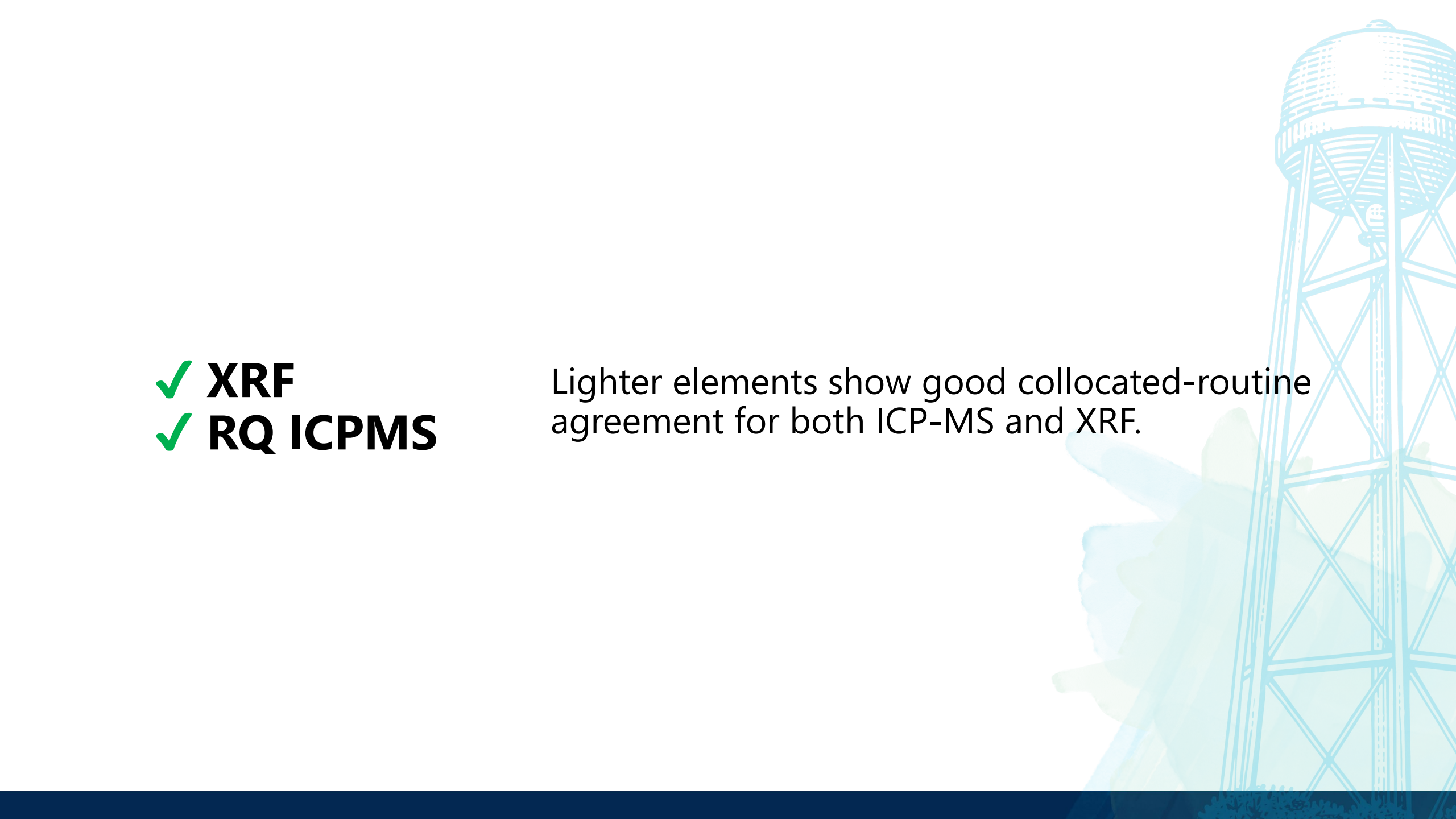
- Na, Mg, Al, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, ~~(and Pb***)~~
- S, Si, Cl, and Br

ICPMS – 5% HNO_3

- Mg, V, Mn, Cu, Zn, and Pb with a dilute acid digestion as described (based on recovery).
- Co, As, Se, and Cd with ICP-MS based on both acceptable recovery and frequency of detection above MDL.
- P, Rb, Sr, Zr, Ag, Sn, Sb, Cs, Ba, and Ce using ICP-MS based on frequency of detection above MDL only.

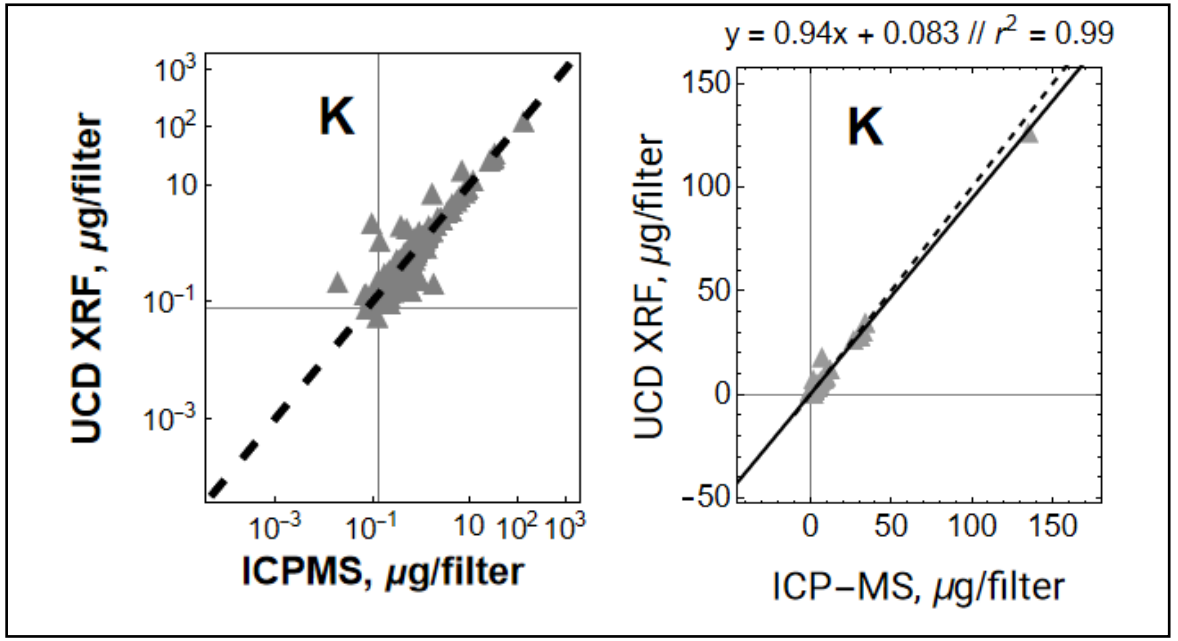
✓ **XRF**
✓ **RQ ICPMS**

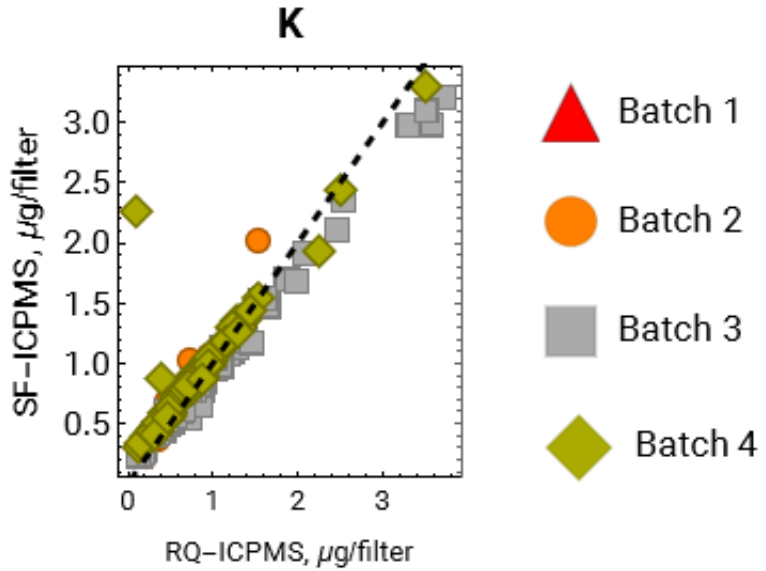
Lighter elements show good collocated-routine agreement for both ICP-MS and XRF.

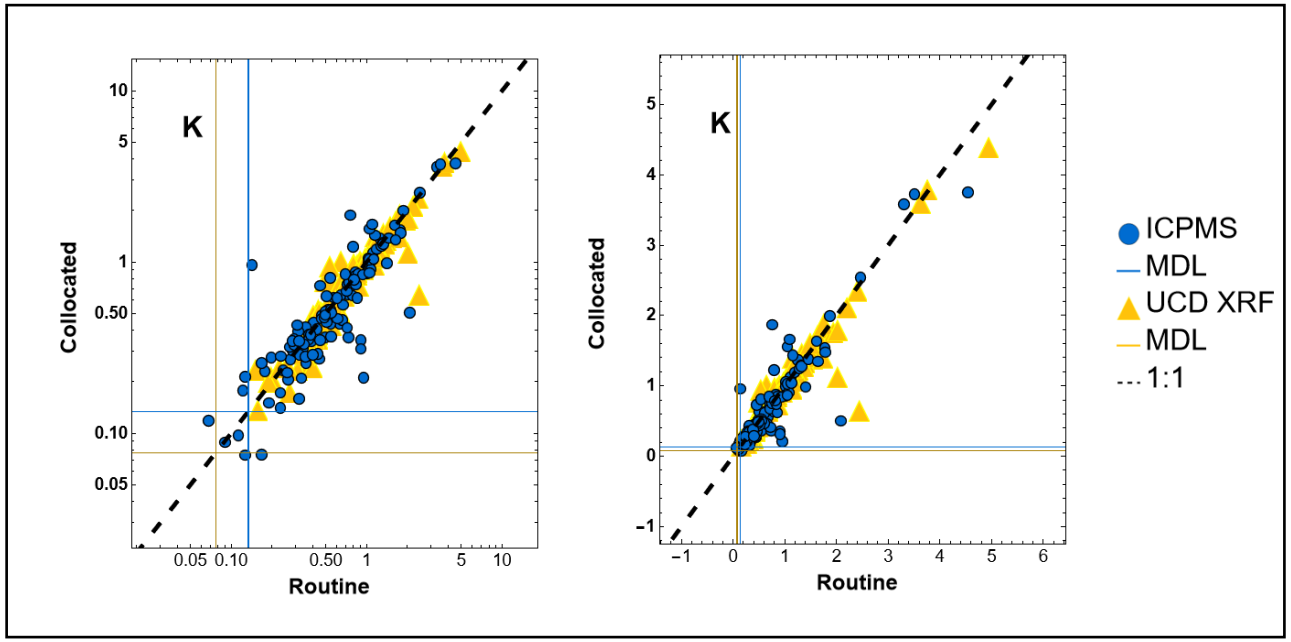


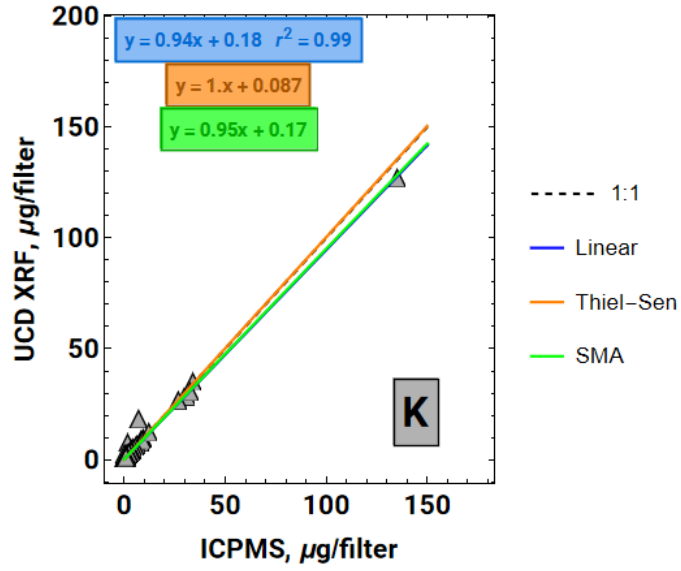
K

XRF > 10% MDL	YES
% above MDL	99%
RQ ICPMS >10% MDL	YES
% above MDL	97%
RQ ICPMS 1648a recovery acceptable? (5% HNO3 + 2 hour hot block digestion)	NO
Which MDL is lower	UCD XRF
Other notes	•OK MDL •OK XRF-ICPMS inter-method



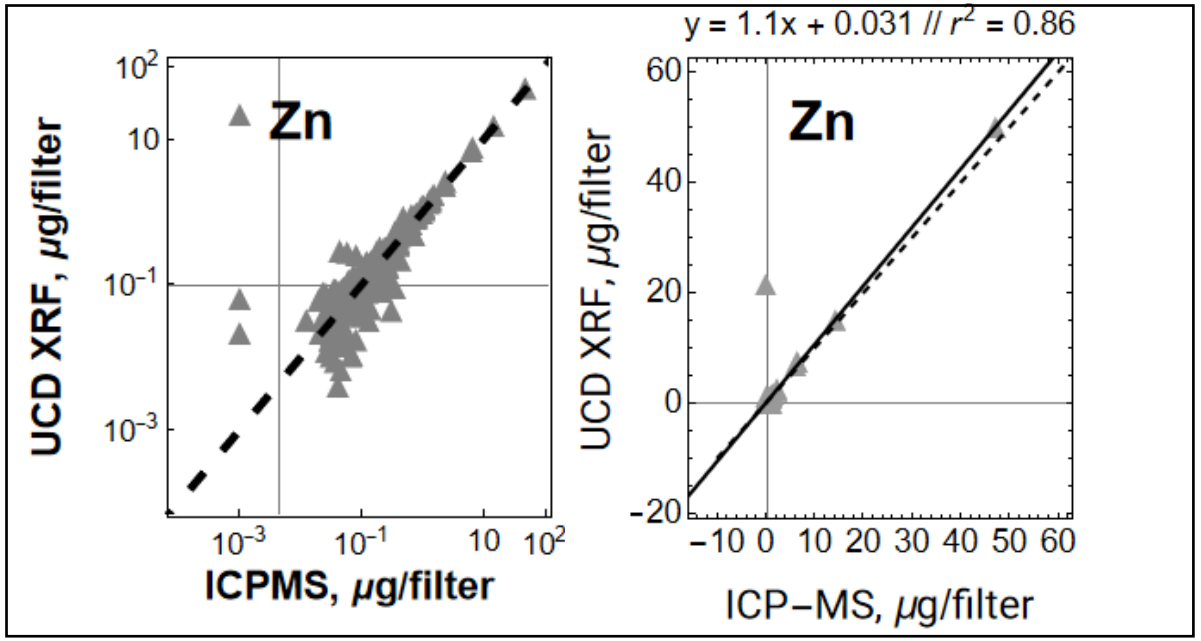


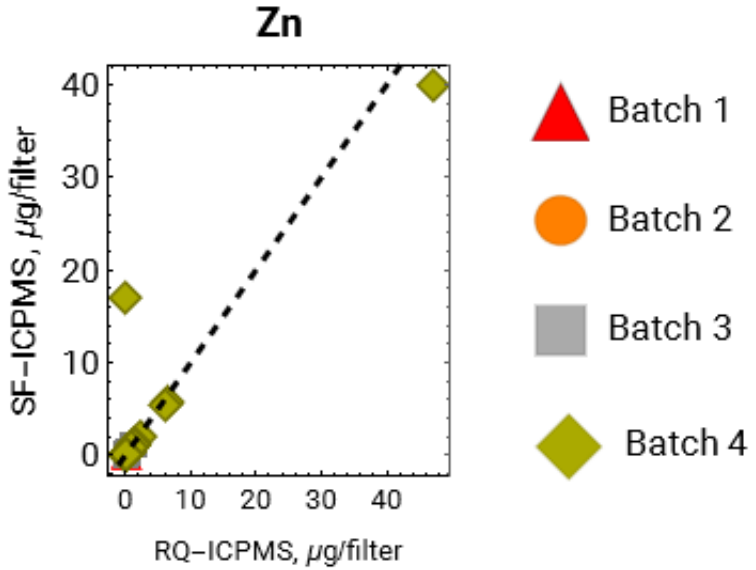


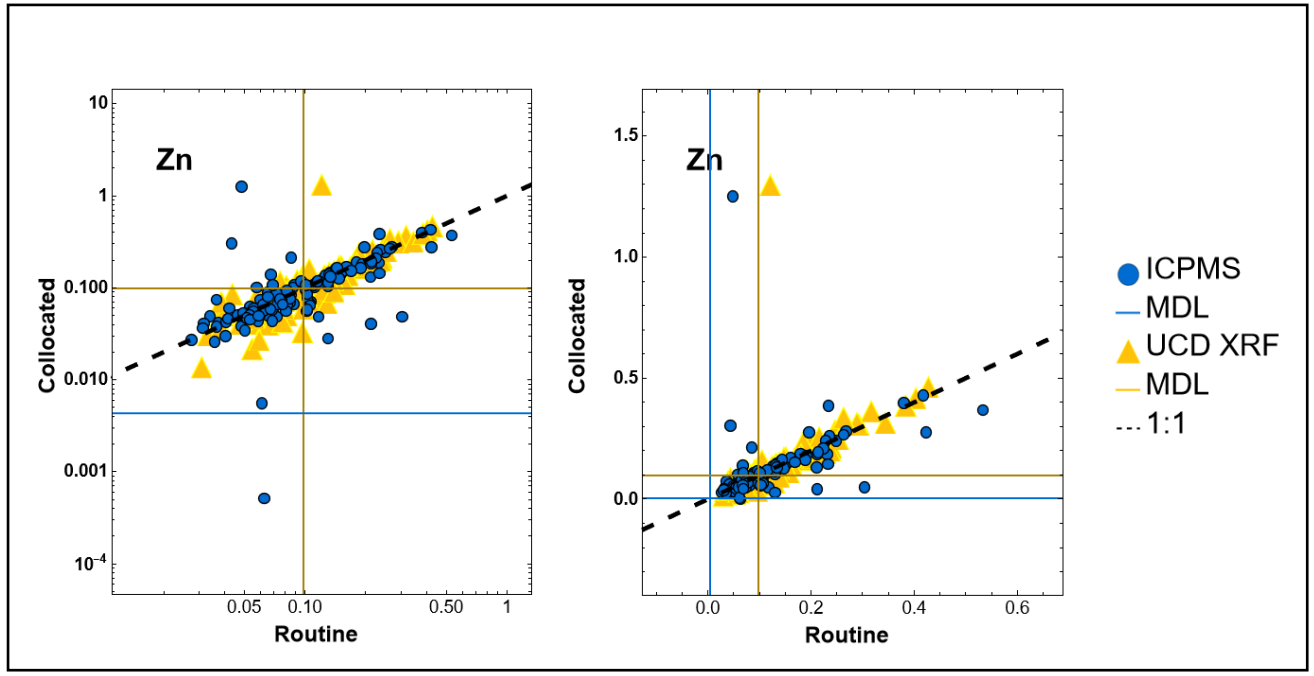


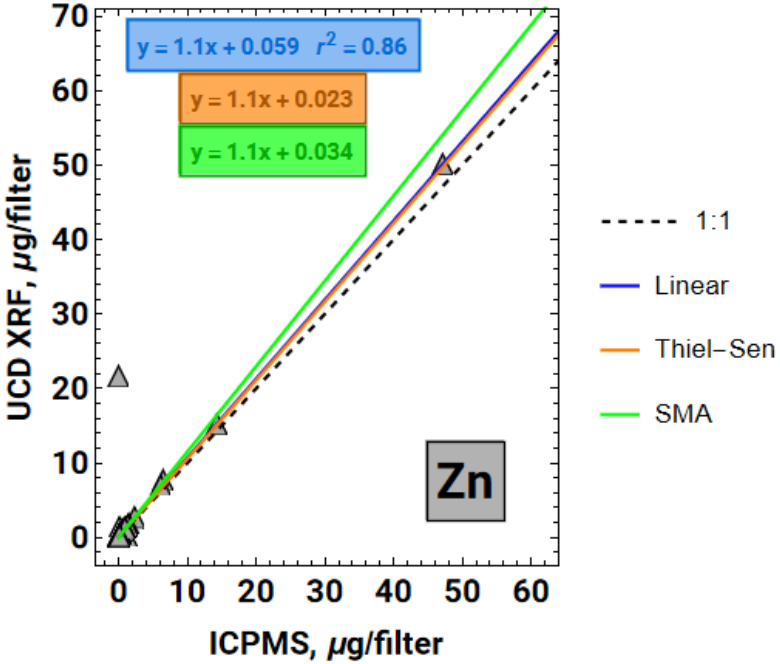
Zn

XRF > 10% MDL	YES
% above MDL	45%
RQ ICPMS >10% MDL	YES
% above MDL	99%
RQ ICPMS 1648a recovery acceptable? (5% HNO3 + 2 hour hot block digestion)	YES
Which MDL is lower	UCD XRF
Other notes	• OK MDL • OK XRF-ICPMS inter-method



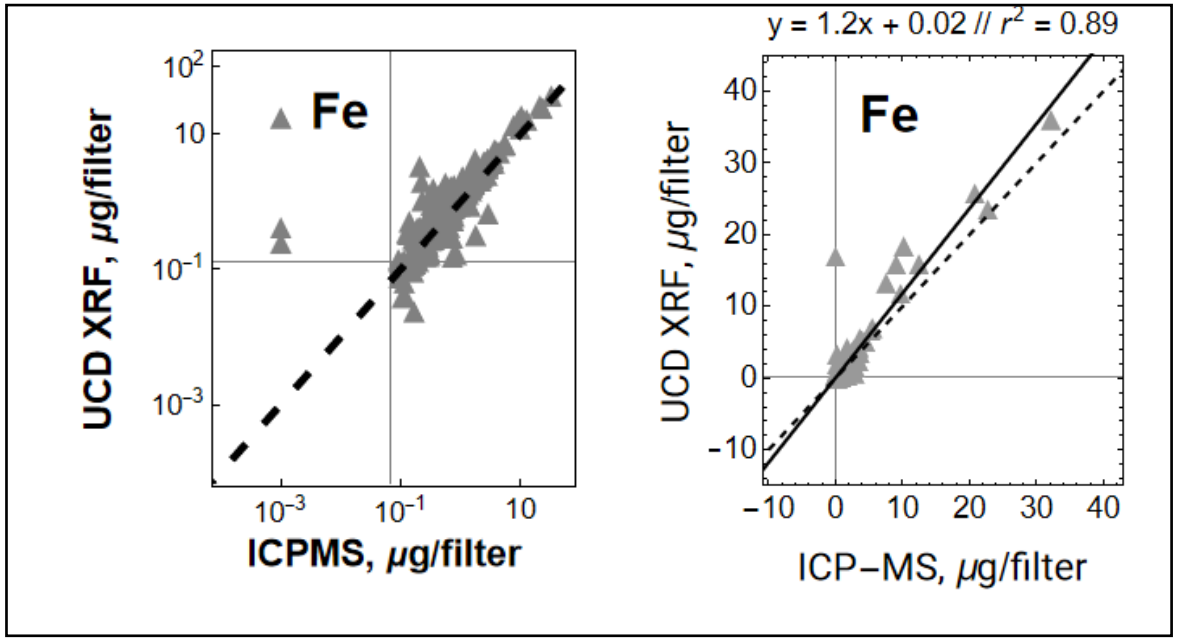


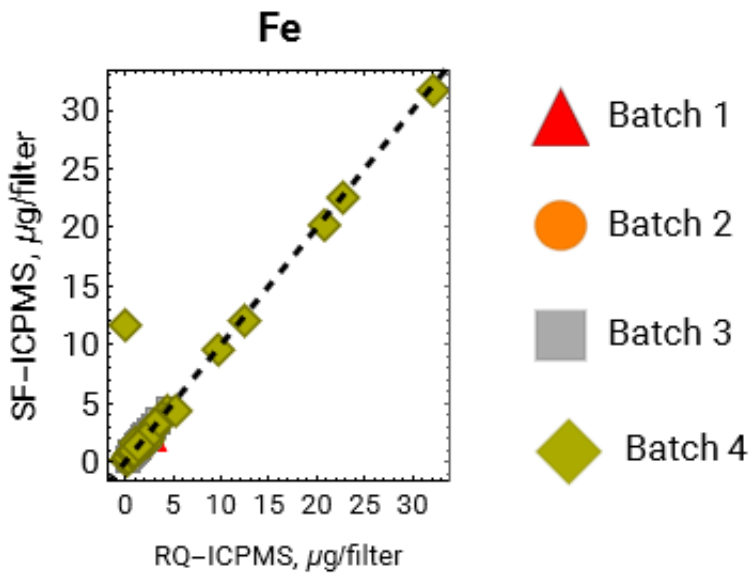


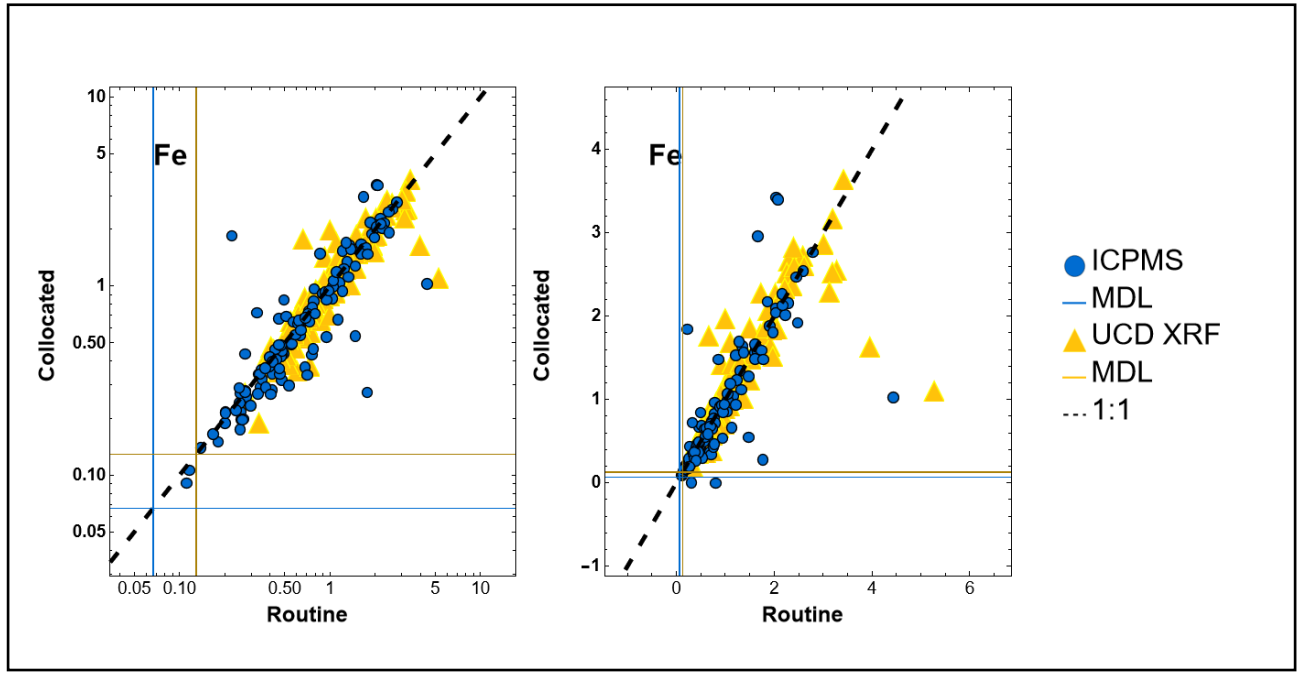


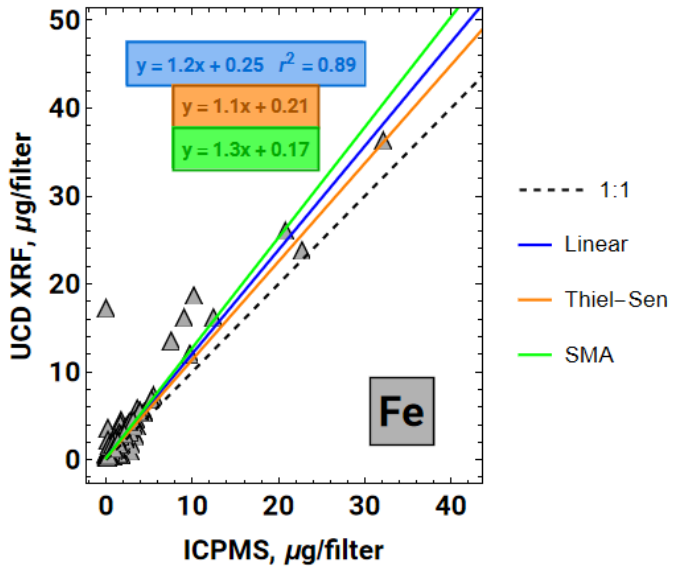
Fe

XRF > 10% MDL	YES
% above MDL	96%
RQ ICPMS > 10% MDL	YES
% above MDL	99%
RQ ICPMS 1648a recovery acceptable? (5% HNO3 + 2 hour hot block digestion)	NO
Which MDL is lower	ICPMS
Other notes	• OK MDL • OK XRF-ICPMS inter-method



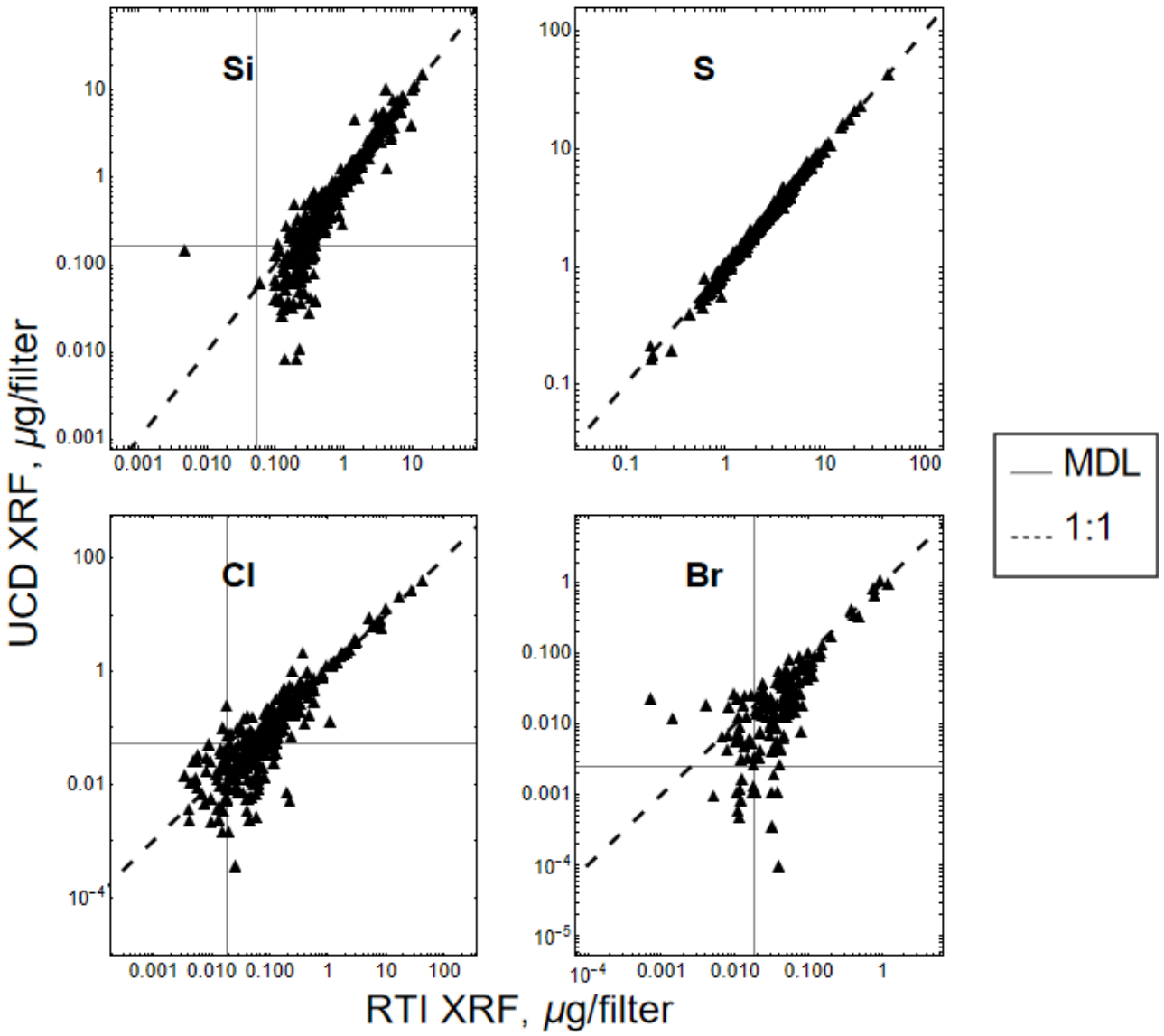






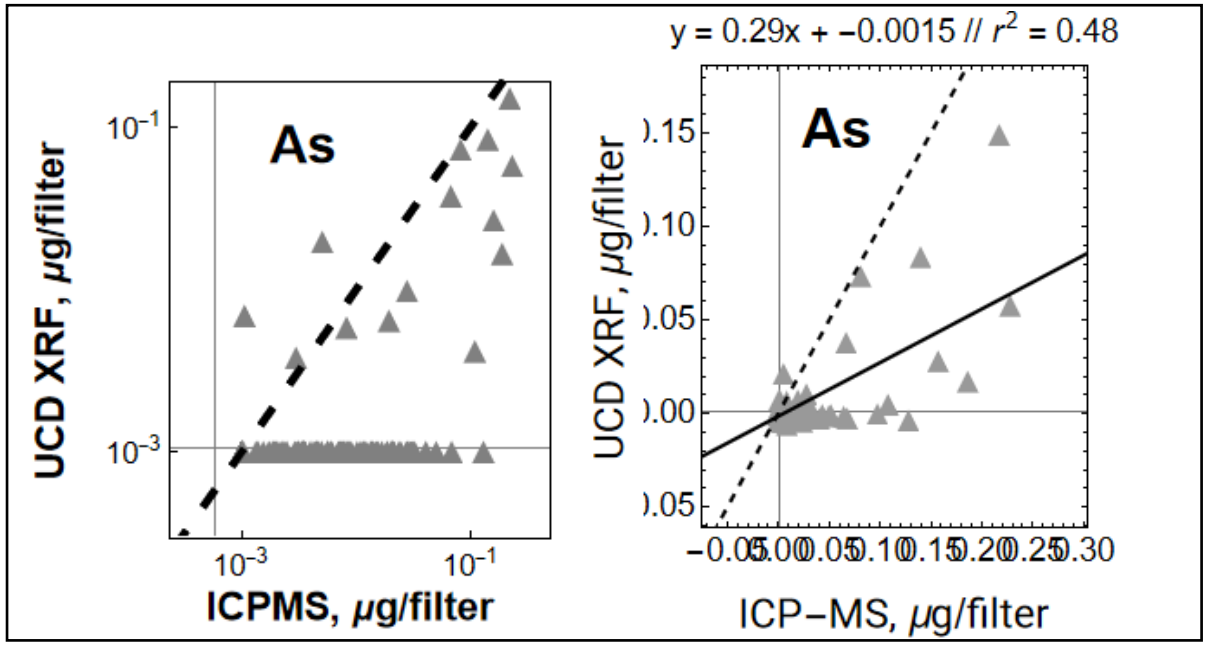
✓ XRF

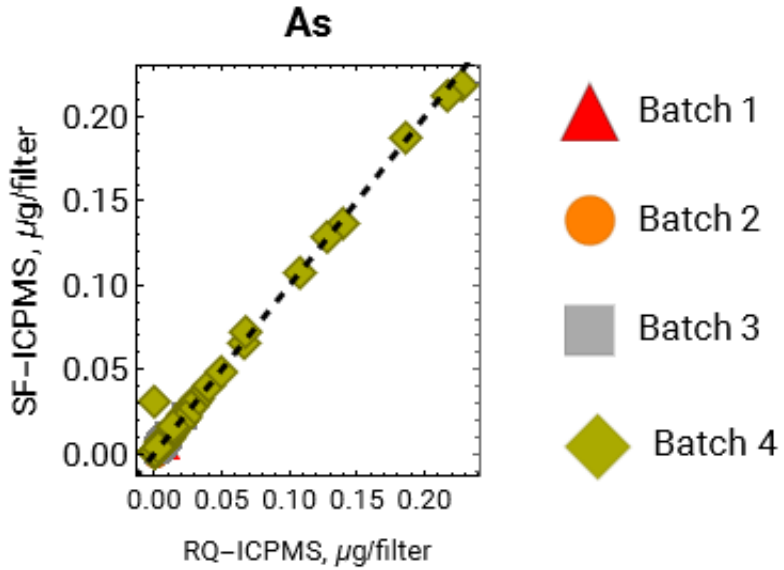
- Polyatomic interferences (S, Si) and detector limitations (S, Br, Cl) make these elements difficult to measure via ICP-MS.
- Since these filters are reanalyzed with RTI XRF, Br and Cl may be 15-20 % different than the original reported UCD XRF concentration due to Br and Cl lost in the vacuum of the XRF.

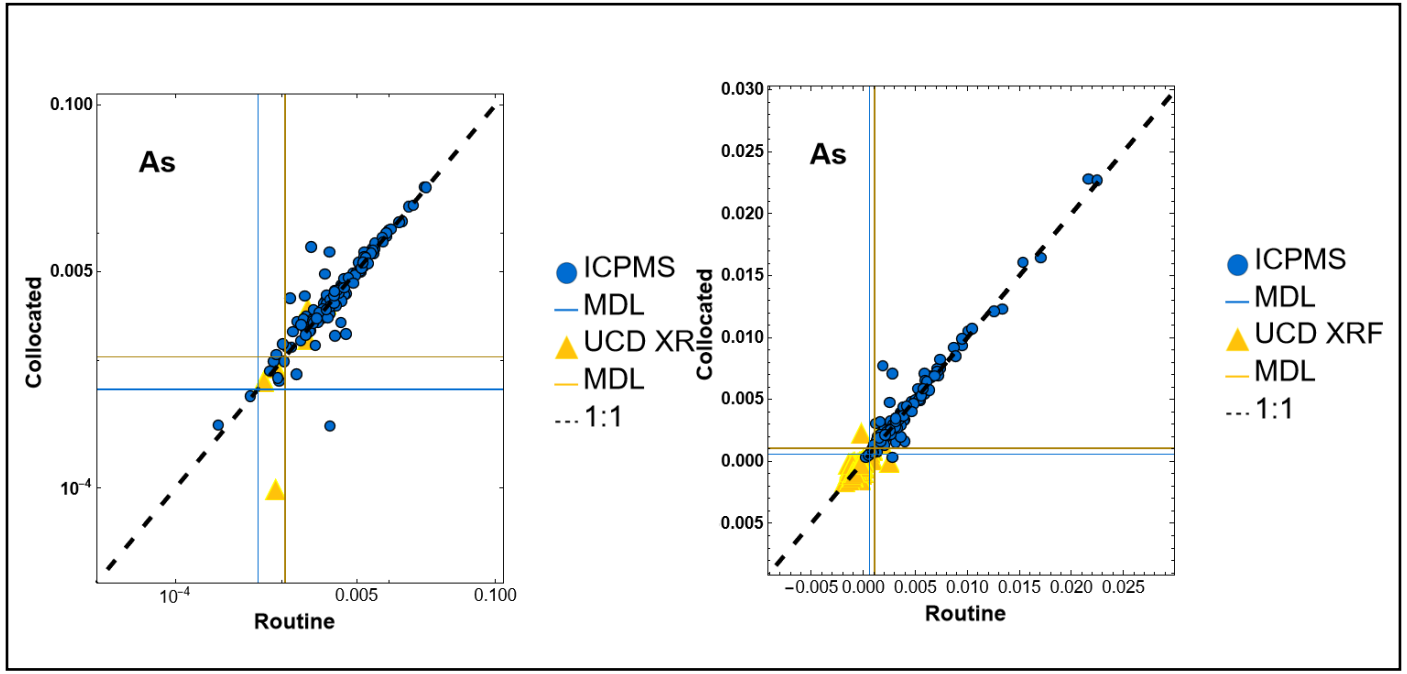


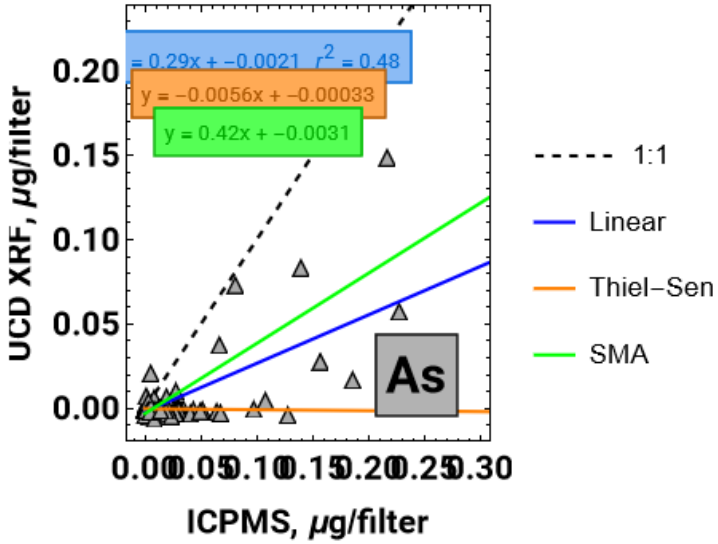
As

XRF > 10% MDL	NO
% above MDL	8%
RQ ICPMS >10% MDL	YES
% above MDL	98%
RQ ICPMS 1648a recovery acceptable? (5% HNO3 + 2 hour hot block digestion)	YES
Which MDL is lower	ICPMS



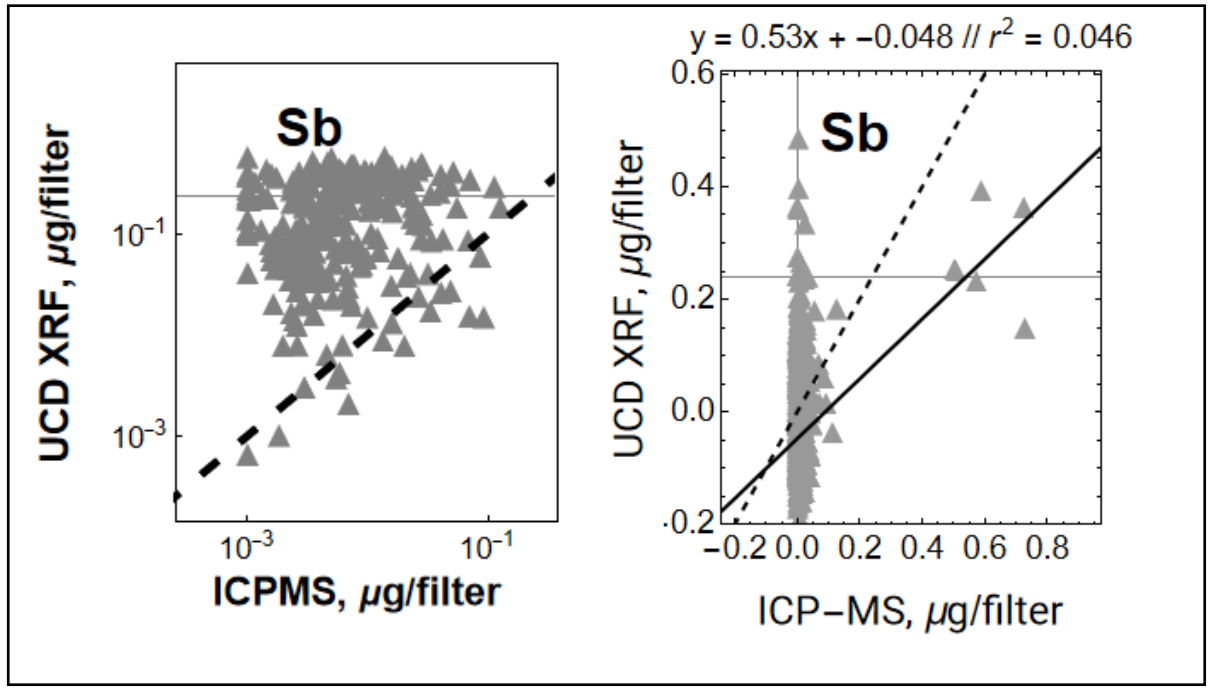


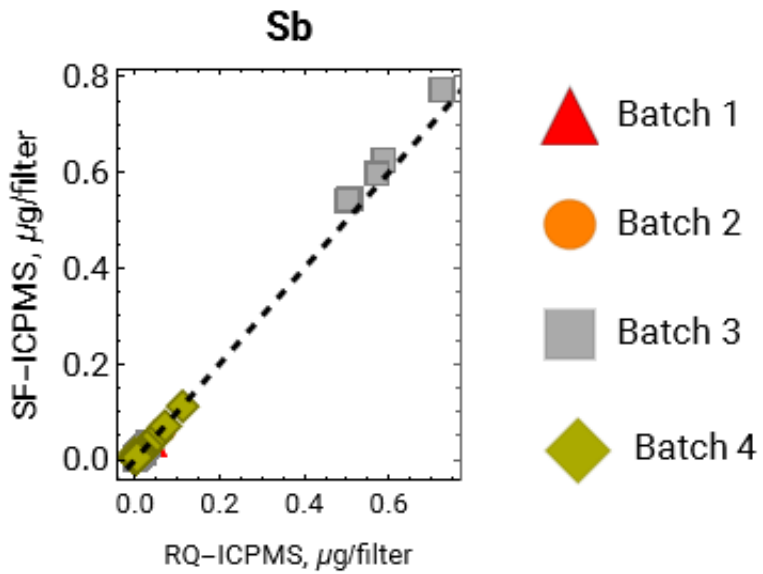


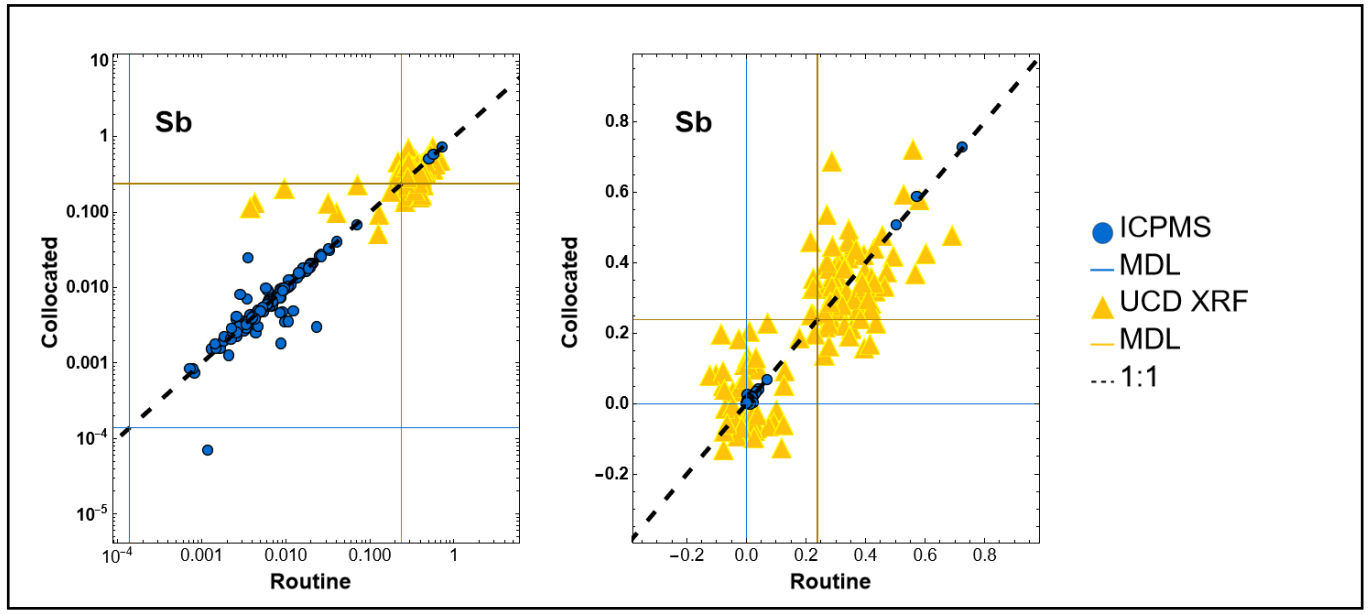


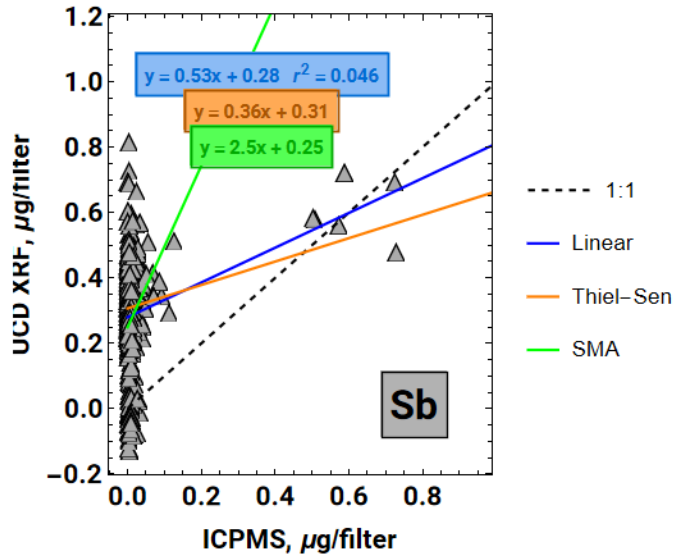
Sb

XRF > 10% MDL	NO
% above MDL	3%
RQ ICPMS >10% MDL	YES
% above MDL	99%
RQ ICPMS 1648a recovery acceptable? (5% HNO3 + 2 hour hot block digestion)	Not evaluated
Which MDL is lower	ICPMS



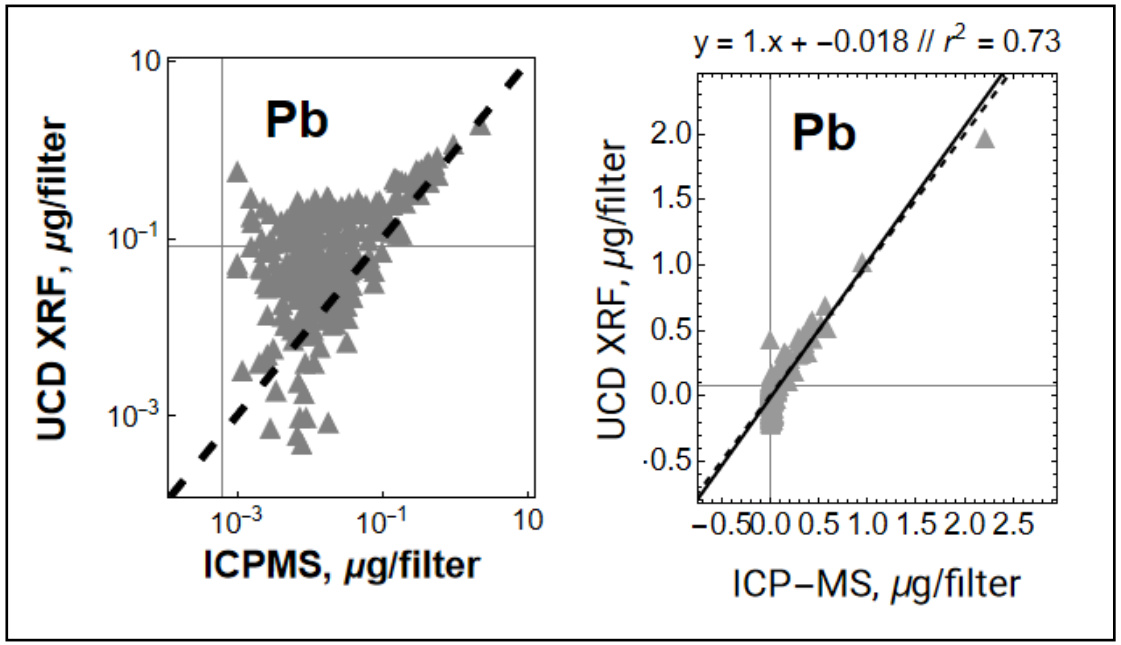


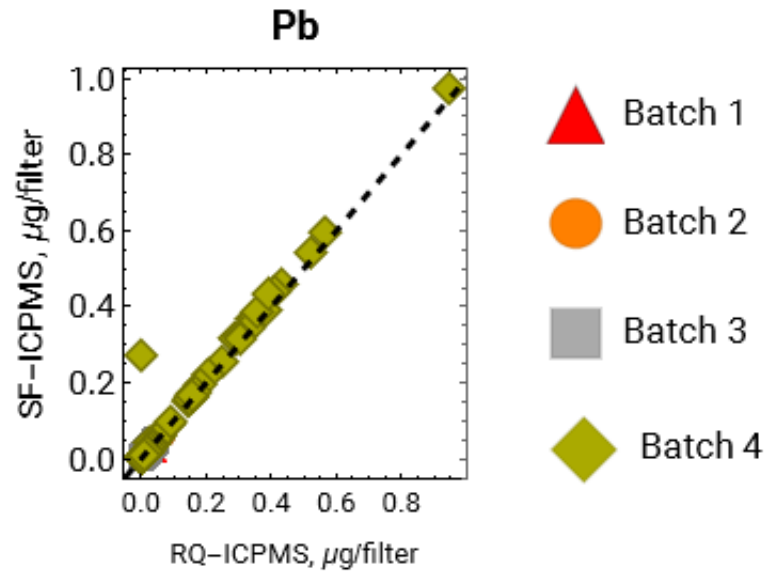


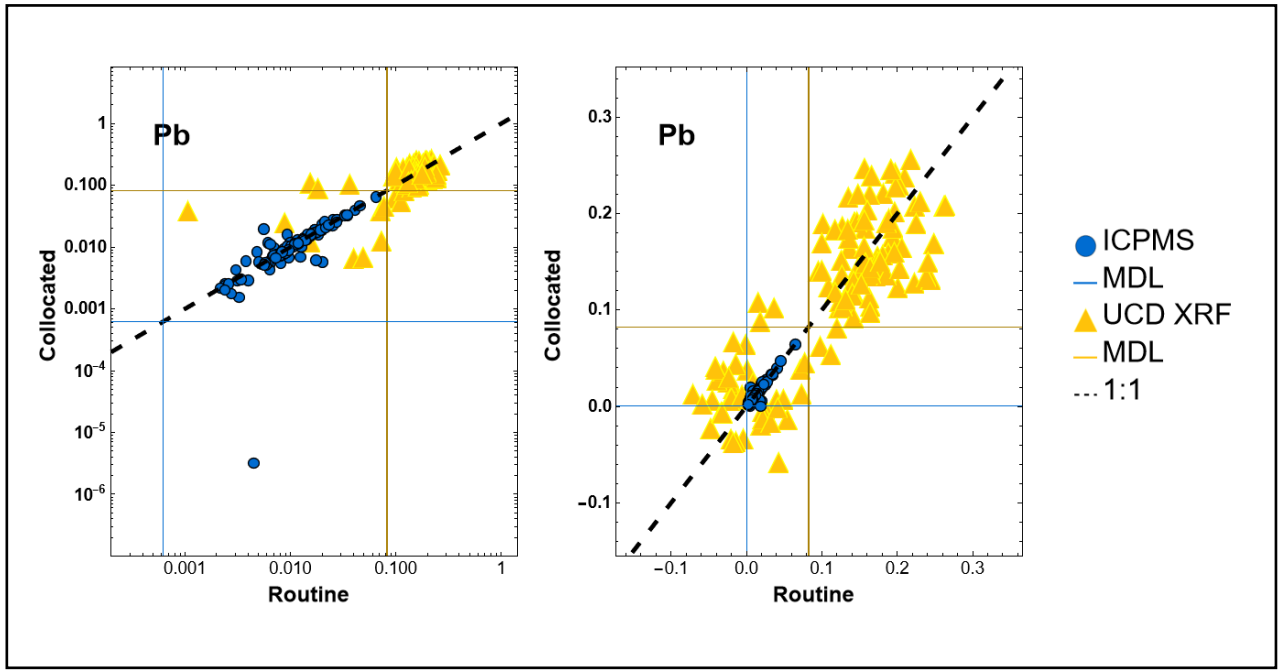


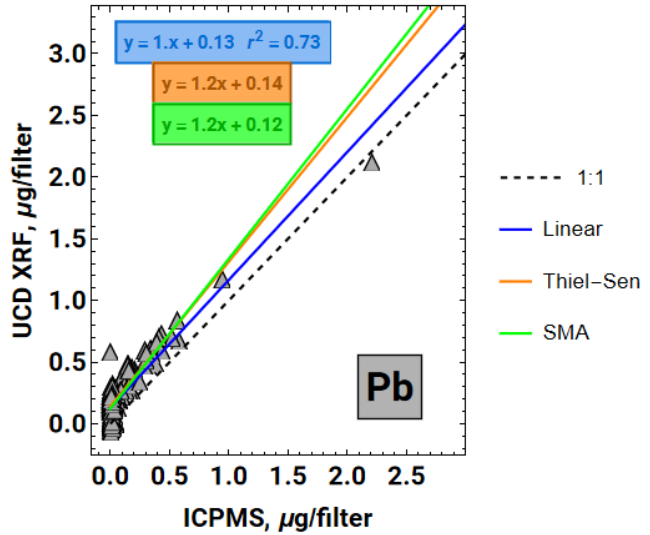
Pb

XRF > 10% MDL	YES
% above MDL	15%
RQ ICPMS > 10% MDL	YES
% above MDL	99%
RQ ICPMS 1648a recovery acceptable? (5% HNO3 + 2 hour hot block digestion)	YES
Which MDL is lower	ICPMS
Other notes	Pb is "noise" above MDL in XRF - ICPMS intercomparison



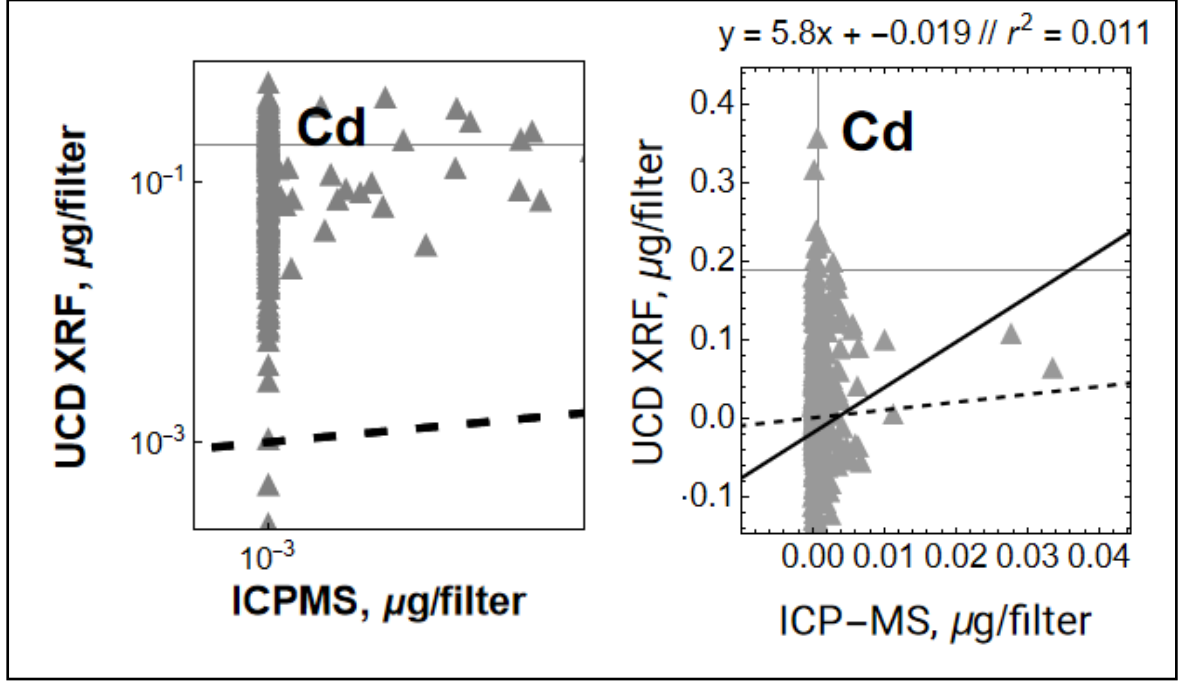


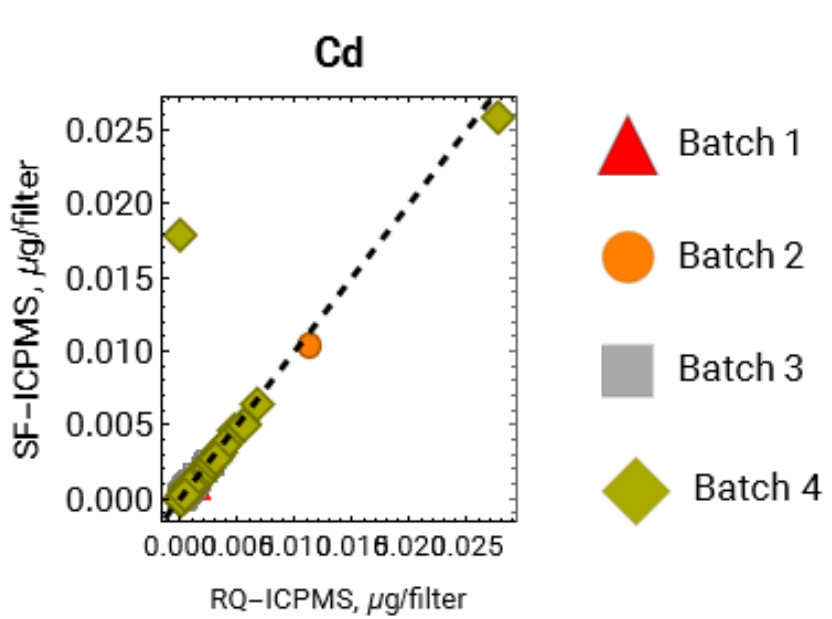


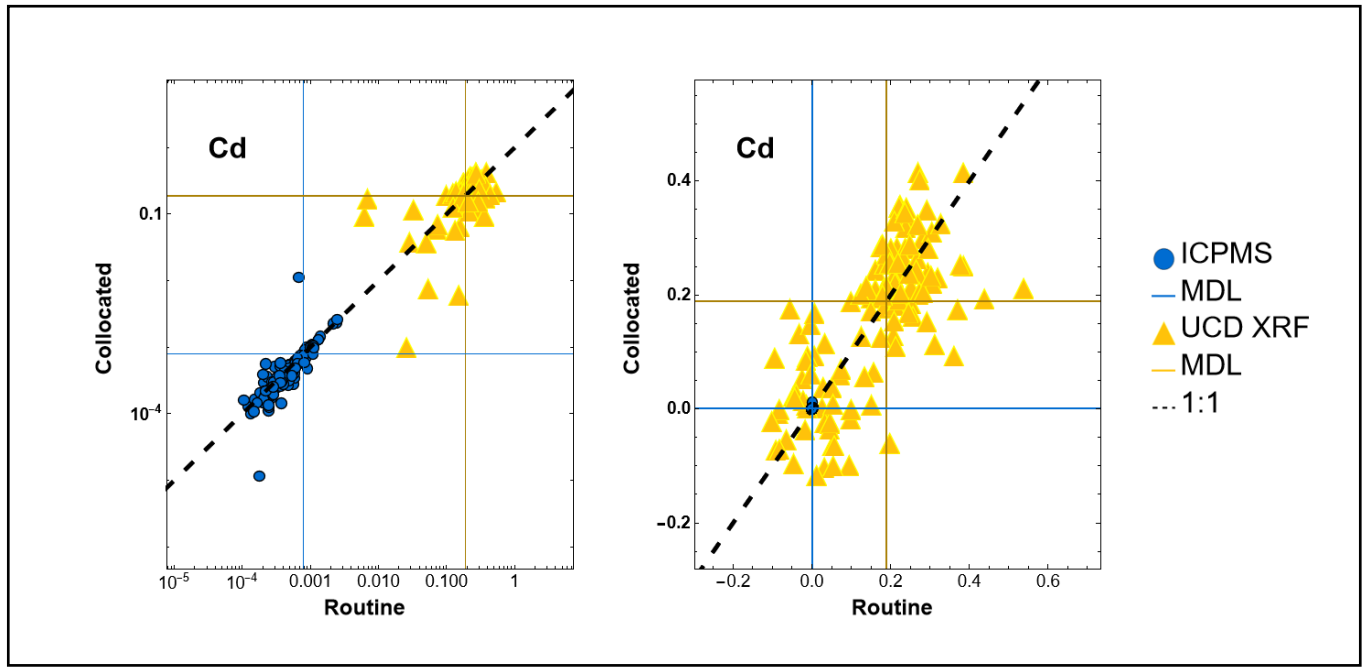


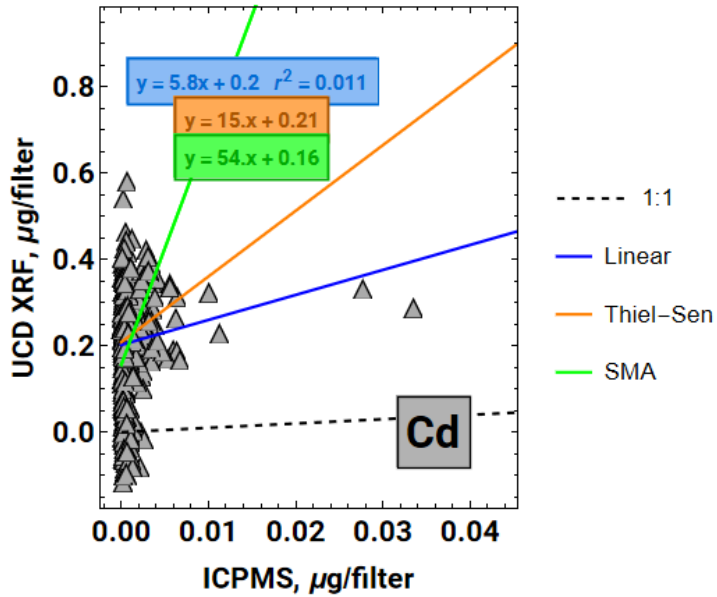
Cd

XRF > 10% MDL	NO
% above MDL	2%
RQ ICPMS >10% MDL	YES
% above MDL	27%
RQ ICPMS 1648a recovery acceptable ? (5% HNO3 + 2 hour hot block digestion)	YES
Which MDL is lower	ICPMS



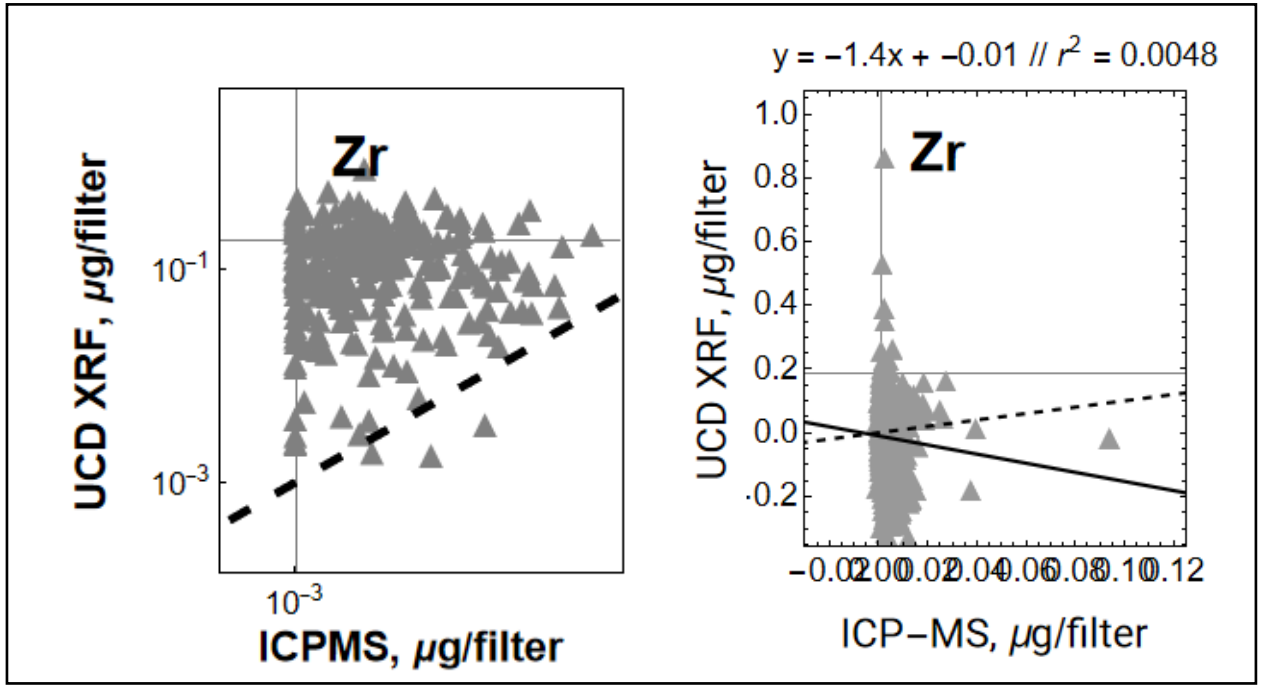


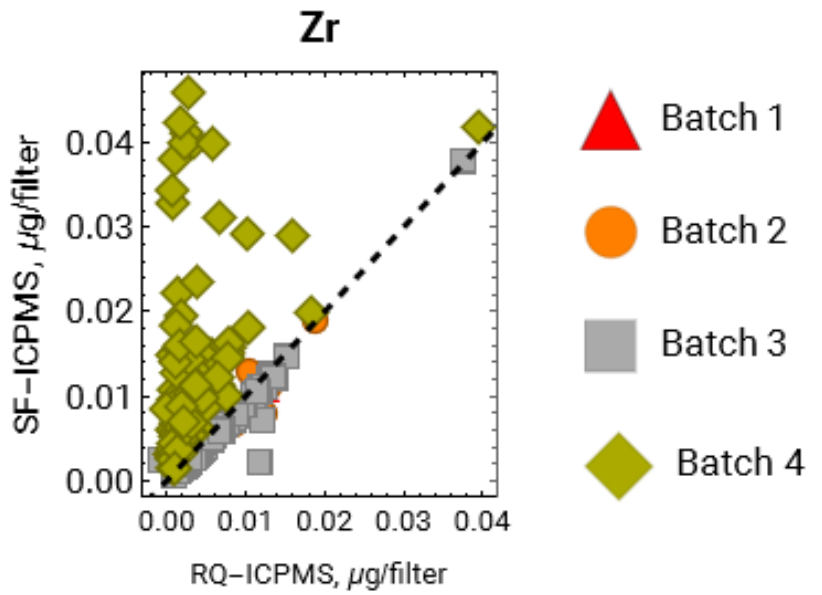


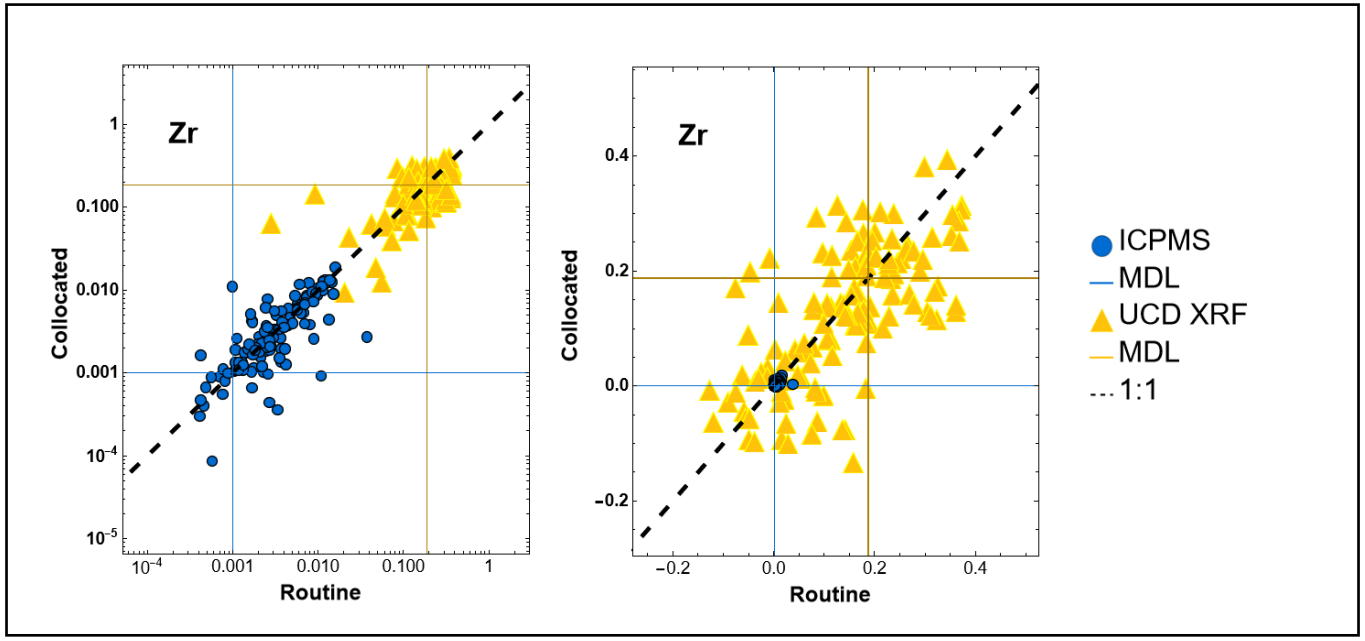


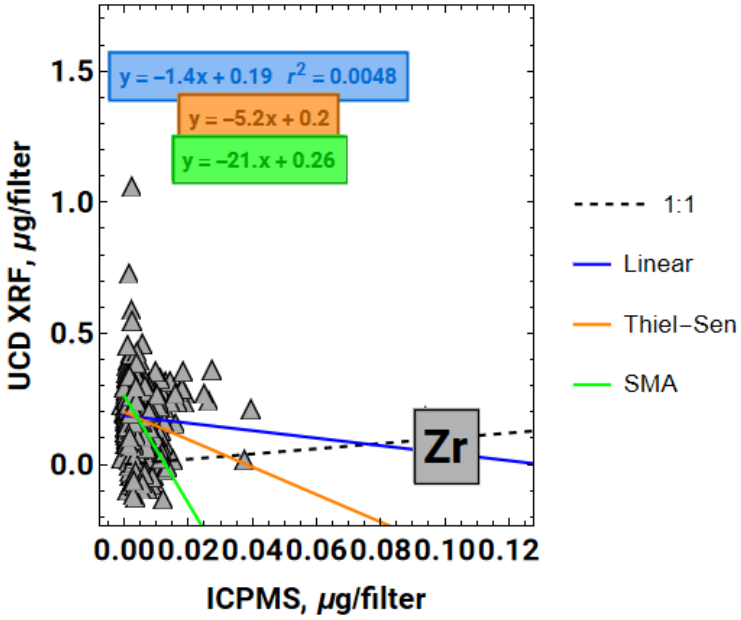
Zr

XRF > 10% MDL	NO
% above MDL	3%
RQ ICPMS >10% MDL	YES
% above MDL	84%
RQ ICPMS 1648a recovery acceptable ? (5% HNO3 + 2 hour hot block digestion)	Not evaluated
Which MDL is lower	ICPMS



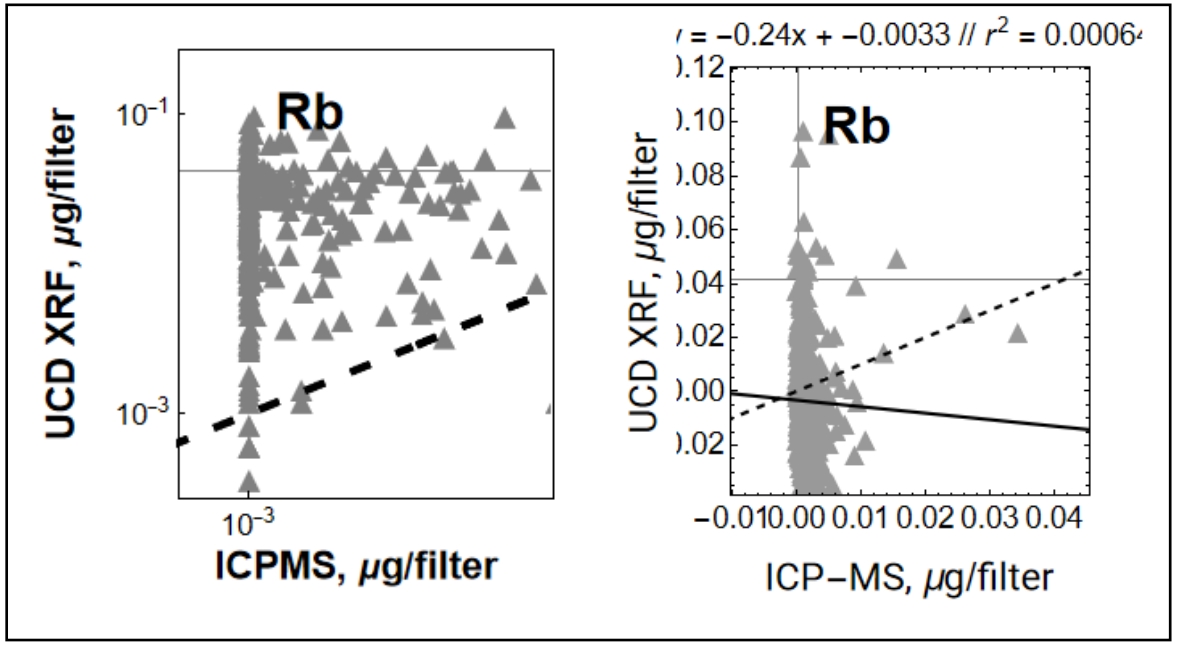


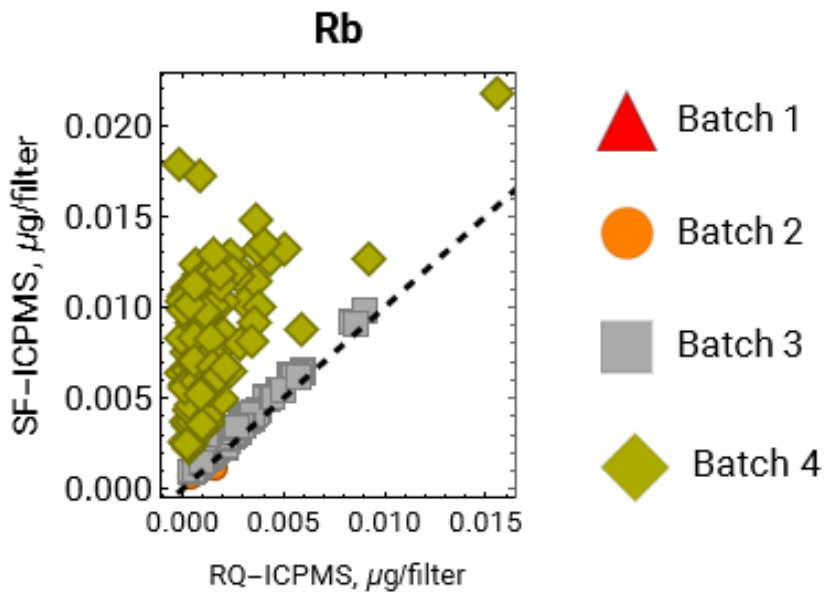


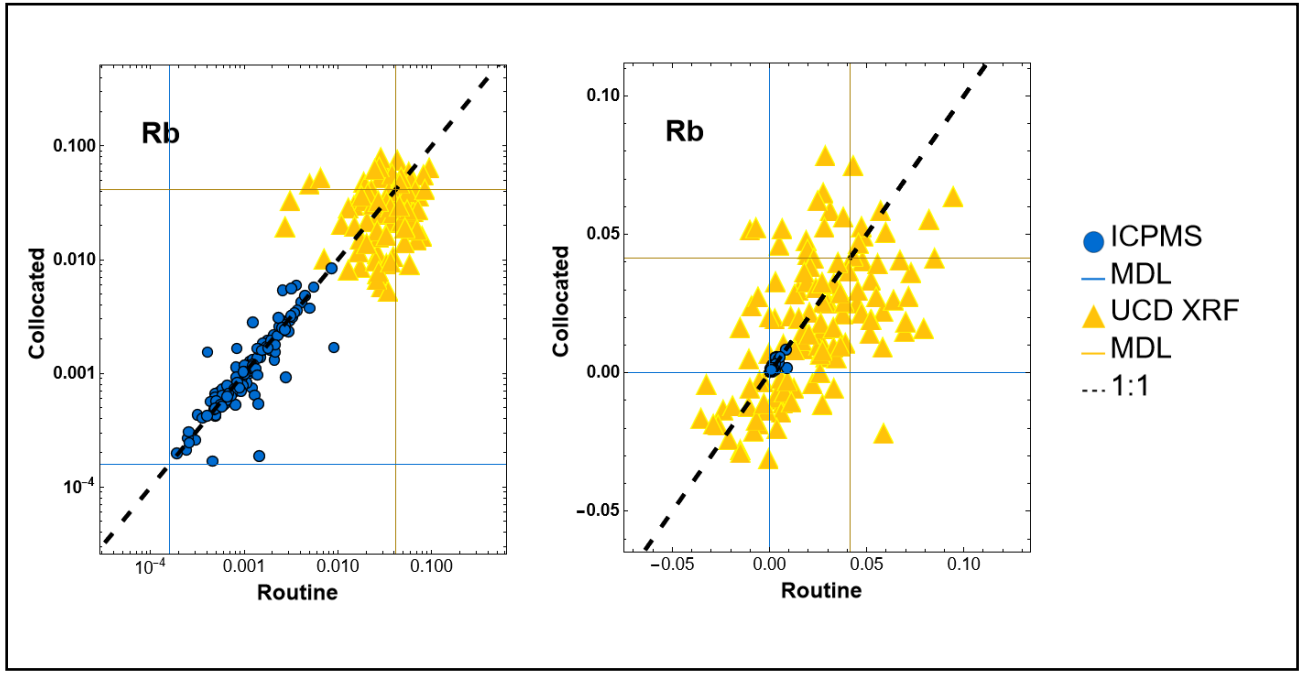


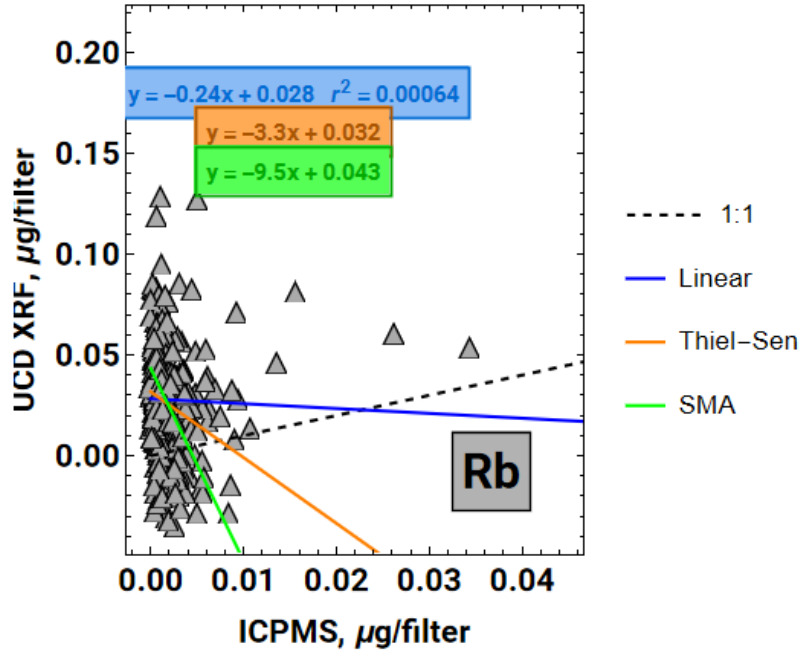
Rb

XRF > 10% MDL	NO
% above MDL	3%
RQ ICPMS >10% MDL	YES
% above MDL	98%
RQ ICPMS 1648a recovery acceptable ? (5% HNO3 + 2 hour hot block digestion)	NO
Which MDL is lower	ICPMS



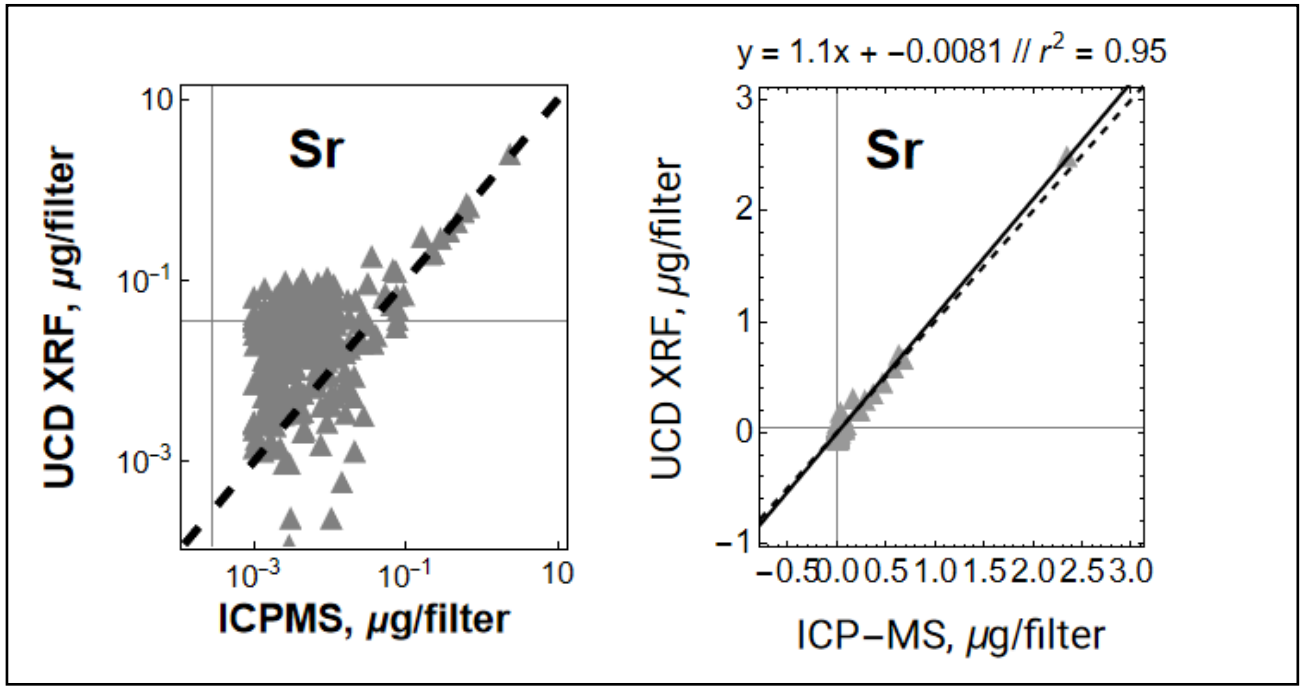


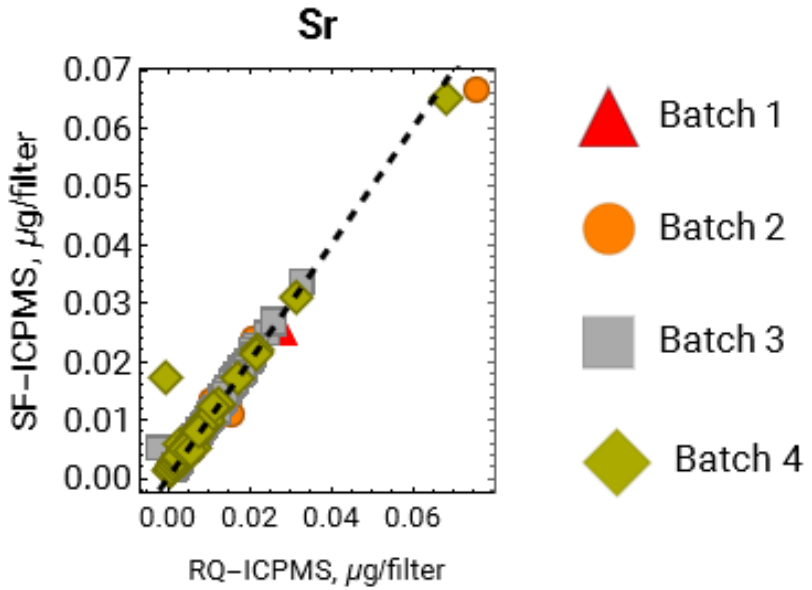


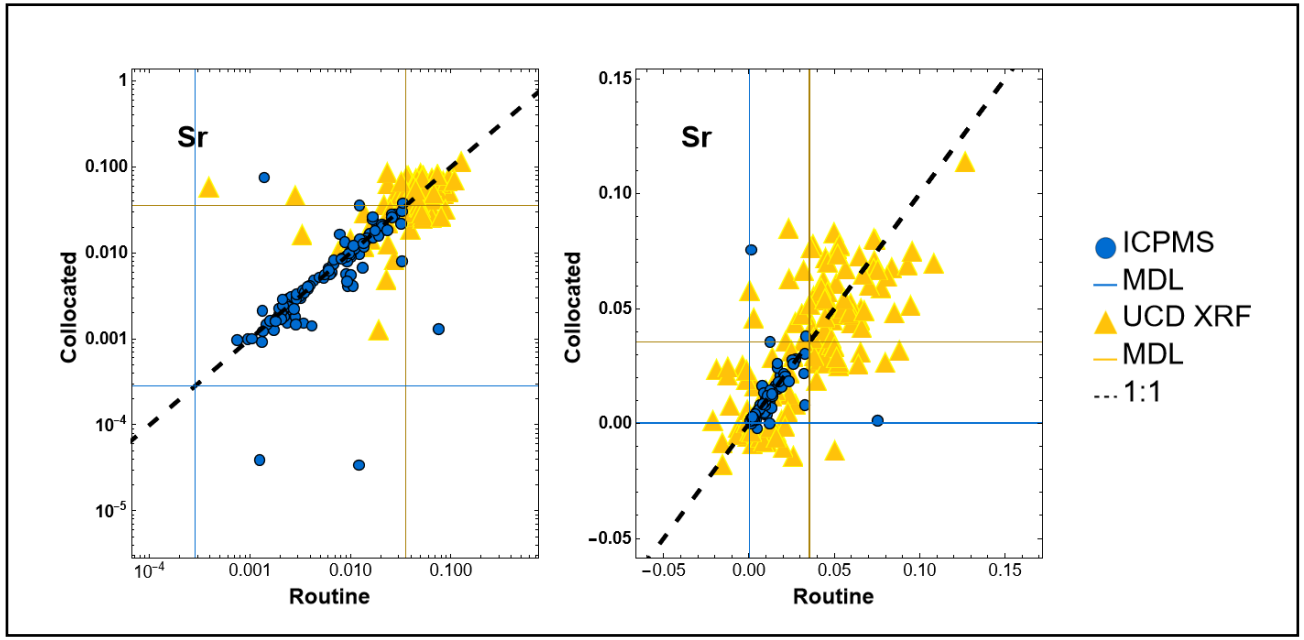


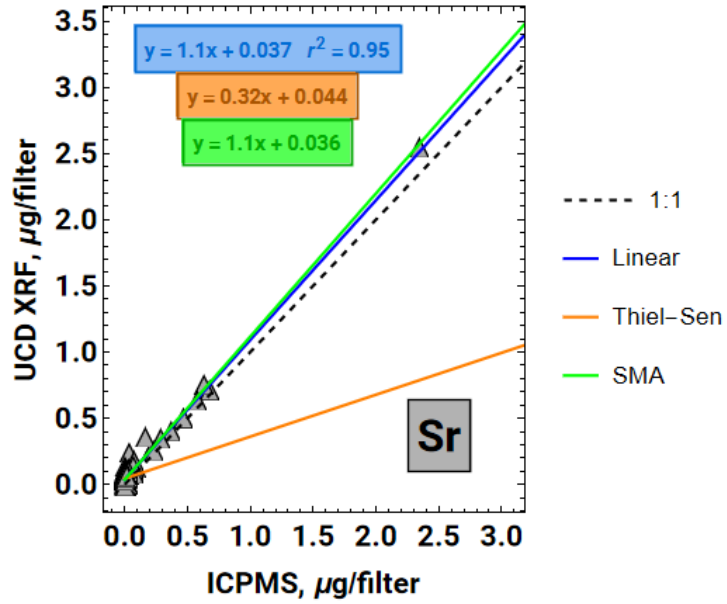
Sr

XRF > 10% MDL	NO
% above MDL	9%
RQ ICPMS > 10% MDL	YES
% above MDL	99%
RQ ICPMS 1648a recovery acceptable? (5% HNO3 + 2 hour hot block digestion)	NO
Which MDL is lower	ICPMS



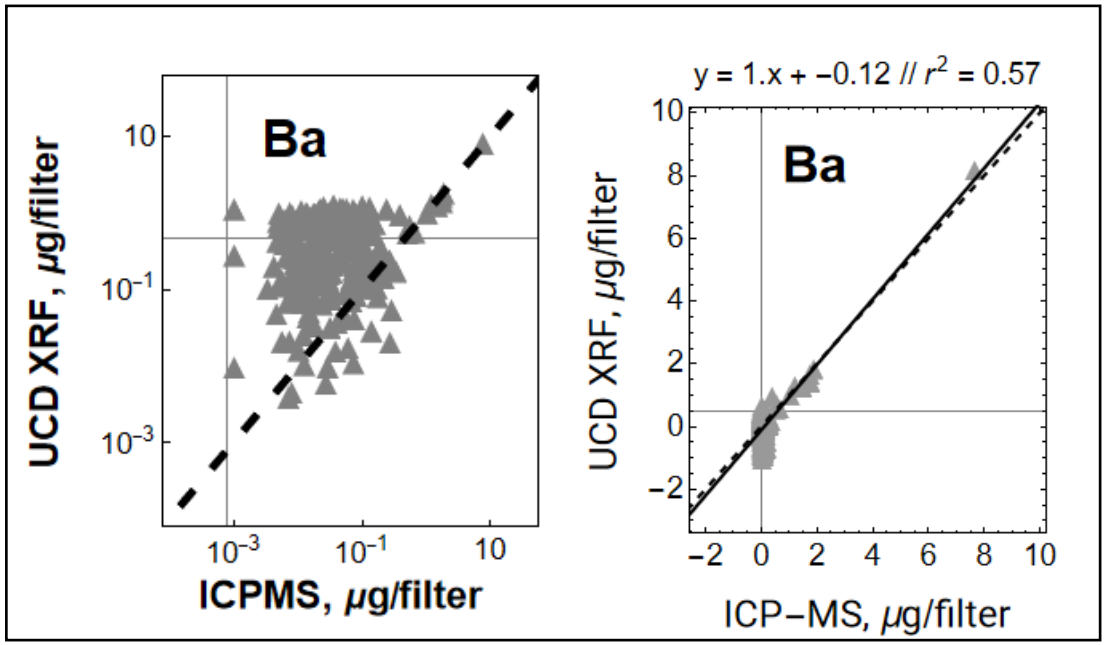


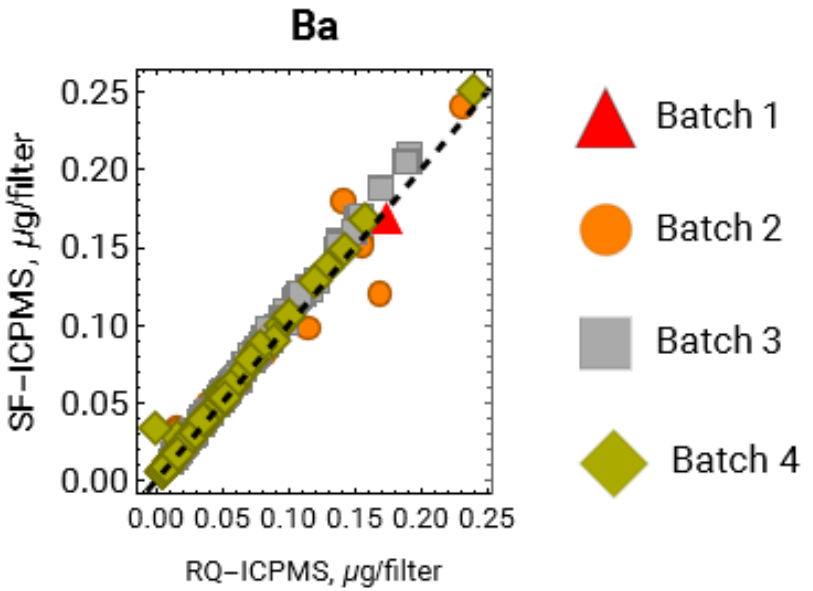


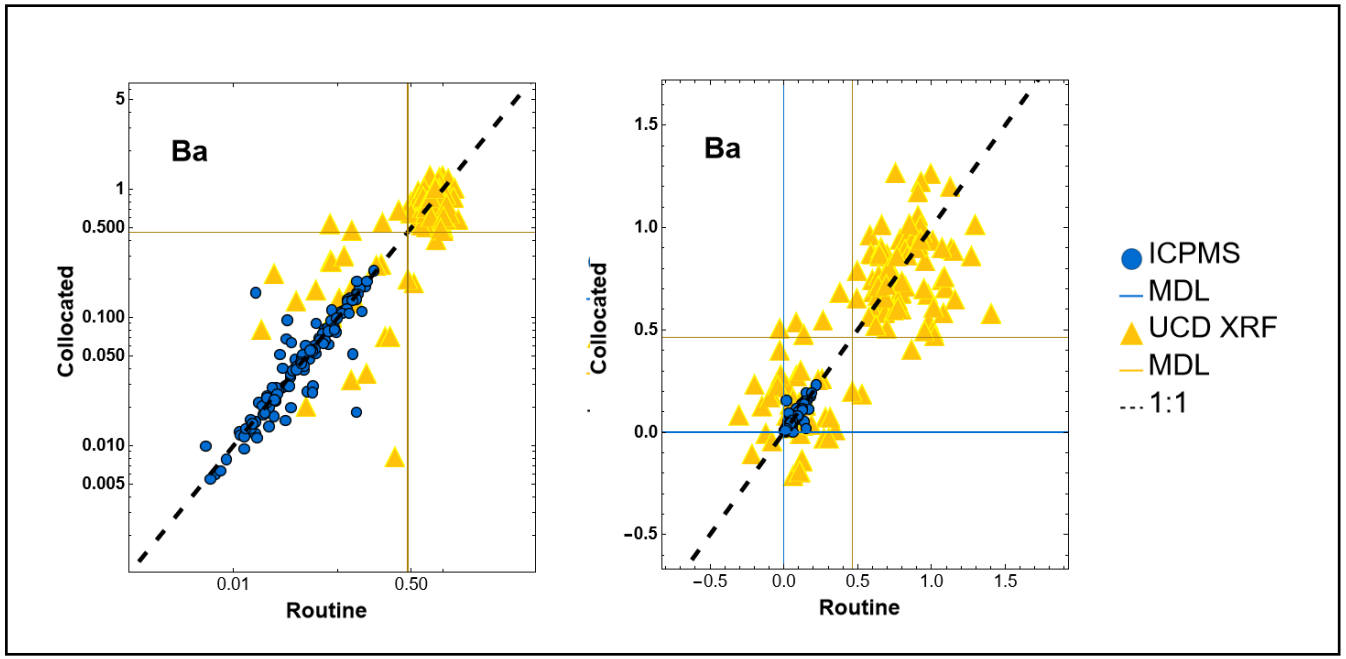


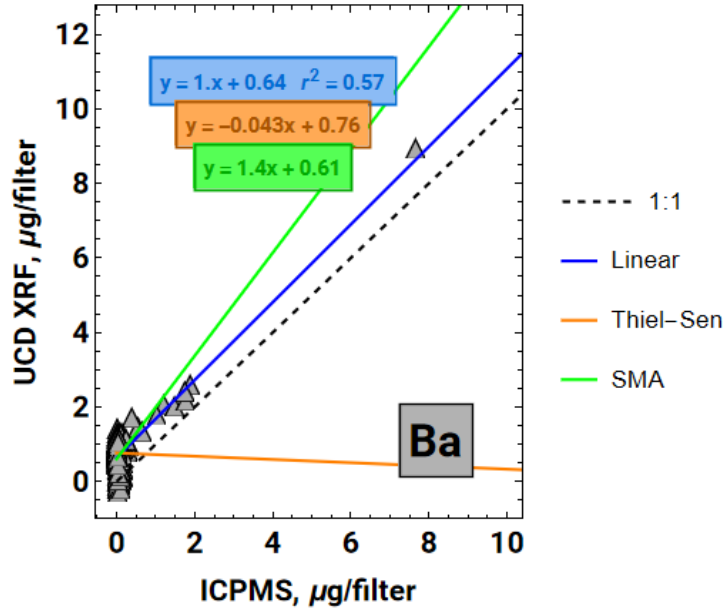
Ba

XRF > 10% MDL	NO
% above MDL	4%
RQ ICPMS >10% MDL	YES
% above MDL	99%
RQ ICPMS 1648a recovery acceptable? (5% HNO3 + 2 hour hot block digestion)	Not evaluated
Which MDL is lower	ICPMS



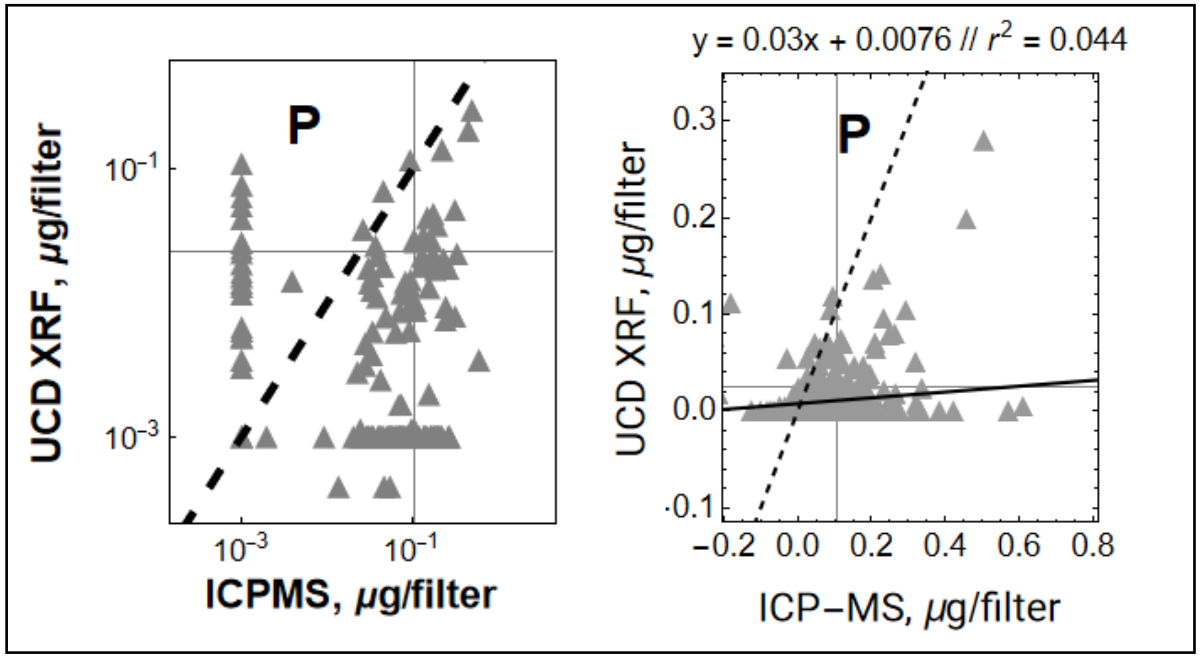


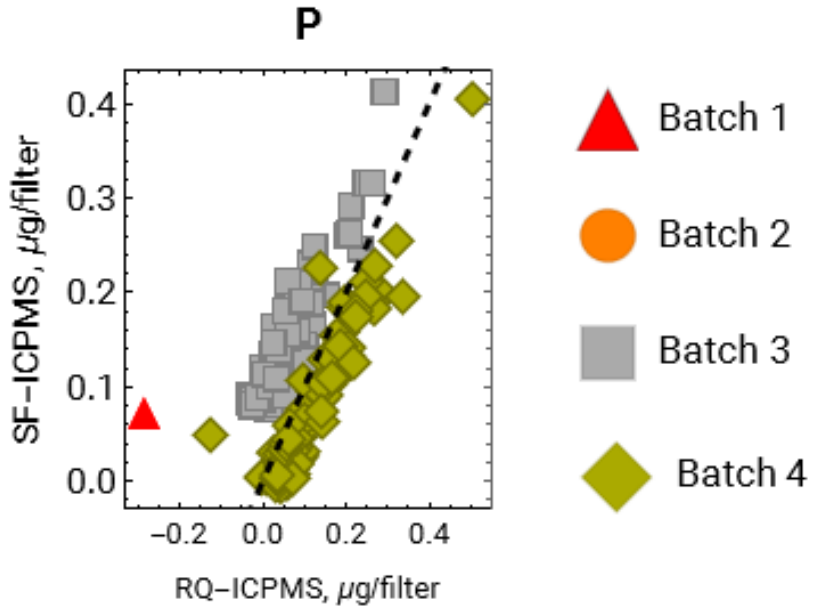


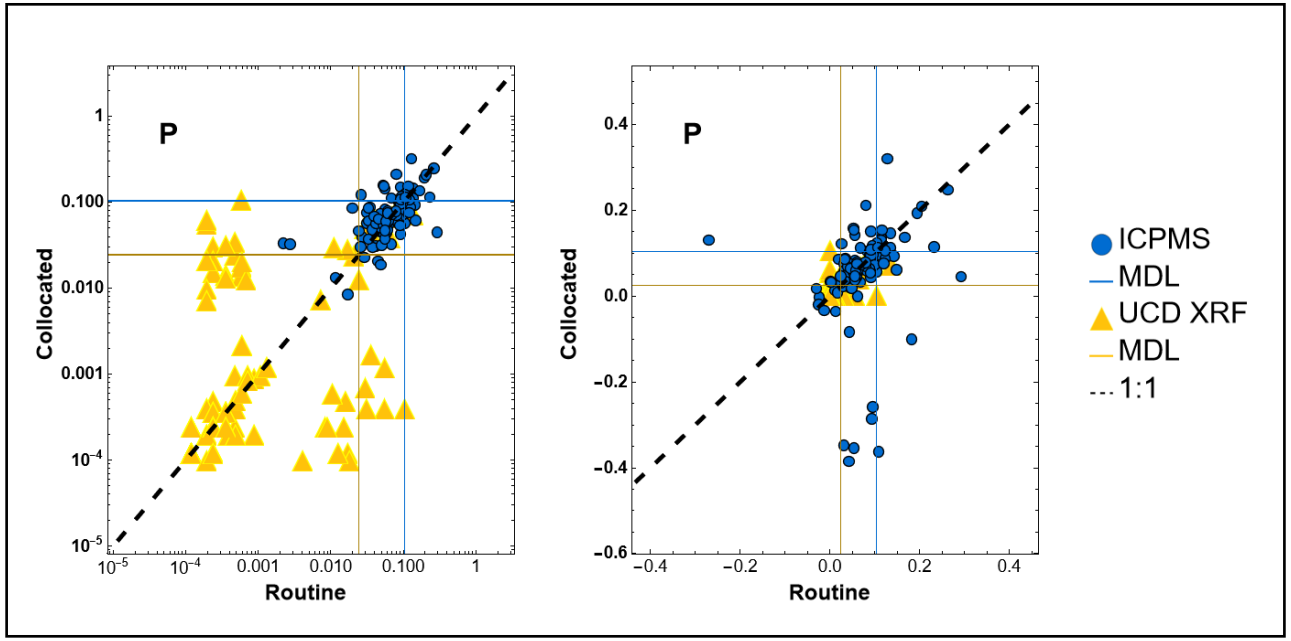


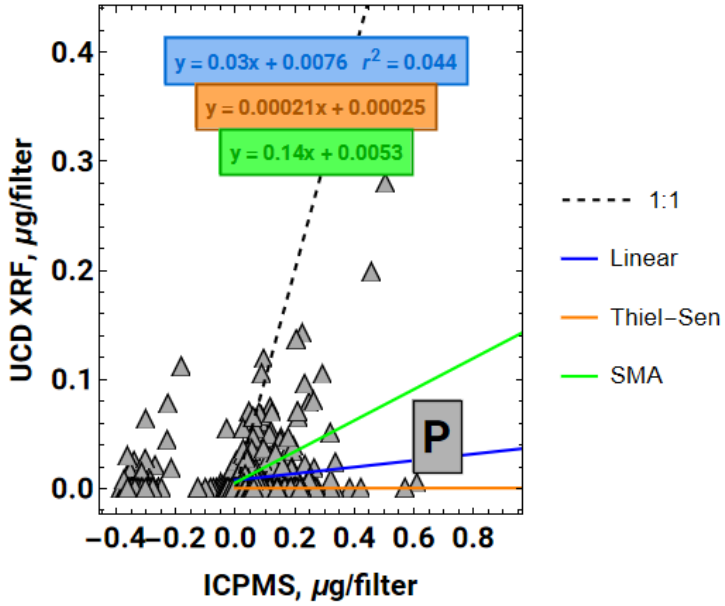
P

XRF > 10% MDL	NO
% above MDL	9.8%
RQ ICPMS > 10% MDL	YES
% above MDL	22%
RQ ICPMS 1648a recovery acceptable ? (5% HNO3 + 2 hour hot block digestion)	Not evaluated
Which MDL is lower	UCD XRF



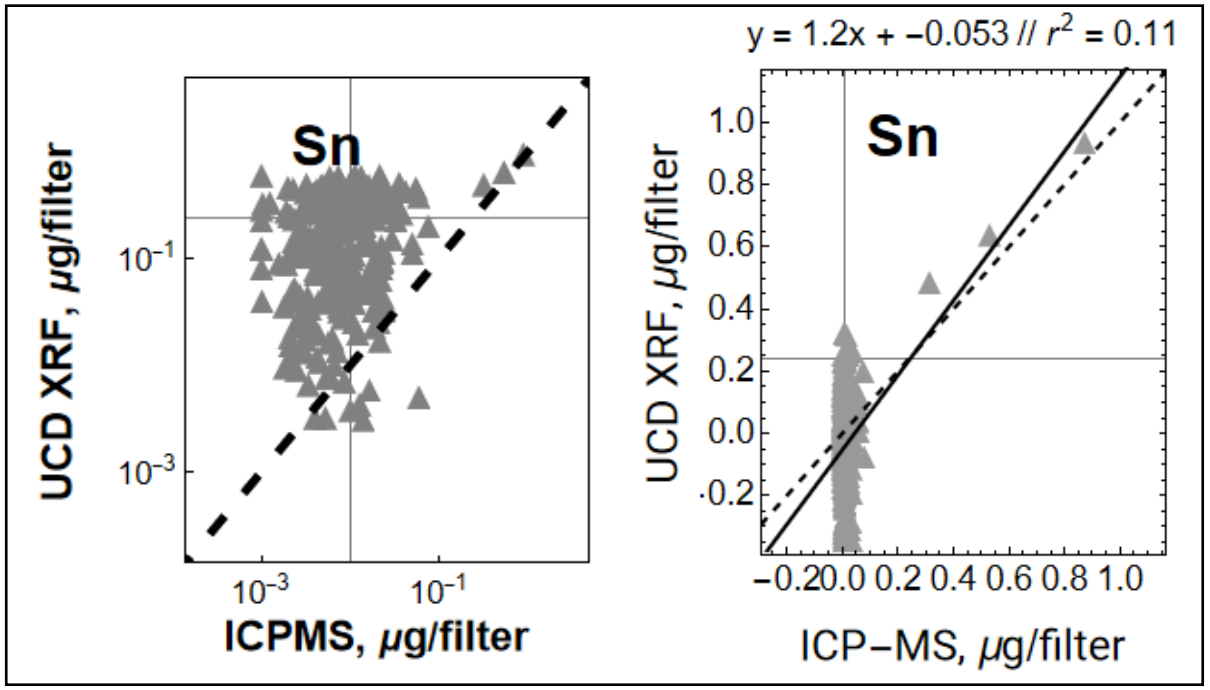


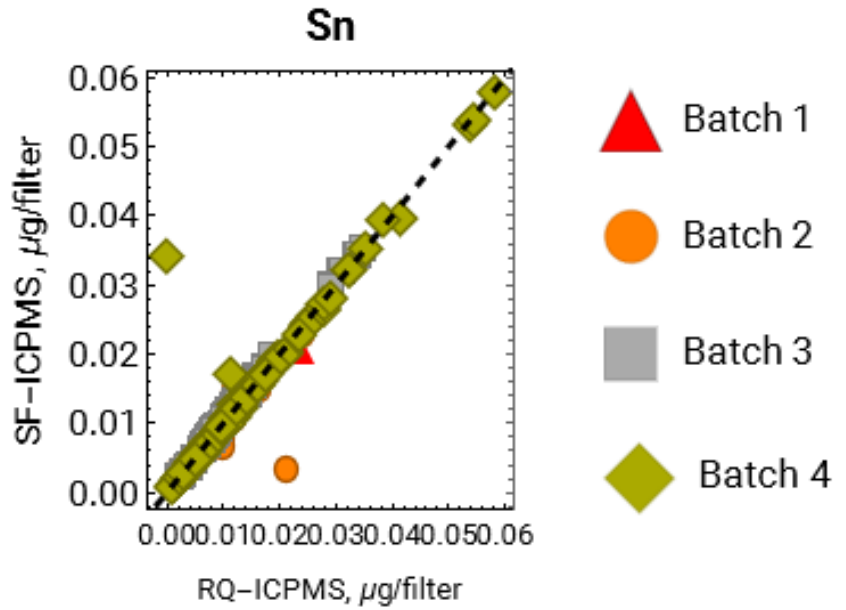


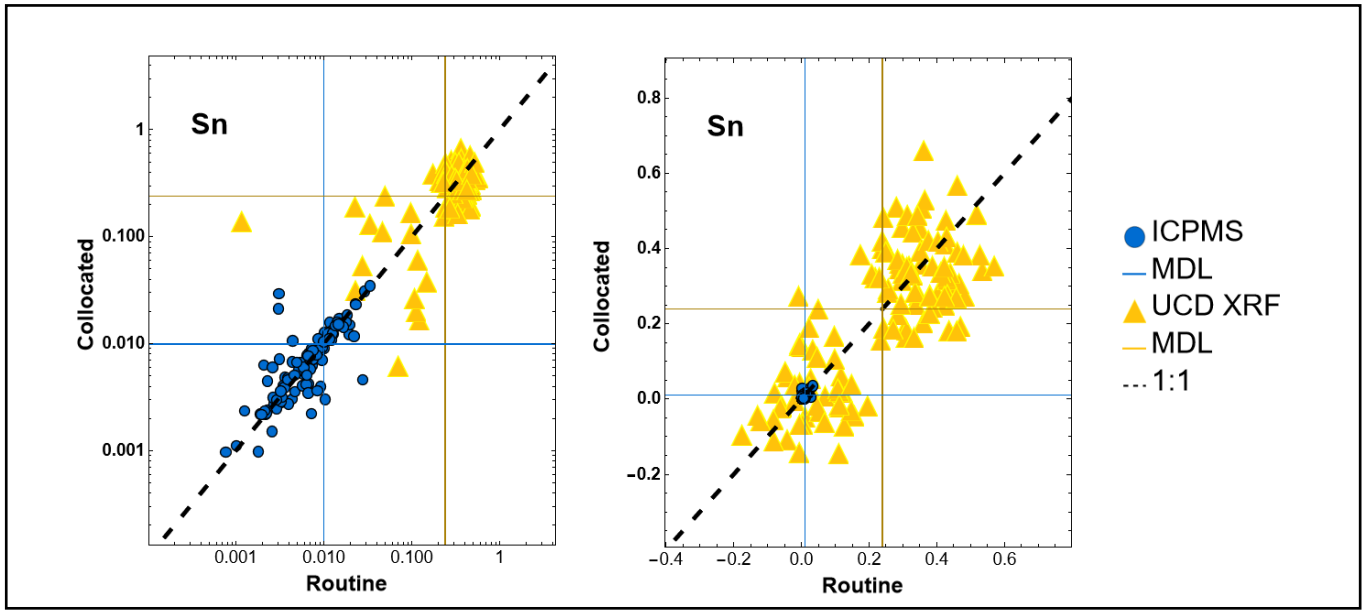


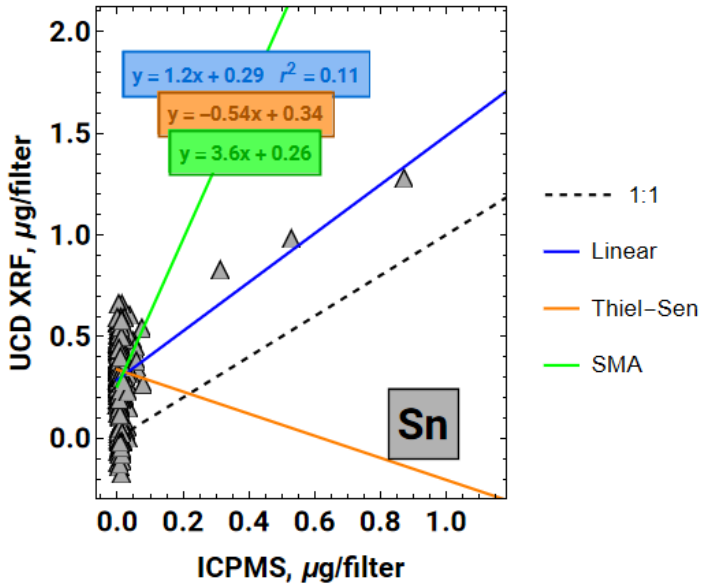
Sn

XRF > 10% MDL	NO
% above MDL	2%
RQ ICPMS > 10% MDL	YES
% above MDL	35%
RQ ICPMS 1648a recovery acceptable ? (5% HNO3 + 2 hour hot block digestion)	Not evaluated
Which MDL is lower	ICPMS



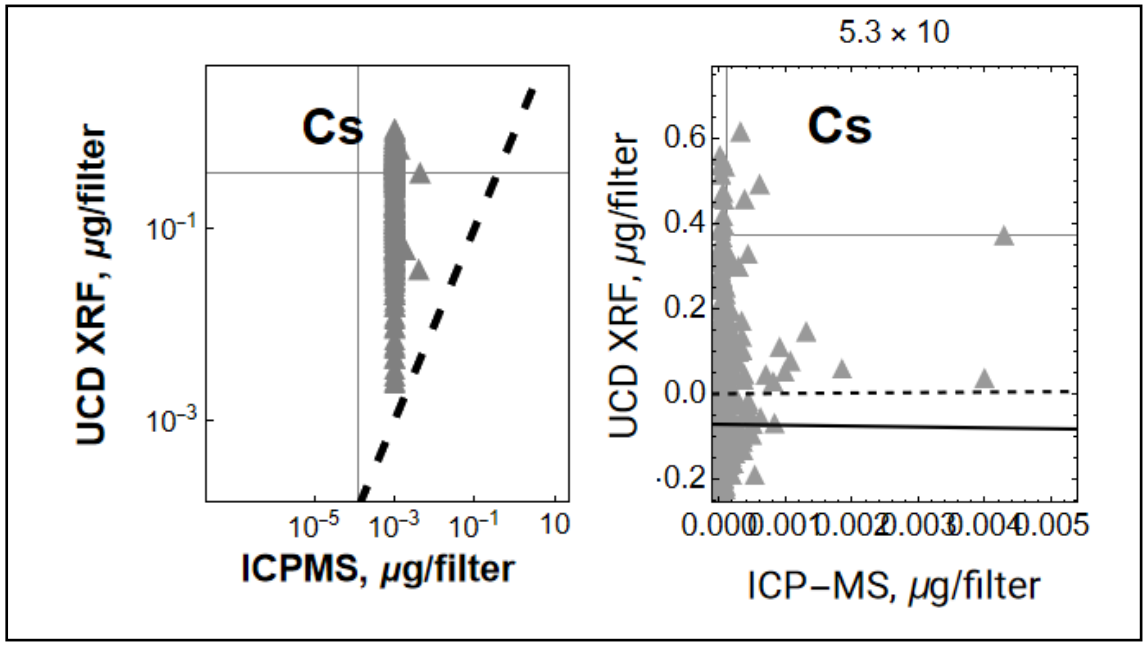


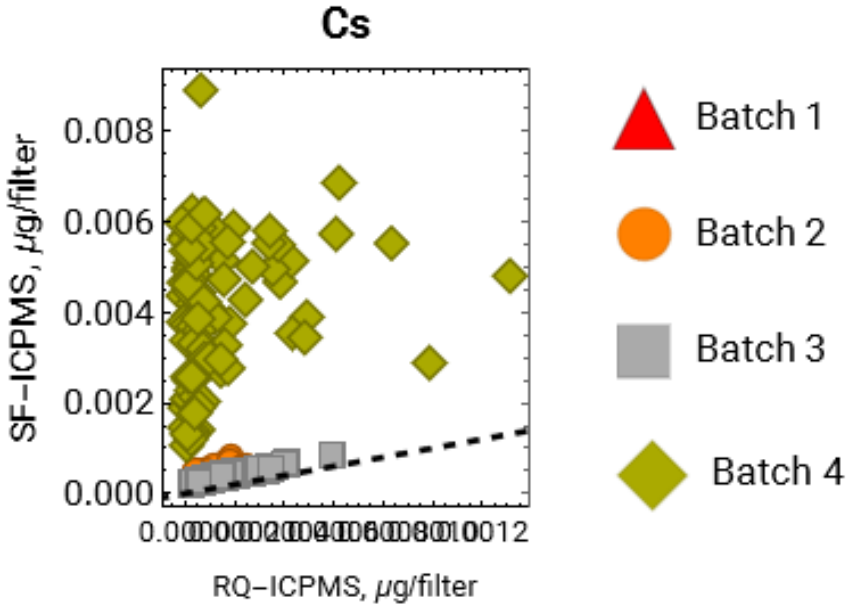


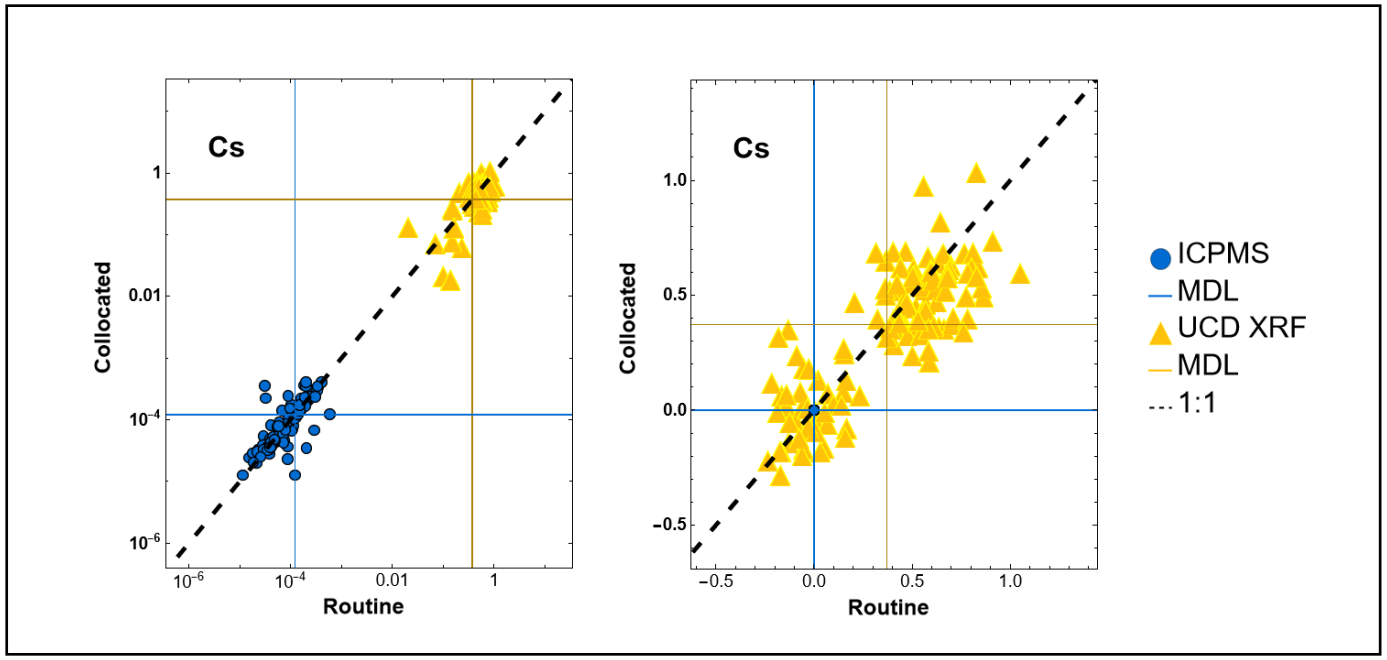


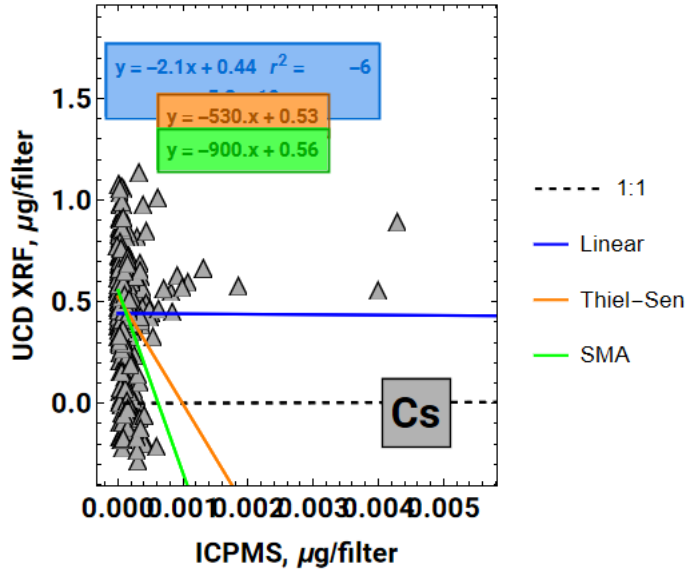
Cs

XRF > 10% MDL	NO
% above MDL	3%
RQ ICPMS >10% MDL	YES
% above MDL	28%
RQ ICPMS 1648a recovery acceptable? (5% HNO3 + 2 hour hot block digestion)	NO
Which MDL is lower	ICPMS



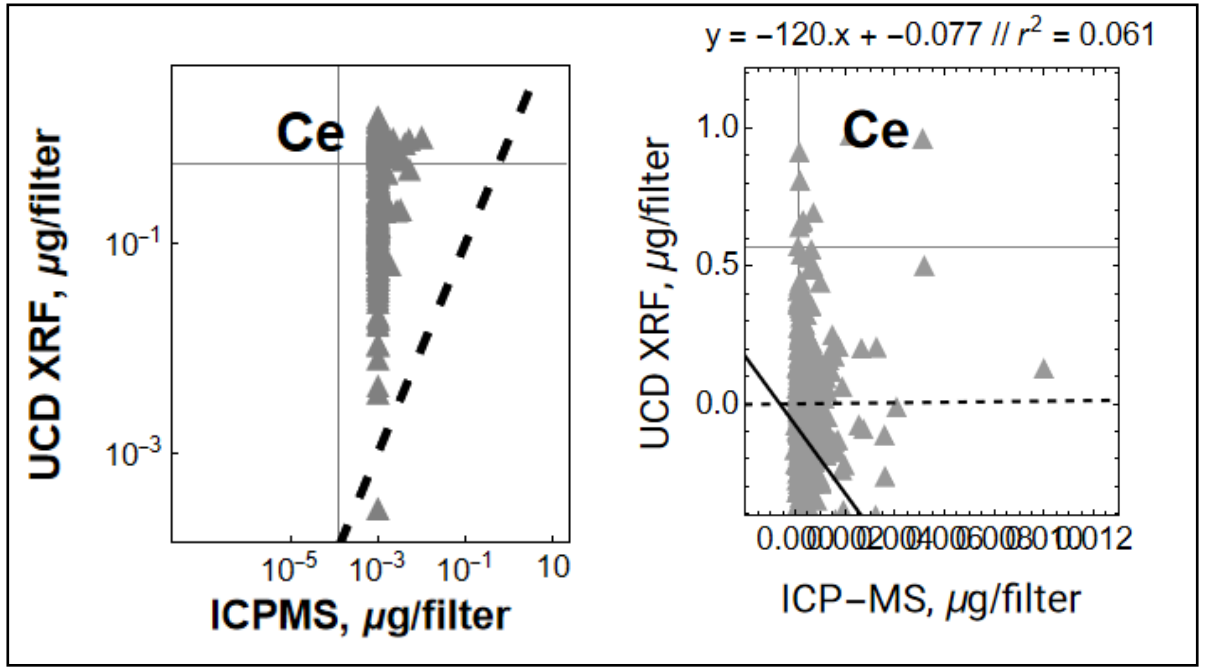


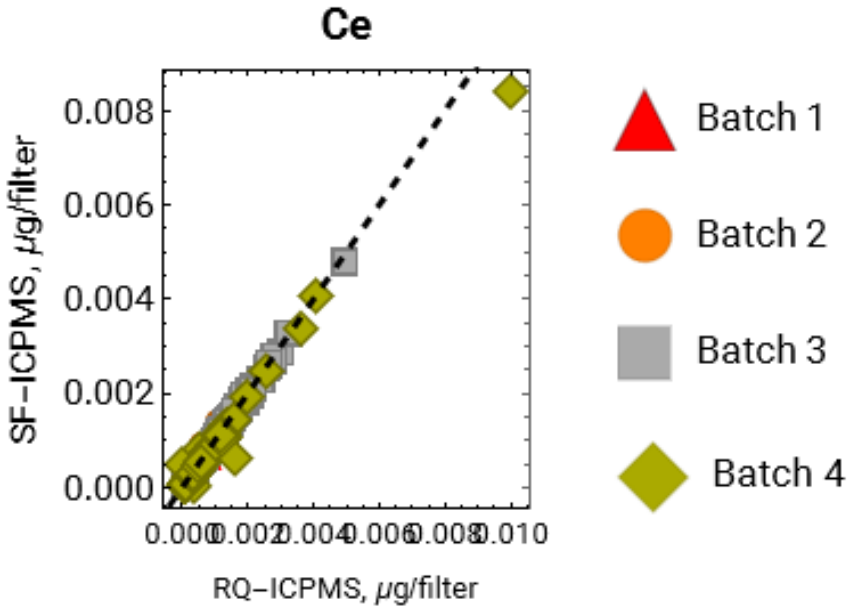


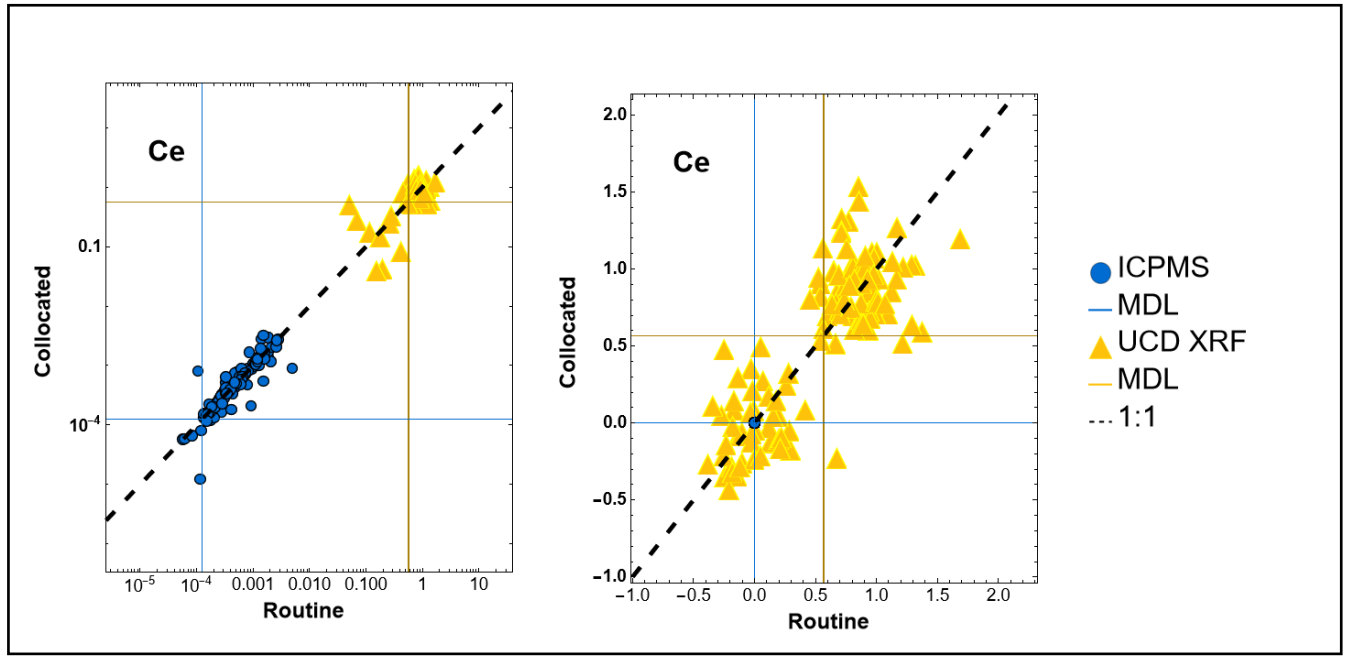


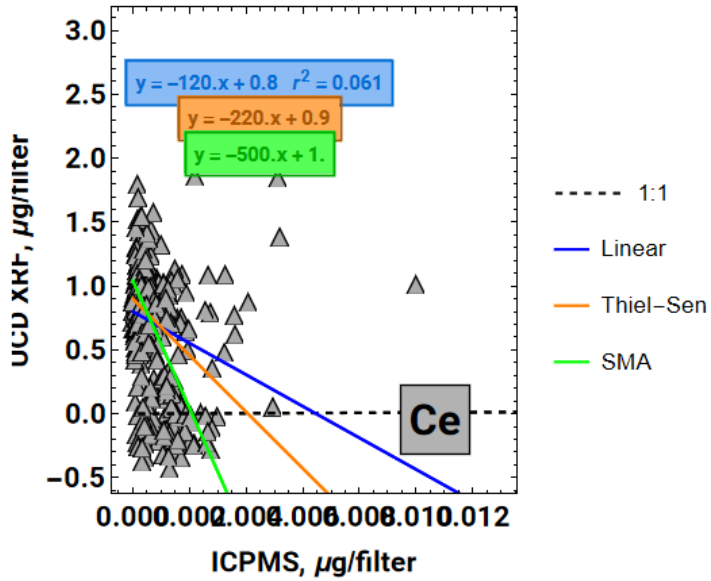
Ce

XRF > 10% MDL	NO
% above MDL	2%
RQ ICPMS >10% MDL	YES
% above MDL	91%
RQ ICPMS 1648a recovery acceptable? (5% HNO3 + 2 hour hot block digestion)	NO
Which MDL is lower	ICPMS



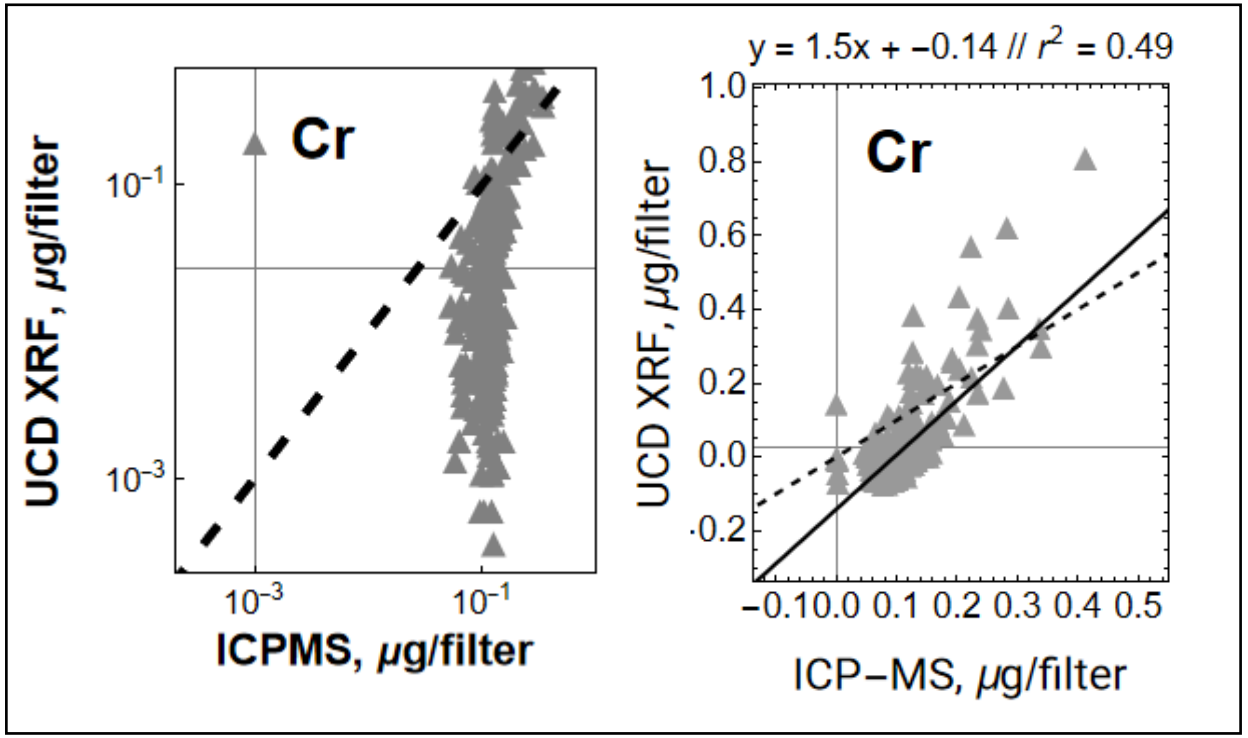


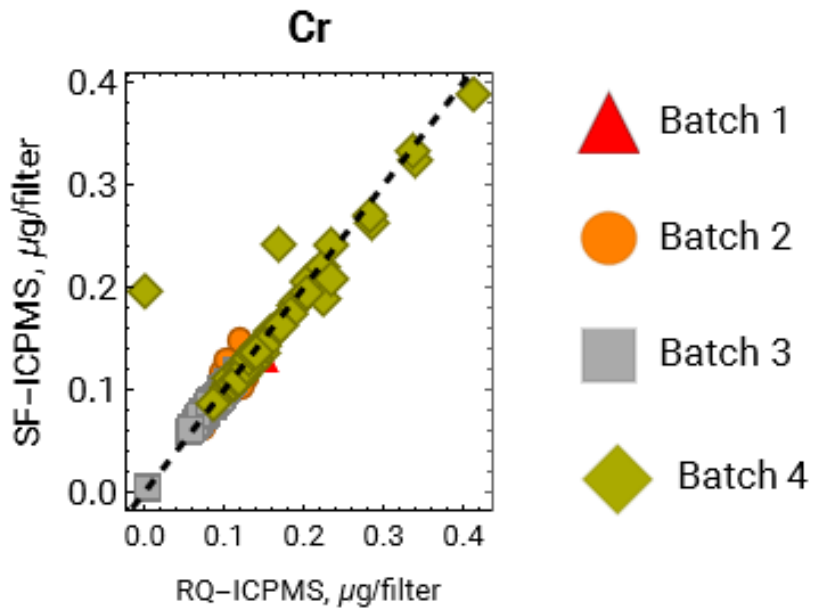


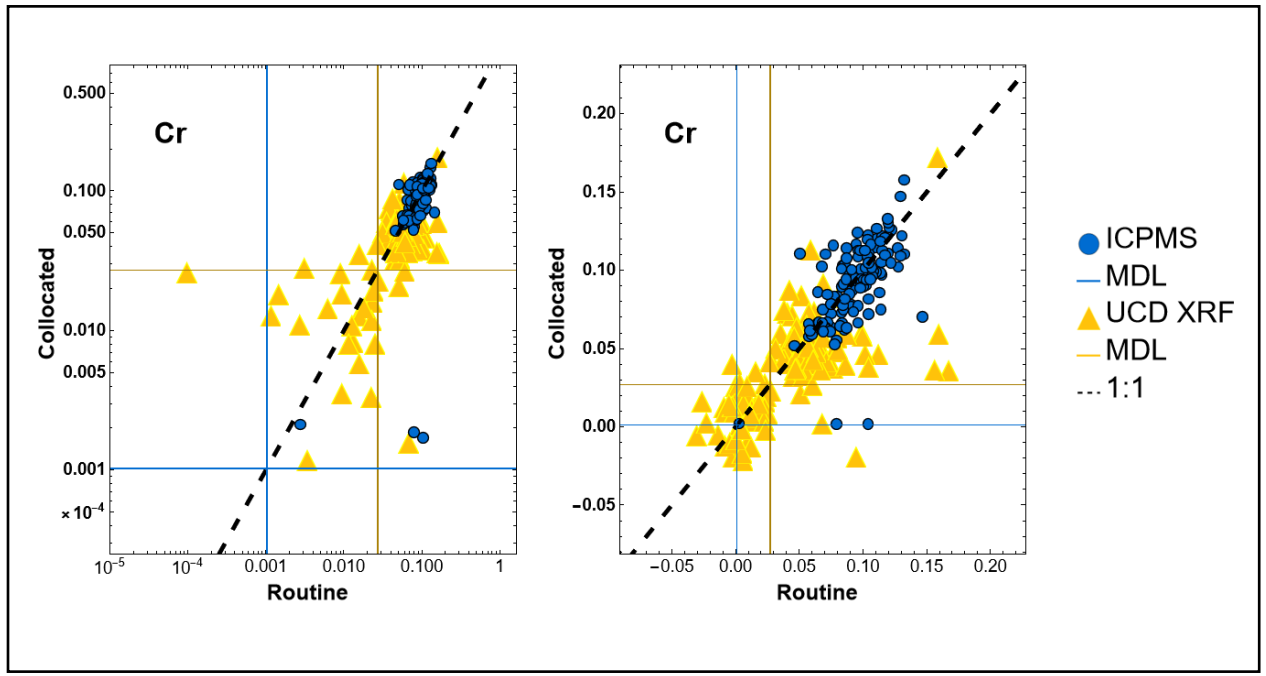


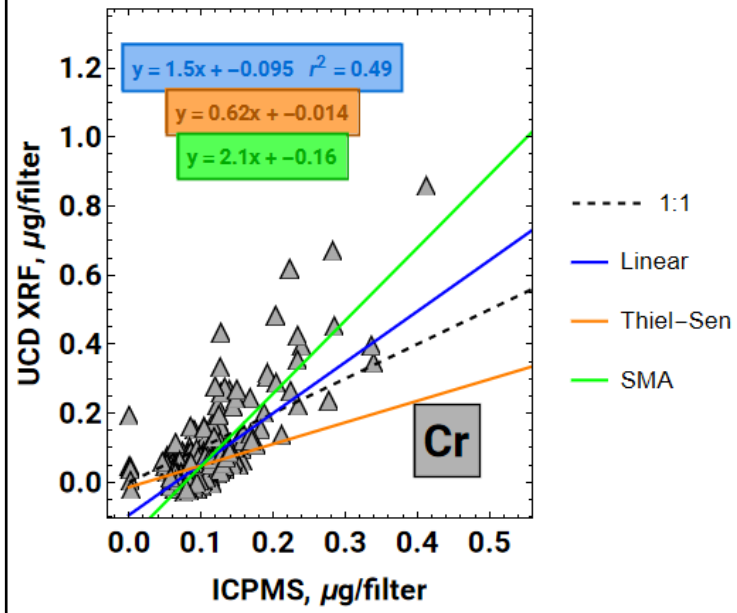
Cr

XRF > 10% MDL	YES
% above MDL	19%
RQ ICPMS >10% MDL	YES
% above MDL	100%
RQ ICPMS 1648a recovery acceptable? (5% HNO3 + 2 hour hot block digestion)	NO
Which MDL is lower	ICPMS
Other notes	• Cr is "noise" above MDL in XRF - ICPMS intercomparison • Cr is known to be better extracted with HF (+microwave digestion?)



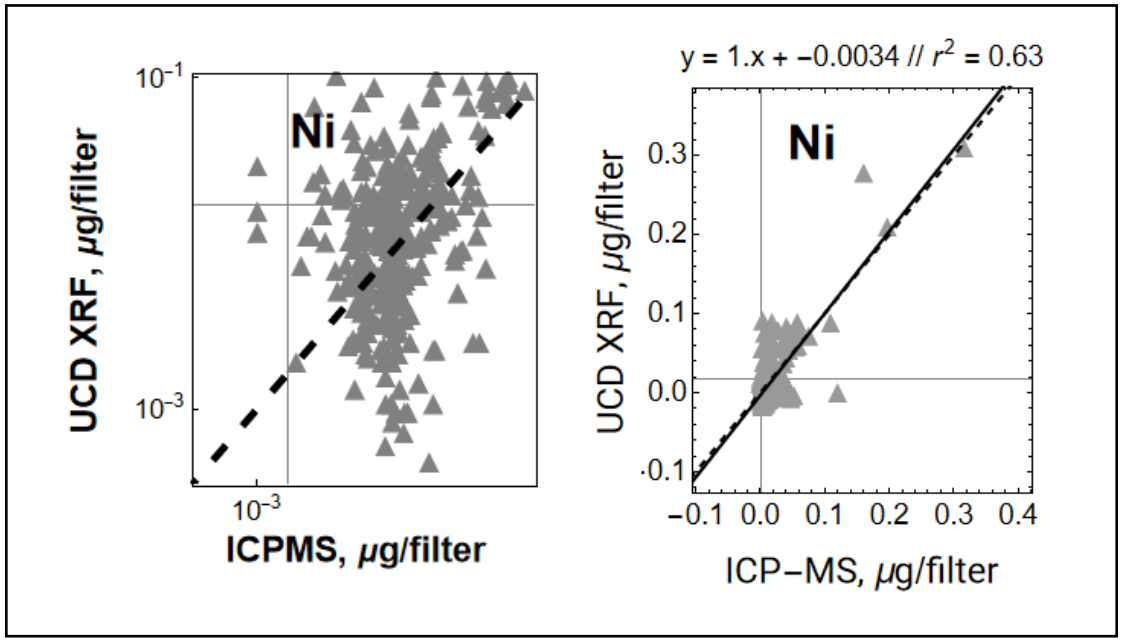


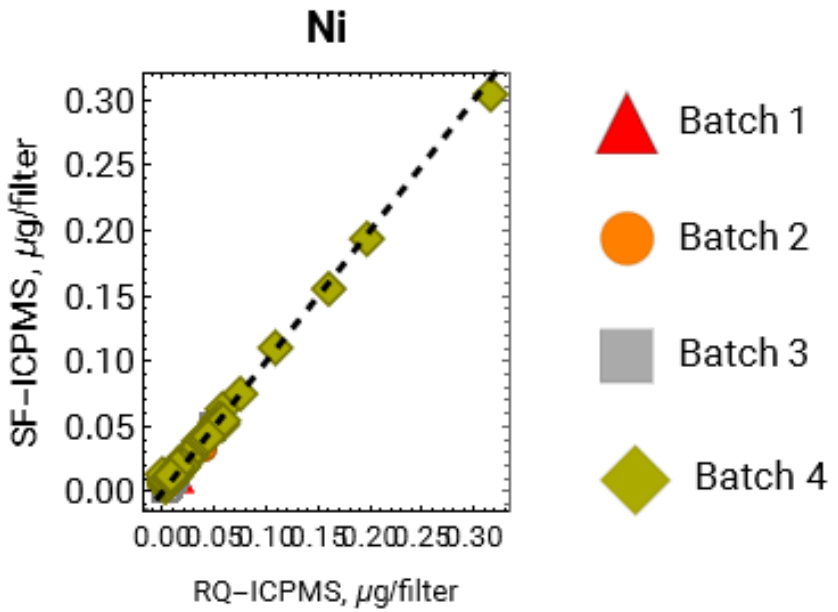


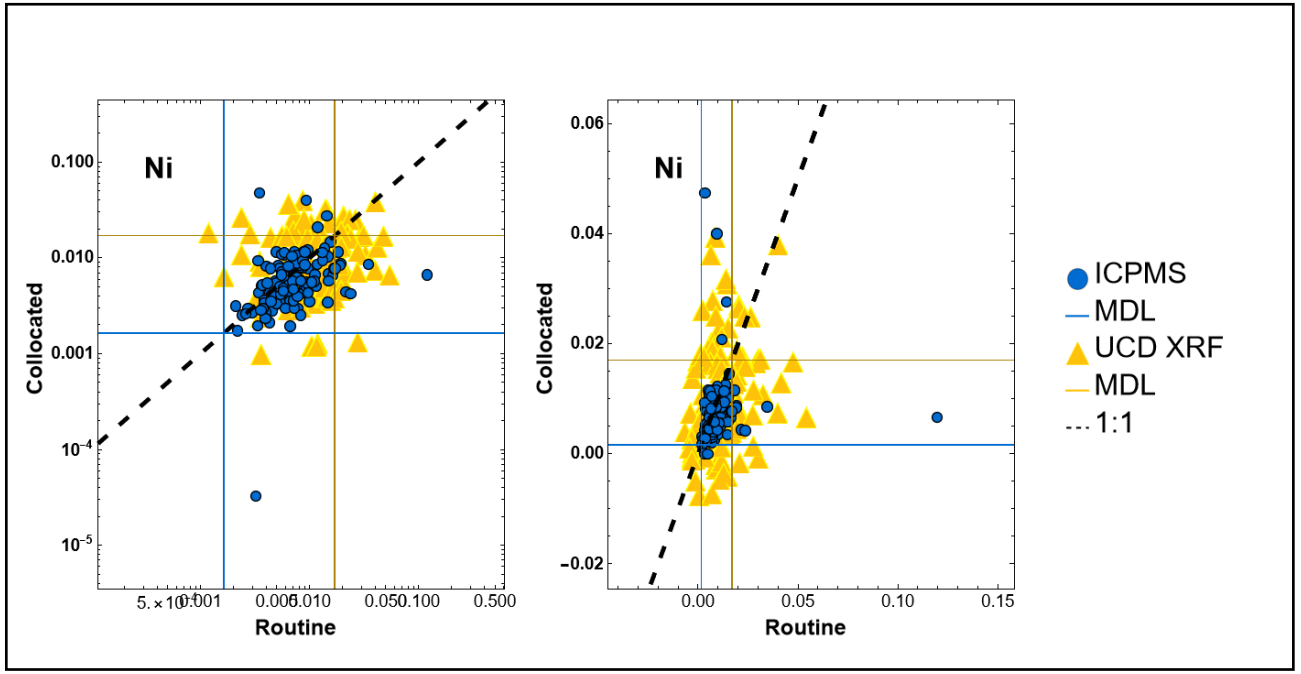


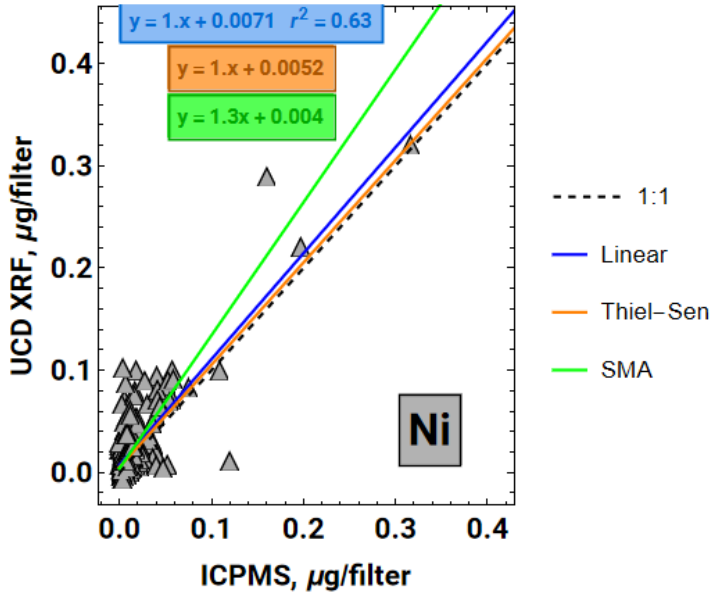
Ni

XRF > 10% MDL	YES
% above MDL	16%
RQ ICPMS > 10% MDL	YES
% above MDL	99%
RQ ICPMS 1648a recovery acceptable? (5% HNO3 + 2 hour hot block digestion)	NO
Which MDL is lower	ICPMS
Other Notes	Ni is known to be better extracted with HF (+ microwave digestion?)



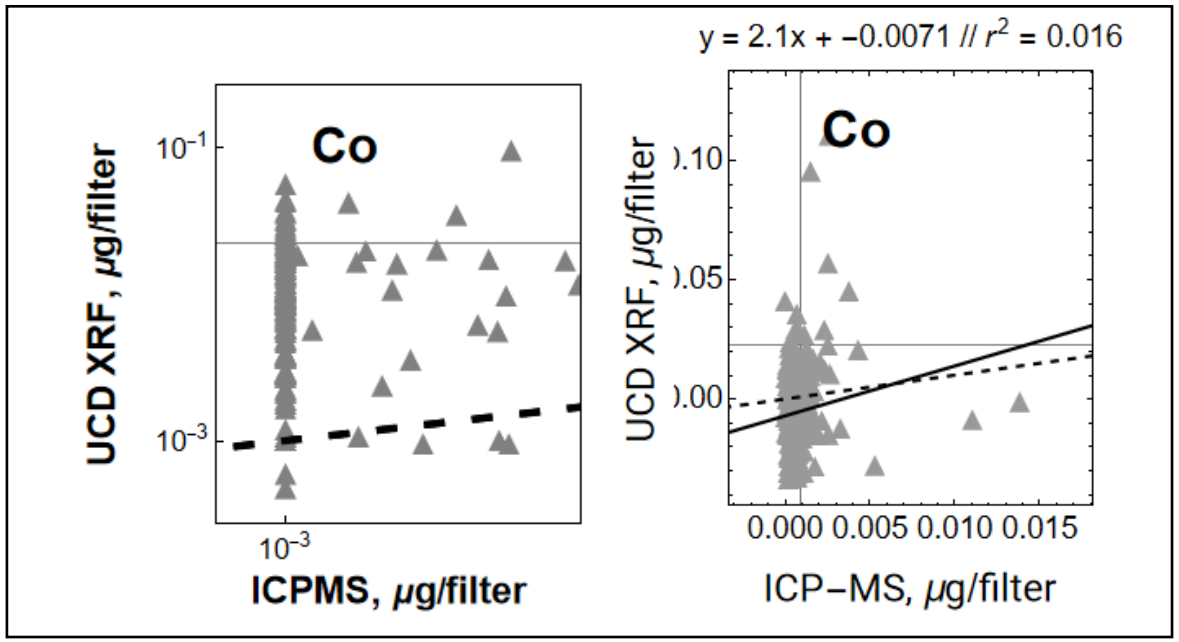


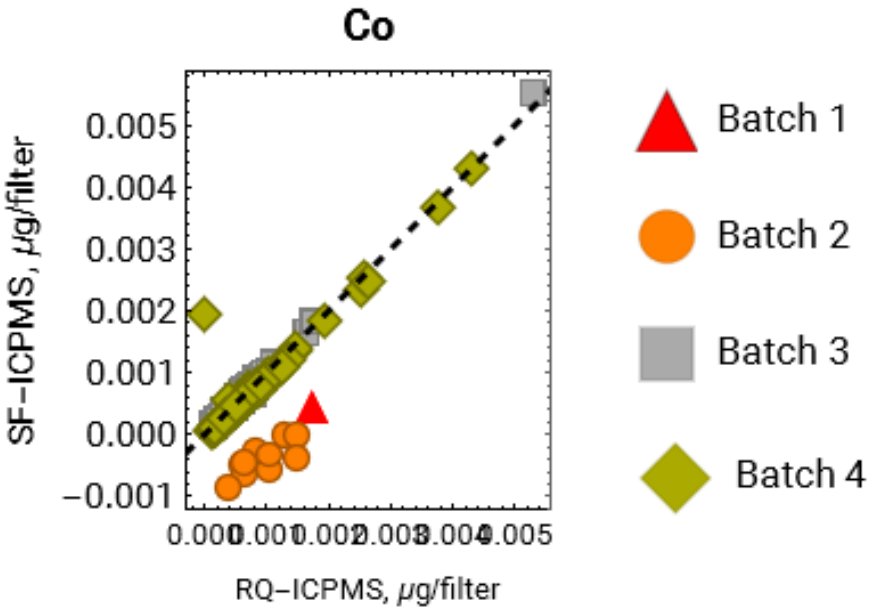


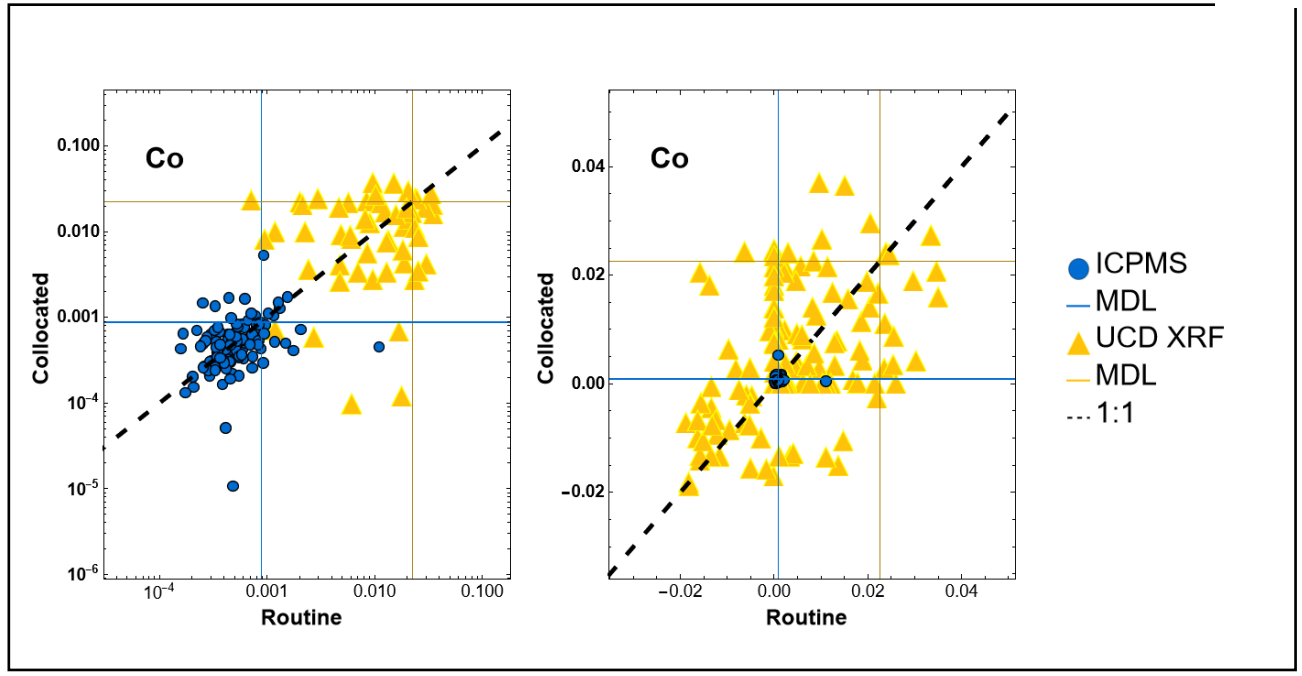


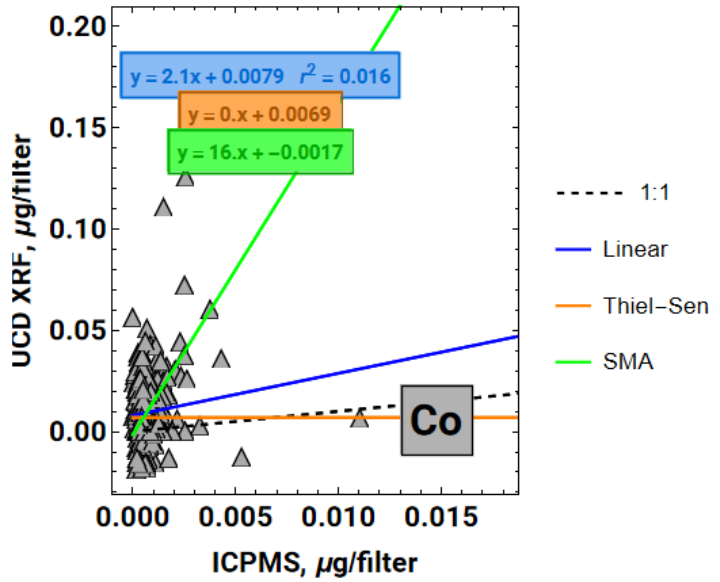
Co

XRF > 10% MDL	NO
% above MDL	2%
RQ ICPMS > 10% MDL	YES
% above MDL	15%
RQ ICPMS 1648a recovery acceptable? (5% HNO3 + 2 hour hot block digestion)	YES
Which MDL is lower	ICPMS



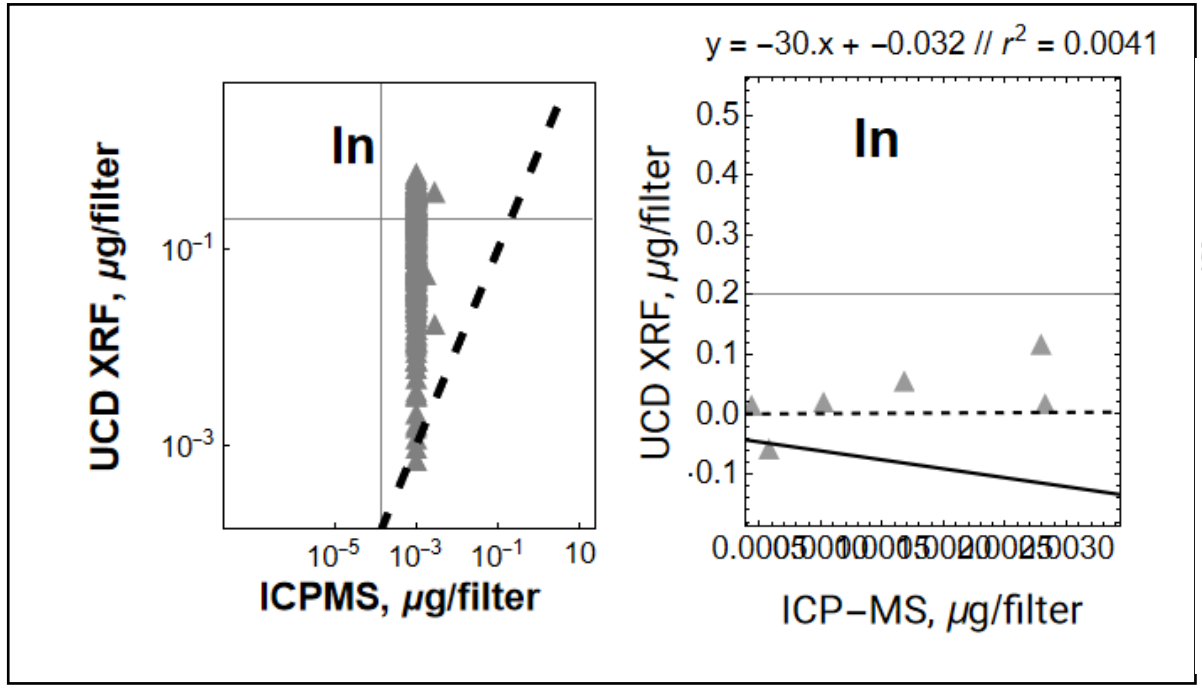


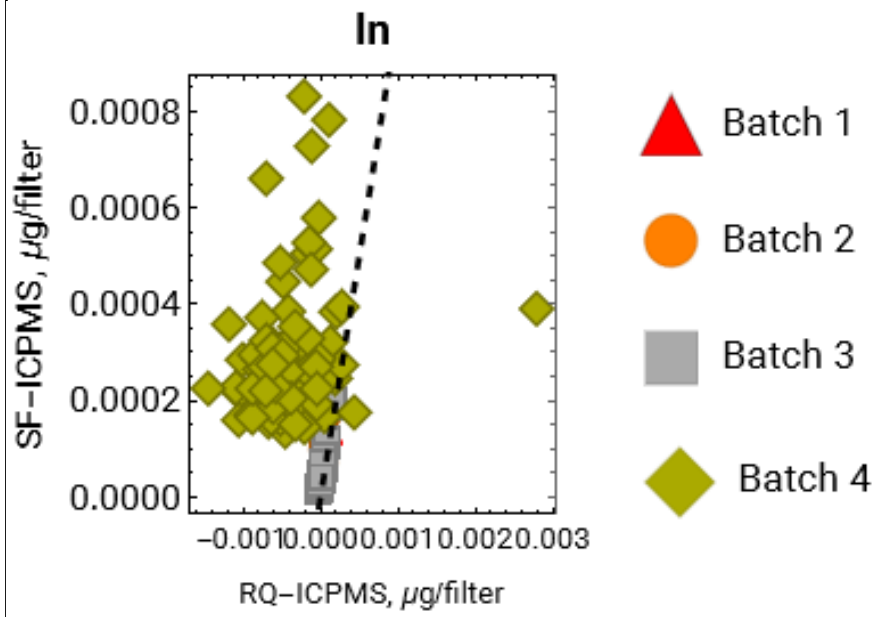


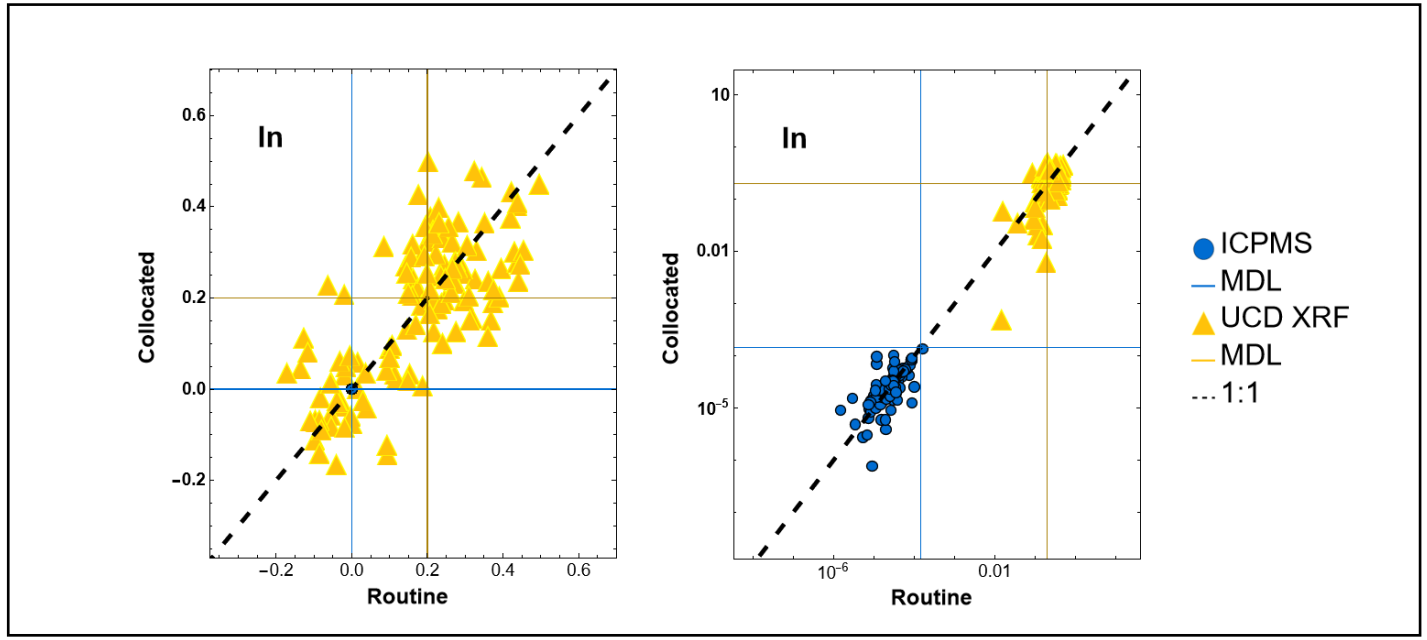


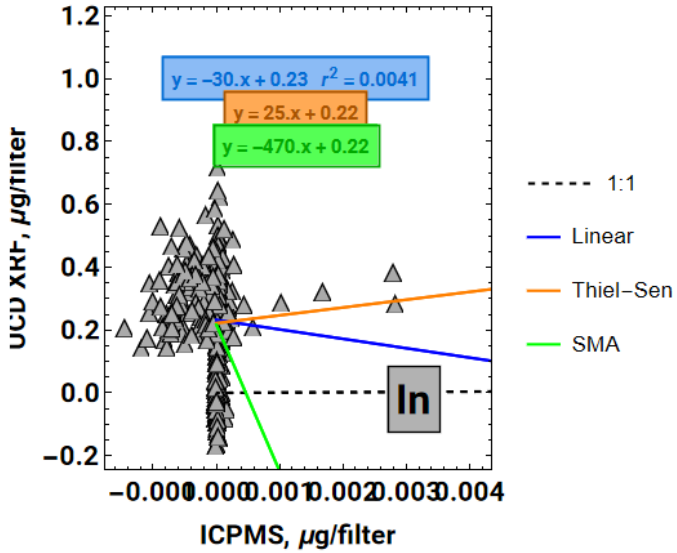
In

XRF > 10% MDL	NO
% above MDL	4%
RQ ICPMS > 10% MDL	NO
% above MDL	4%
RQ ICPMS 1648a recovery acceptable ? (5% HNO3 + 2 hour hot block digestion)	Not evaluated
Which MDL is lower	ICPMS









Considerations:

- **Were the elements detected?**

  Intra-method: Method detection limits

- **Are the reported concentrations reliable?**

  Inter-method: XRF-ICPMS intercomparison

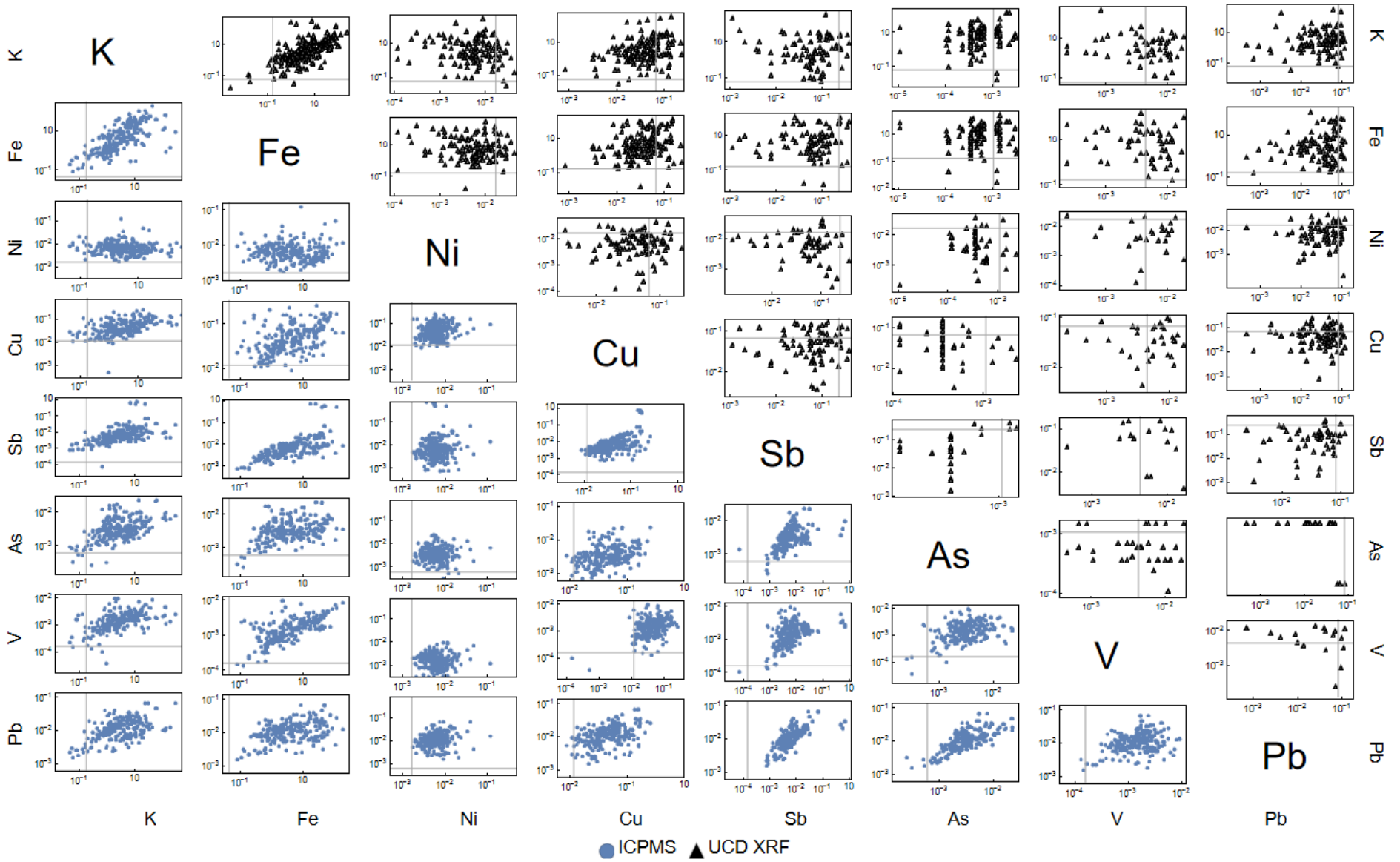
  Intra-method: inter-elemental comparison; collocated samples (precision)

- **Was the ICPMS extraction complete?**

  Evaluated using reference materials (NIST SRM 1648a, 1633)

Intra-method, inter-elemental

- Pairs selected from *a priori* knowledge of the elements' association.
- Elements from common source are often correlated: soil elements (K, Fe, Cu) or elements that may be from anthropogenic urban sources (Sb, As, Pb, Cu, Ni, Cr, V).
- ICPMS inter-element correlations are much tighter than UCD XRF correlations → better intra-method measurement precision for ICPMS.



The plots to the left of the diagonal show ICPMS results only. The plots to the right of the diagonal show XRF results only.

Comparison of Recoveries – RTI ICPMS and Canada NAPS

See: *Validation of a Simple Microwave-Assisted Acid Digestion Method Using Microvessels for Analysis of Trace Elements in Atmospheric $PM_{2.5}$ in Monitoring and Fingerprinting Studies*. Celo, V., Dabek-Zlotorynska, E., Mathieu, D., Okonskaia, I. The Open Chemical and Biochemical Methods Journal, 2010. http://dx.doi.org/10.2174/1875038901003010143

Canada NAPS (Celo, 2010)

- 2 mL 40% HNO_3
- microwave 1 min 165 °C, then 15 min 175 °C

XRF: 22 elements (Al, Si, S, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Zn, Se, Br, Rb, Sr, Cd, Sn, Cu, Cs, Ba, Pb)

ICPMS: 20 metals (Ag, Al, As, Ba, Be, Cd, Co, Cu, Fe, Mn, Mo, Ni, Pb, Se, Sb, Sn, Sr, Tl, V, Zn)

This study

- 25 mL 5.0 % HNO_3
- Heated graphite block for two hours at 95 ± 5 °C

Elements (star denotes non certified)	**Canada NAPS recovery (Celo, 2010)**	**This study**					
		T1-5x	T2-5x	T3-5x	T1-100x	T2-100x	T3-100x
Al	50				26	26	29
Ti*	28	10	10	10			
V	**83**	**86**	**93**	**94**			
Cr	30	15	12	17			
Mn	**94**	76	75	**81**			
Fe	**82**				46	46	51
Co	**81**	**100**	**102**	**108**			
Ni	**89**	58	59	63			
Cu	**97**	**83**	**82**	**86**			
Zn	**116**				**87**	**88**	**97**
As	**104**	**99**	**97**	**104**			
Se	**107**	**88**	**84**	**88**			
Cd	**107**	**85**	**85**	**92**			
Sb	74	67	66	70			
Ba	**82**						
Ce	62	45	45	47			
Pb	**101**				**94**	**96**	**102**

Elements not listed were not reported in the table of recoveries in Celo, 2010 (excludes Mo and La)

Atomic Number	Element	XRF > 10% MDL?	% above MDL	RQ ICPMS > 10 % MDL?	RQ ICPMS 1648a recovery acceptable? (5% HNO3 + 2 hour hot block digestion)	Notes	RECOMMENDATION	CANADA NAPS
4	**Be**							ICPMS
11	Na	YES	43	YES	NO		XRF	
12	Mg	YES	28	YES	YES (1 out of 3 trials)		XRF or ICPMS	
13	Al	YES	42	YES	NO		XRF	XRF, ICPMS
14	Si	YES	78	NO (not measured)	NO (not measured)		XRF	XRF
15	P	NO	10	YES	not evaluated		ICPMS	
16	S	YES	100	NO (not measured)	not evaluated		XRF	XRF
17	Cl	YES	50	NO (not measured)	not evaluated		XRF	
19	K	YES	99	YES	NO	OK MDL, OK XRF-ICPMS inter-method	XRF	XRF
20	Ca	YES	94	YES	NO	OK with SF ICPMS	XRF	XRF
22	Ti	YES	52	YES	NO		XRF	XRF
23	V	YES	17	YES	YES		XRF or ICPMS	XRF, ICPMS
24	Cr	YES	19	YES	NO	Cr is "noise" above MDL in XRF - ICPMS intercomparison; Cr is known to be better extracted with HF (+microwave digestion?)	XRF	XRF
25	Mn	YES	16	YES	YES		XRF or ICPMS	XRF, ICPMS
26	Fe	YES	96	YES	NO	OK MDL, OK XRF-ICPMS inter-method	XRF	XRF, ICPMS
27	Co	NO	2	YES	YES		ICPMS	ICPMS
28	Ni	YES	16	YES	NO	Ni is known to be better extracted with HF (+ microwave digestion?)	XRF	XRF, ICPMS
29	Cu	YES	20	YES	YES		XRF or ICPMS	XRF, ICPMS
30	Zn	YES	45	YES	YES	OK MDL, OK XRF-ICPMS inter-method	XRF or ICPMS	XRF, ICPMS
33	As	NO	8	YES	YES		ICPMS	ICPMS
34	Se	NO	5	YES	YES		ICPMS	XRF, ICPMS
35	Br	YES	37	NO	not evaluated		XRF	XRF
37	Rb	NO	3	YES	NO		ICPMS	XRF
38	Sr	NO	9	YES	NO		ICPMS	XRF, ICPMS
40	Zr	NO	3	YES	not evaluated		ICPMS	
42	**Mo**							ICPMS
47	Ag	NO	1	YES	YES		ICPMS	ICPMS
48	Cd	NO	2	YES	YES		ICPMS	XRF, ICPMS
49	In	NO	4	NO	not evaluated		neither	
50	Sn	NO	2	YES	not evaluated		ICPMS	XRF, ICPMS
51	Sb	NO	3	YES	not evaluated		ICPMS	ICPMS
55	Cs	NO	3	YES	NO		ICPMS	XRF
56	Ba	NO	4	YES	not evaluated		ICPMS	XRF, ICPMS
58	Ce	NO	2	YES	NO		ICPMS	
81	**Tl**							ICPMS
82	Pb	YES	15	YES	YES	Pb is "noise" above MDL in XRF - ICPMS intercomparison	XRF or ICPMS	XRF, ICPMS

Appendix: All elements

Guide to the plots

In all plots, dashed line is 1:1
Solid lines are fits

- Were the measurements above the **UCD XRF MDL at least 10 %** of the time?
- Out of N=594, what % of were measurements above the stated **UCD XRF MDL**?
- Were the measurements above the **ICPMS MDL** at least 10 % of the time?
- Out of N=594, what % of were measurements above the stated **ICPMS MDL**?

- Did the element have an **acceptable recovery** based on the digestion of **SRM 1648a**?

- Which of the MDL for this element is lower, **UCD XRF MDL or ICPMS MDL?**

***Inter*-method:** XRF on y, ICPMS on x
or vice versa

***Intra*-method:** XRF on both y and x
or ICPMS on both y and x

Excludes S, Si, Br, Cl

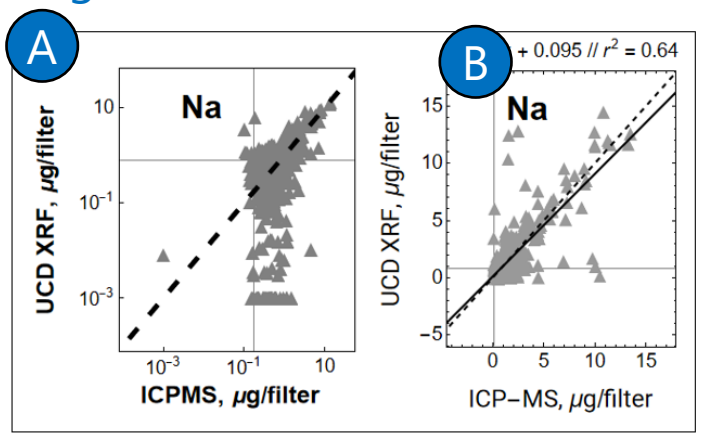
Inter-method comparison (N=594*)

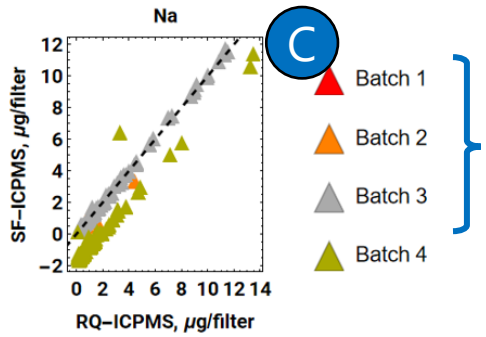
log scale linear scale

SF-RQ ICPMS comparison (N=94)

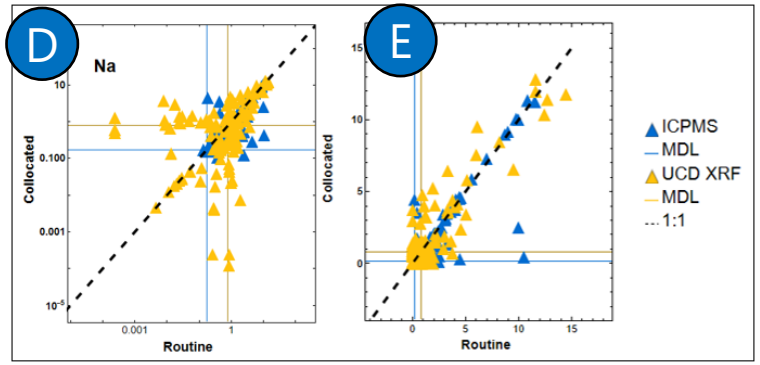
Na

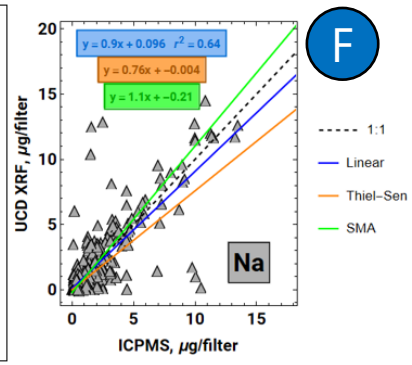
XRF > 10% MDL	YES
% above MDL	43%
RQ ICPMS >10% MDL	YES
% above MDL	96%
RQ ICPMS 1648a recovery acceptable? (5% HNO3 + 2 hour hot block digestion)	NO
Which MDL is lower	ICPMS





Batches based on when sent to RTI





log scale linear scale

Collocated, intra-method (N= 248*)

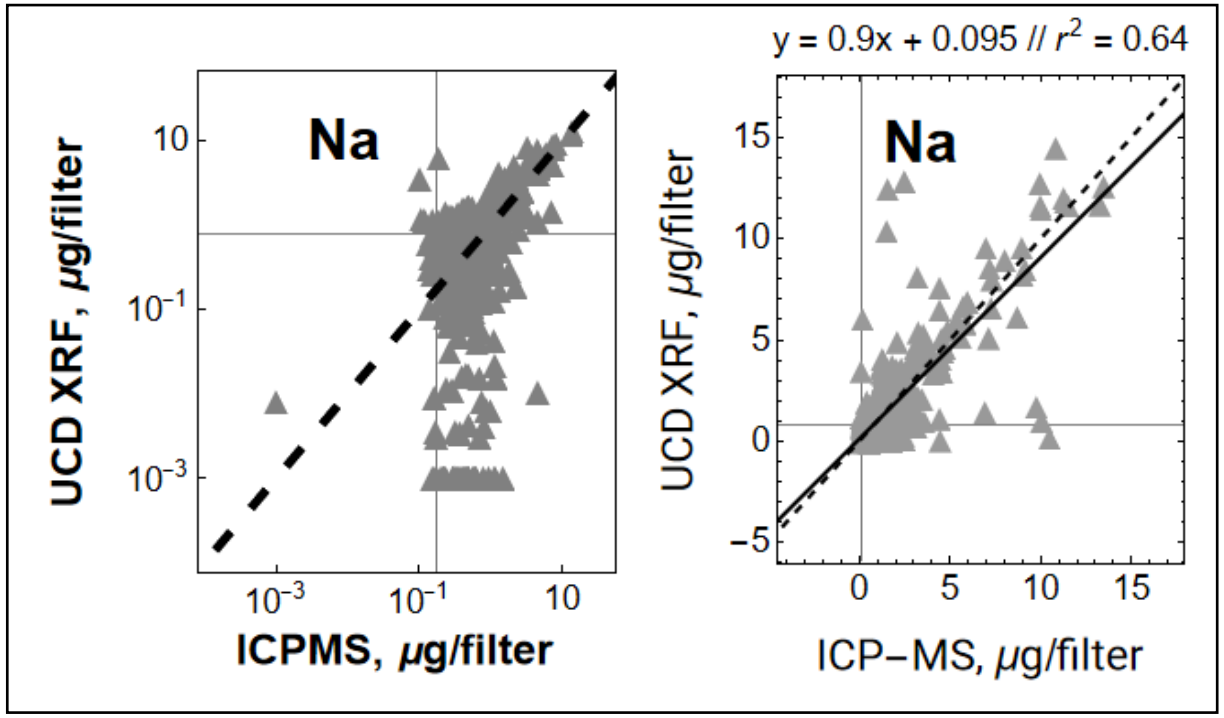
Various fits for inter-method comparison (N= 594*)

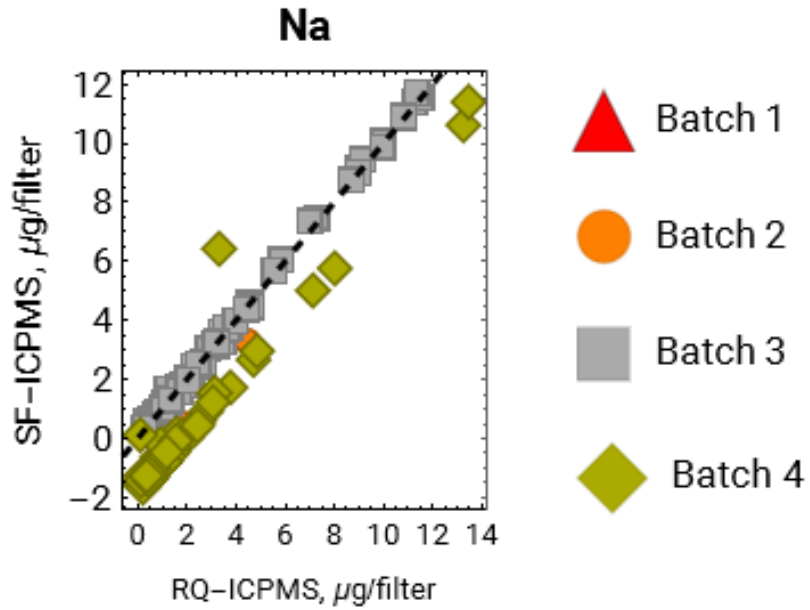
A more detailed version of plot B

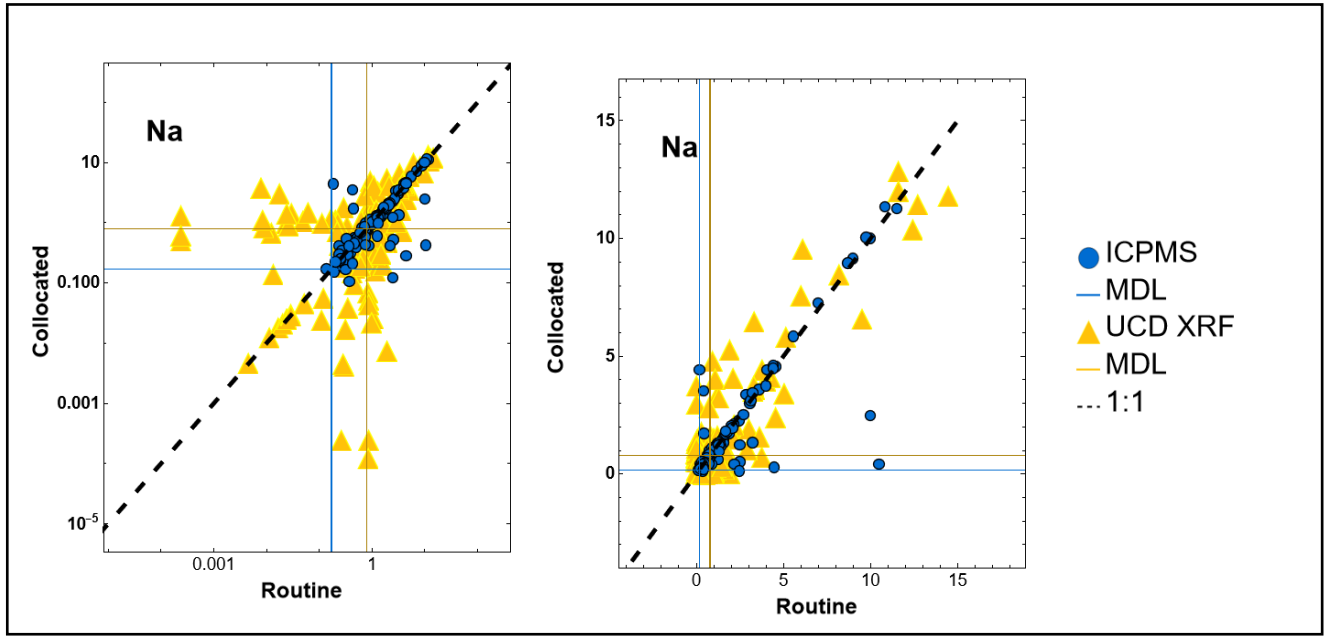
* N will be less for log scale plots, as they don't show negative or zero values

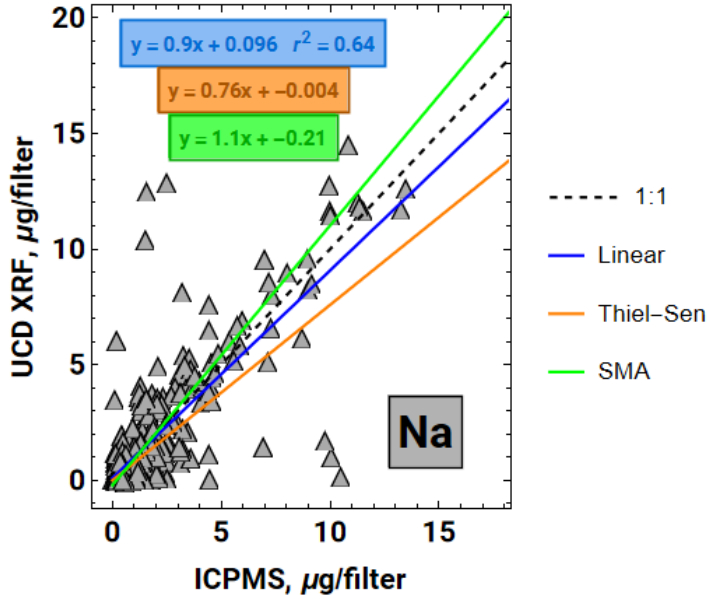
Na

XRF > 10% MDL	YES
% above MDL	43%
RQ ICPMS >10% MDL	YES
% above MDL	96%
RQ ICPMS 1648a recovery acceptable? (5% HNO3 + 2 hour hot block digestion)	NO
Which MDL is lower	ICPMS



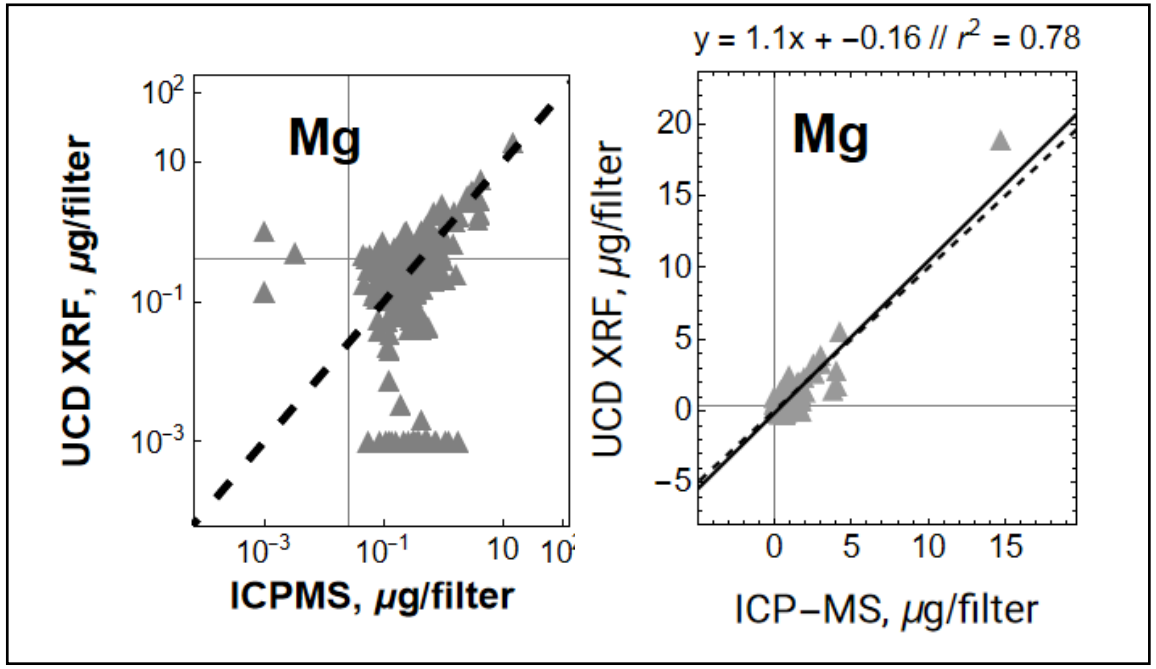


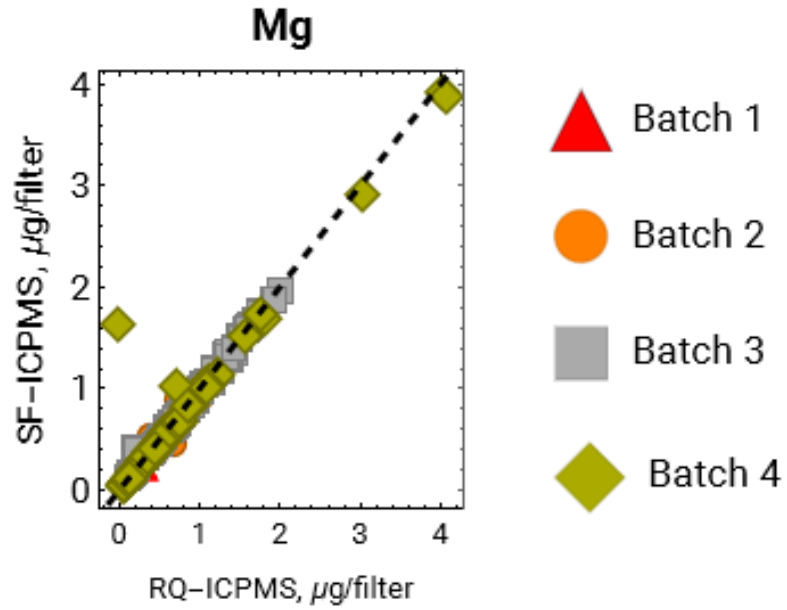


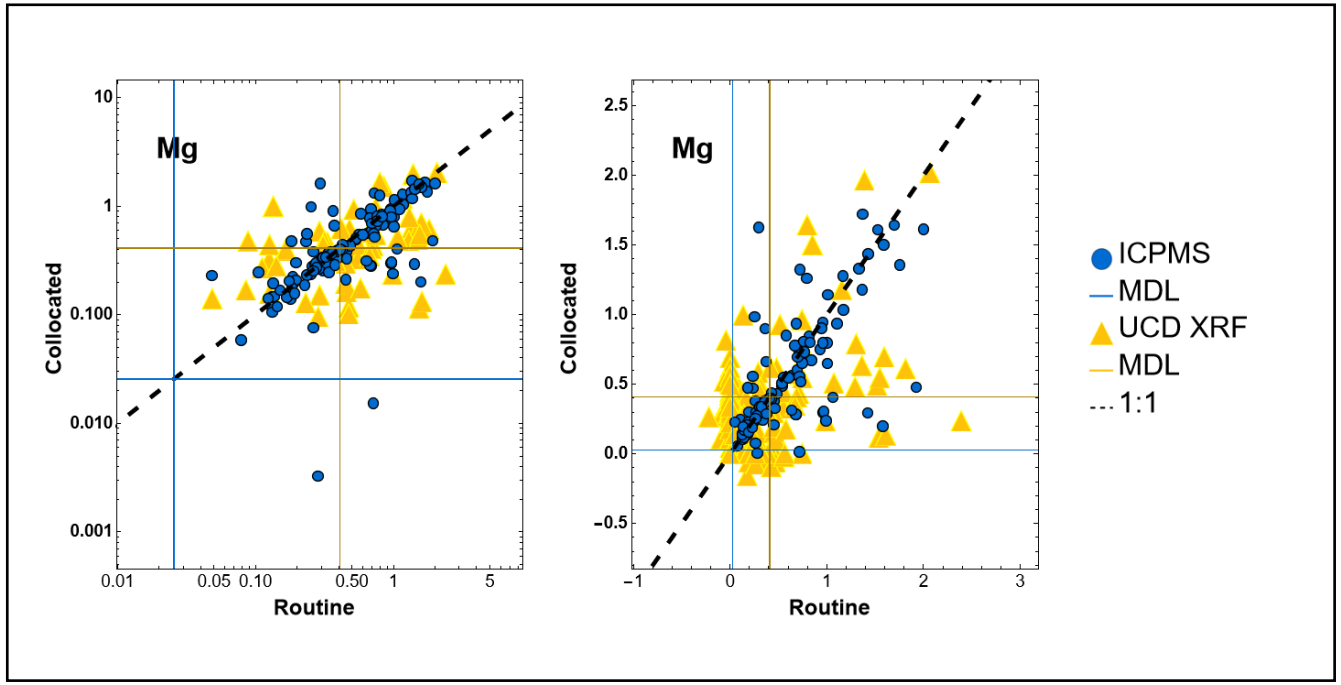


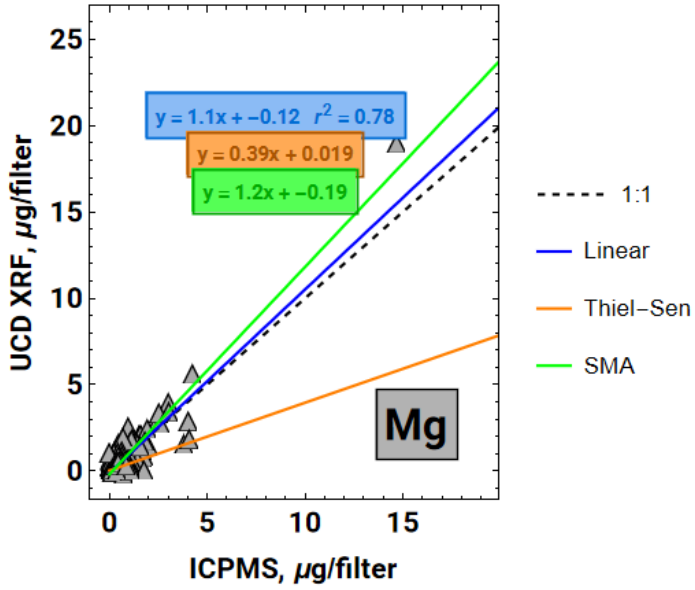
Mg

XRF > 10% MDL	YES
% above MDL	28%
RQ ICPMS >10% MDL	YES
% above MDL	99%
RQ ICPMS 1648a recovery acceptable? (5% HNO3 + 2 hour hot block digestion)	YES (1 out of 3 trials)
Which MDL is lower	ICPMS



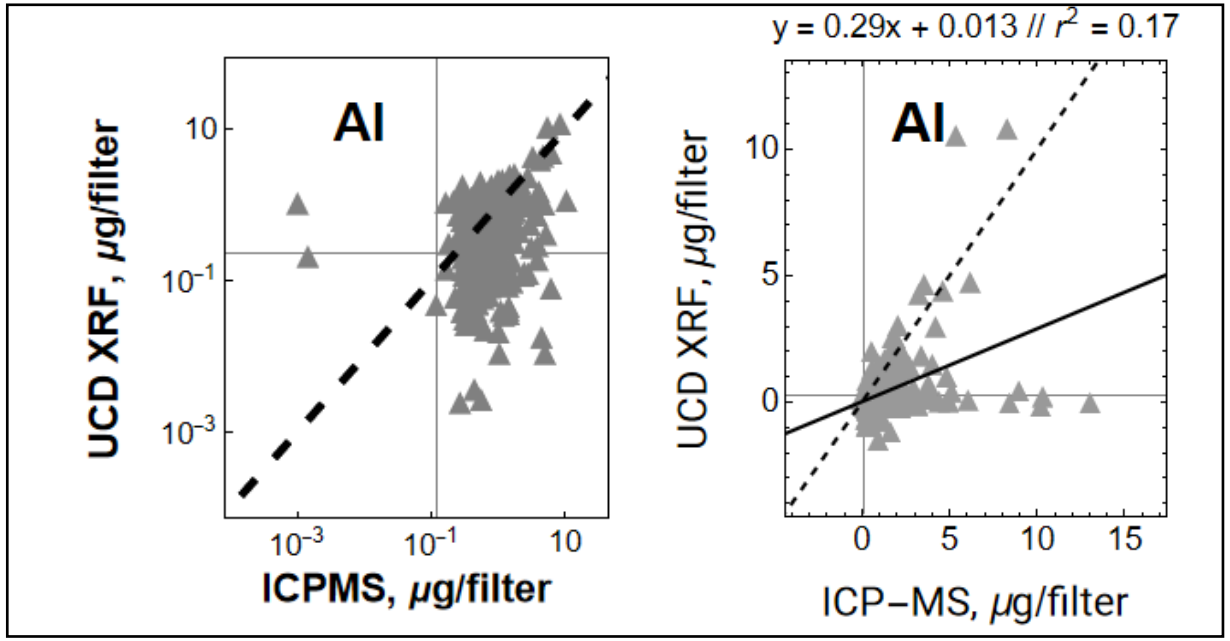


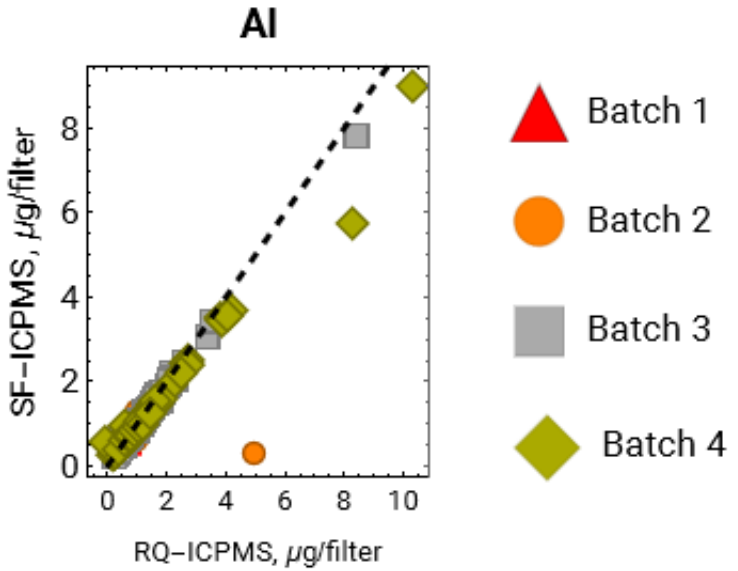


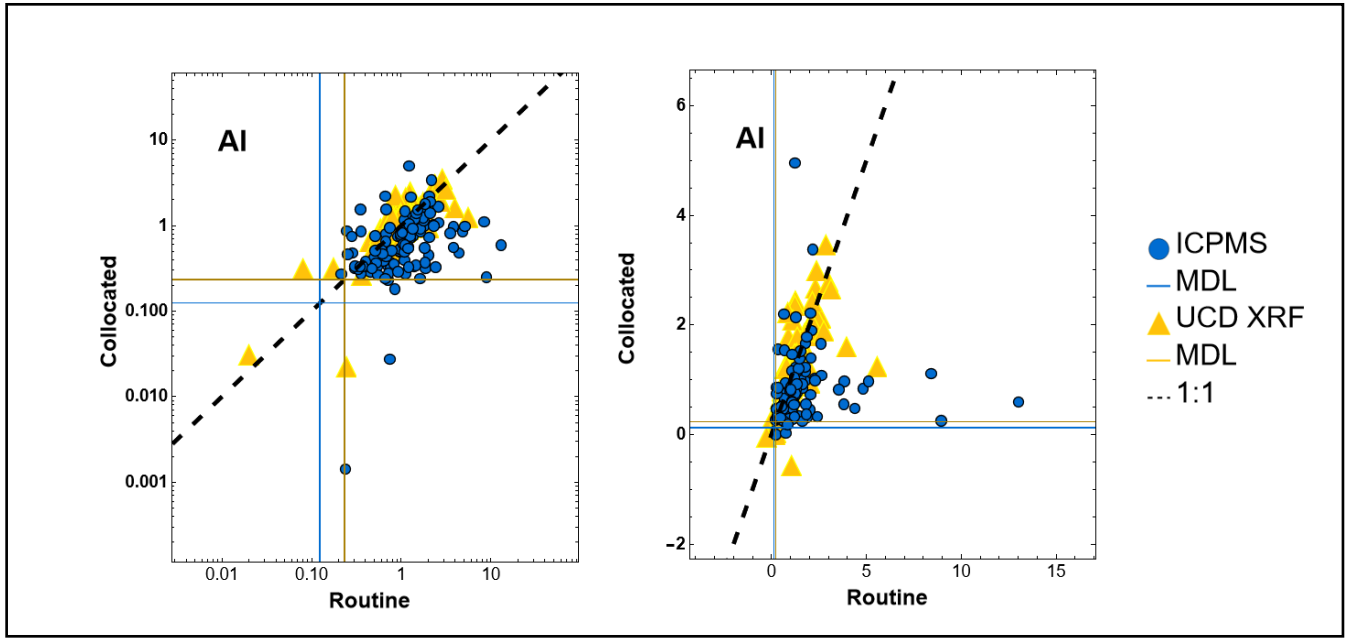


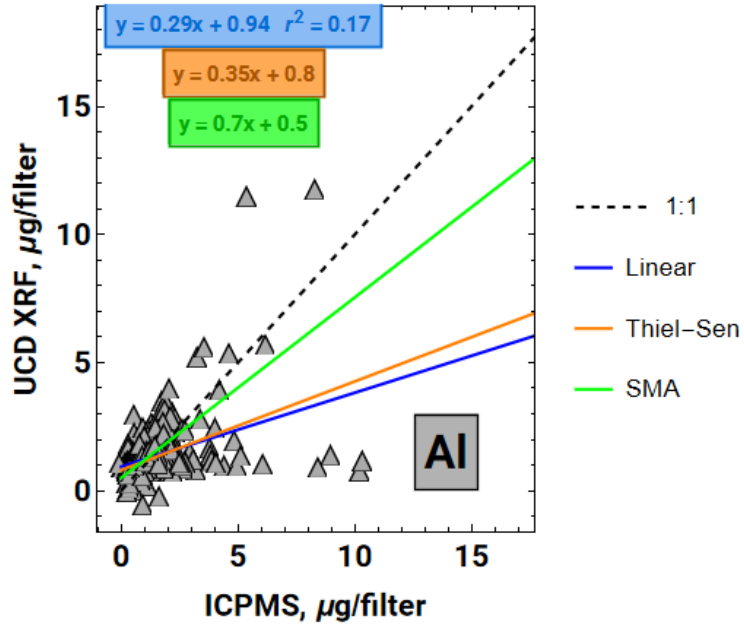
Al

XRF > 10% MDL	YES
% above MDL	42%
RQ ICPMS > 10% MDL	YES
% above MDL	99%
RQ ICPMS 1648a recovery acceptable ? (5% HNO3 + 2 hour hot block digestion)	NO
Which MDL is lower	ICPMS



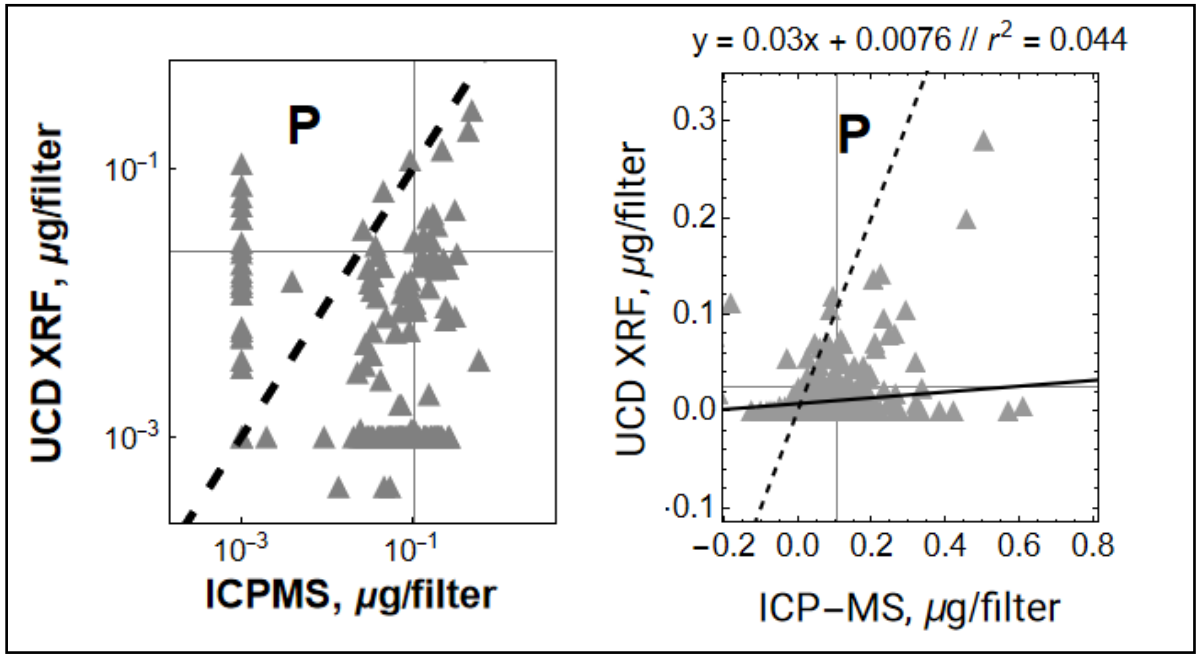


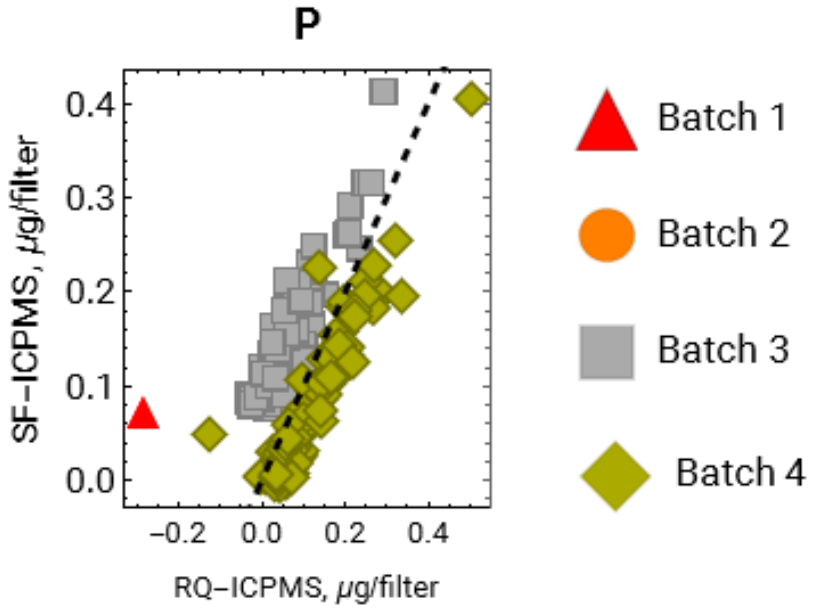


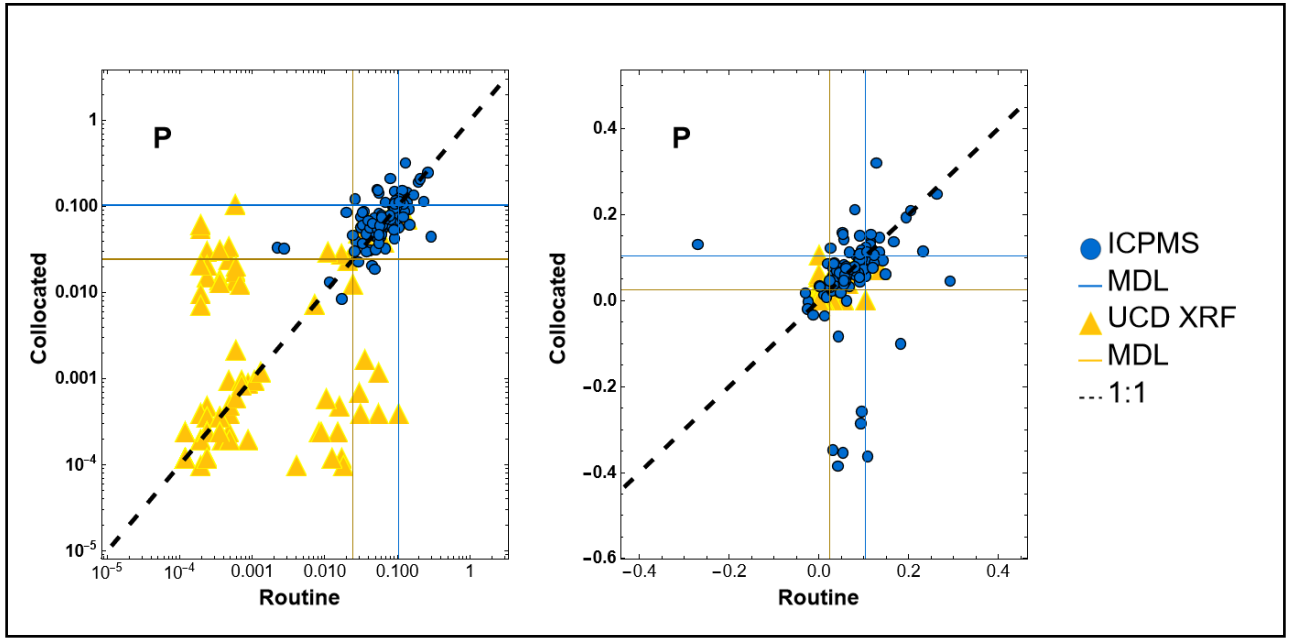


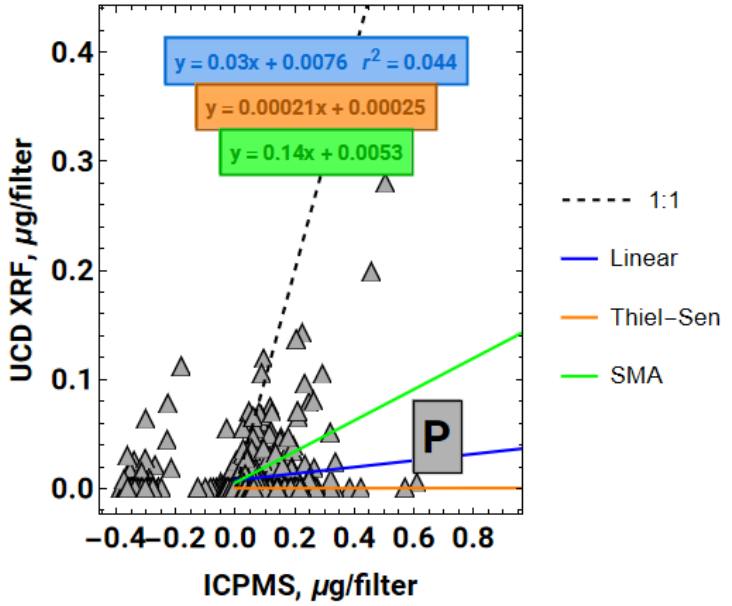
P

XRF > 10% MDL	NO
% above MDL	9.8%
RQ ICPMS > 10% MDL	YES
% above MDL	22%
RQ ICPMS 1648a recovery acceptable ? (5% HNO3 + 2 hour hot block digestion)	Not evaluated
Which MDL is lower	UCD XRF



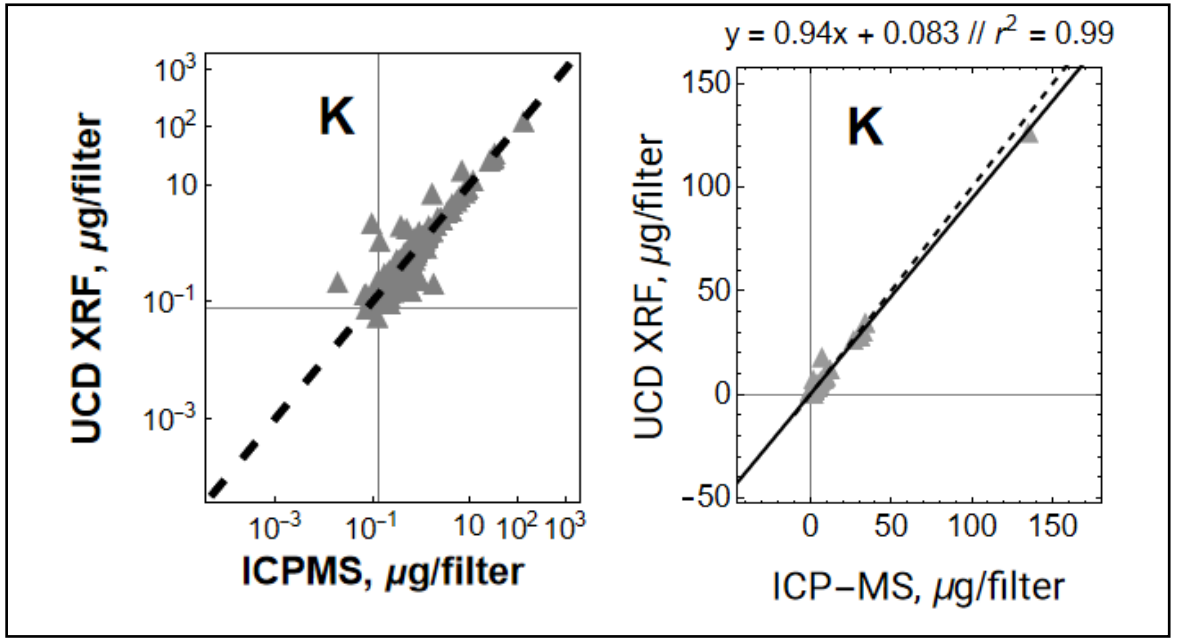


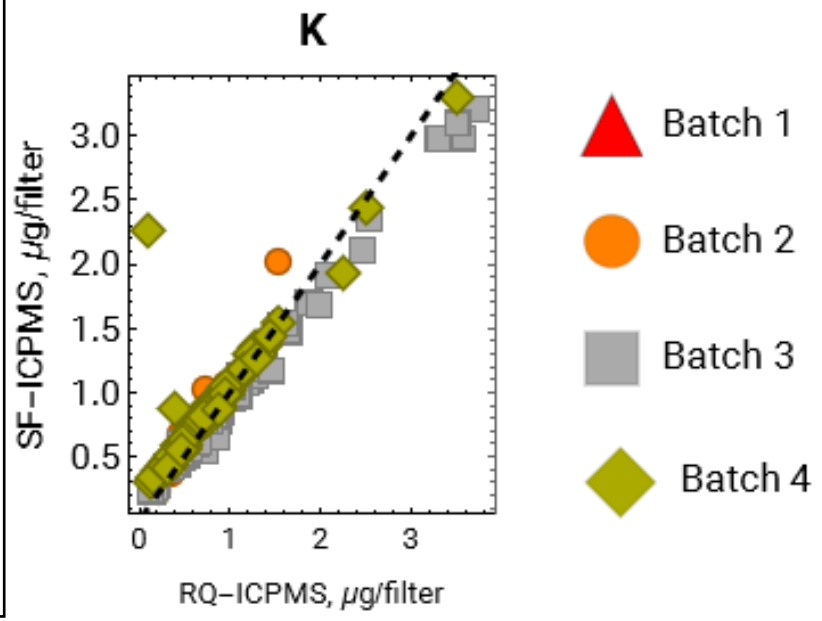


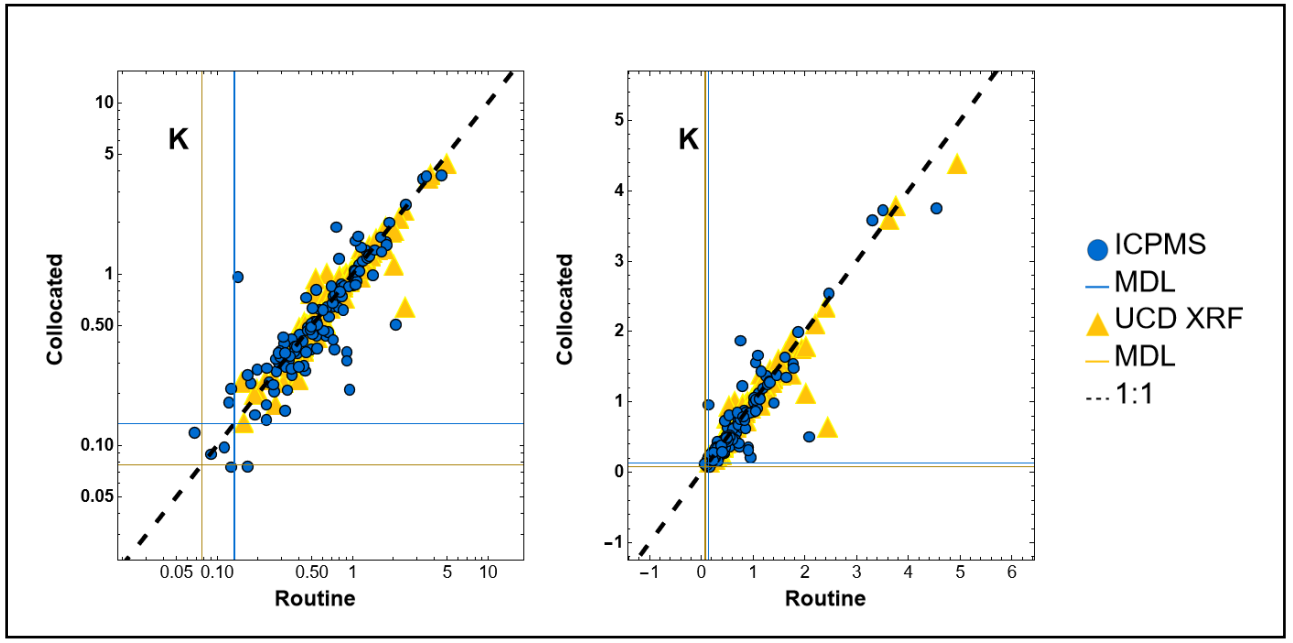


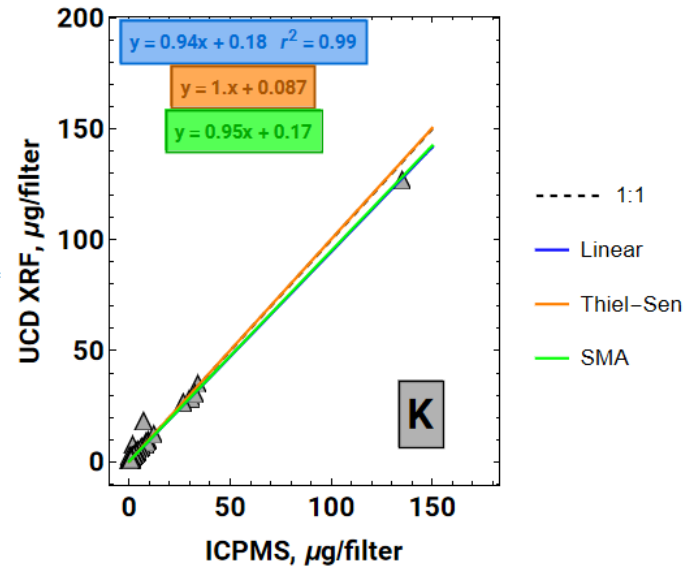
K

XRF > 10% MDL	YES
% above MDL	99%
RQ ICPMS >10% MDL	YES
% above MDL	97%
RQ ICPMS 1648a recovery acceptable ? (5% HNO3 + 2 hour hot block digestion)	NO
Which MDL is lower	UCD XRF
Other notes	•OK MDL •OK XRF-ICPMS inter-method



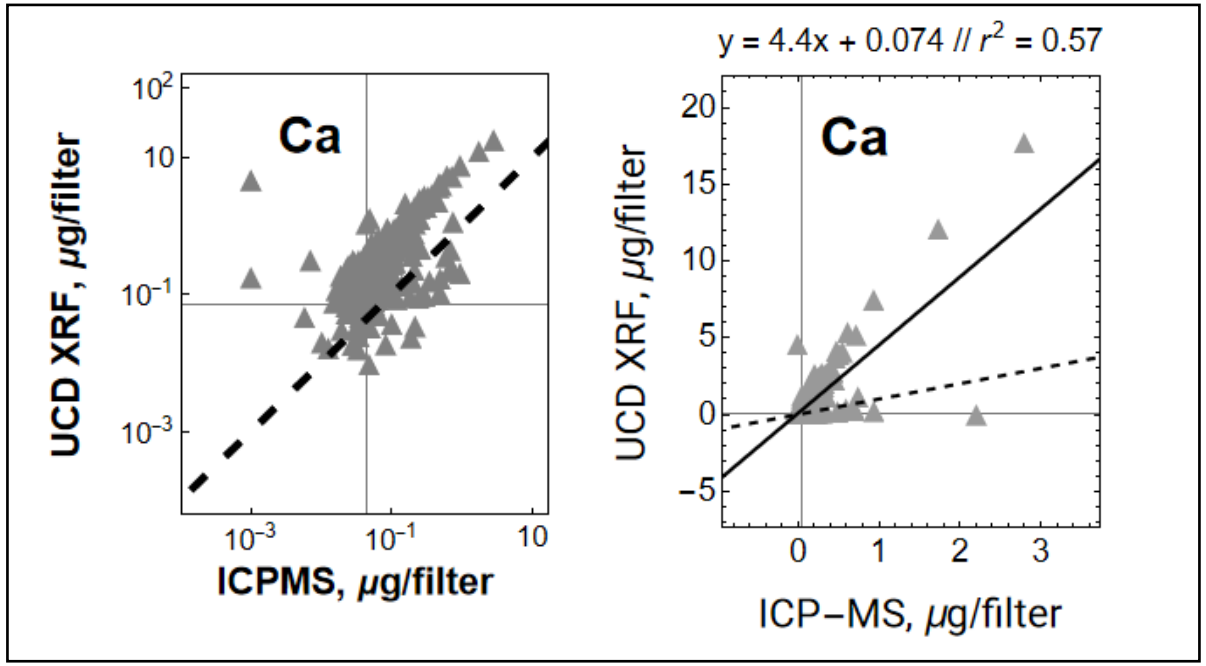


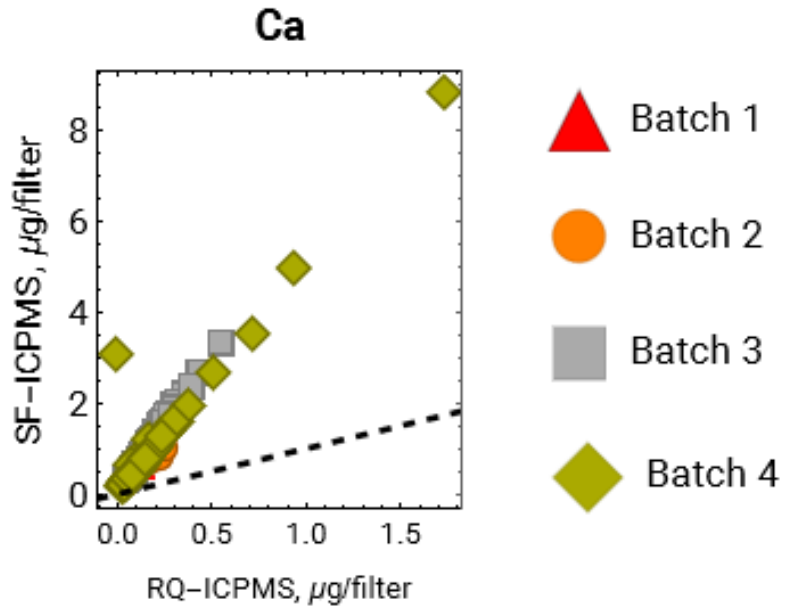


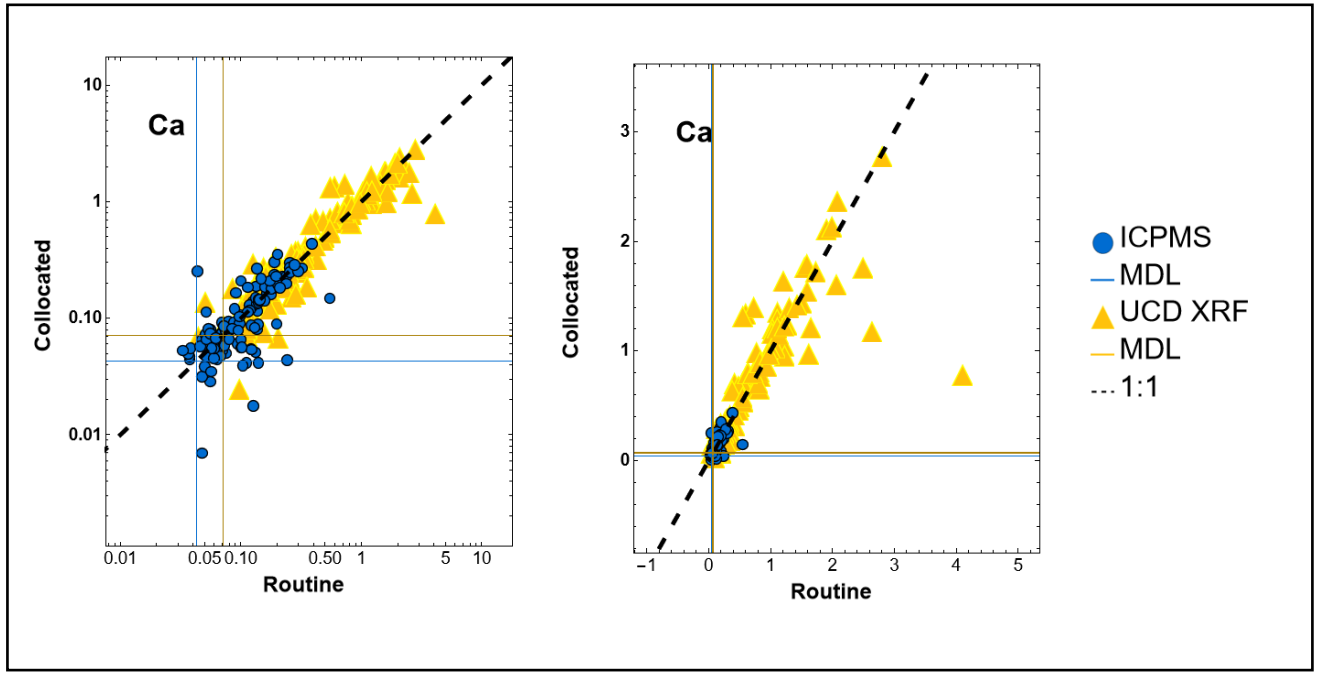


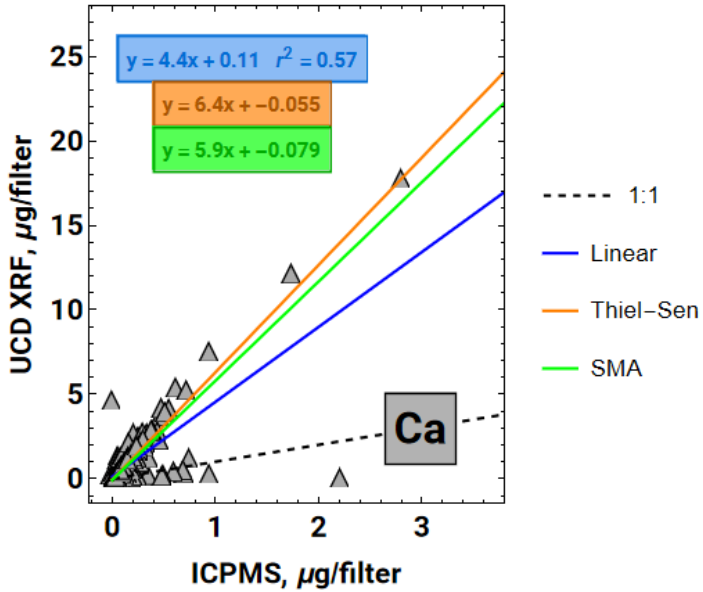
Ca

XRF > 10% MDL	YES
% above MDL	94%
RQ ICPMS >10% MDL	YES
% above MDL	88%
RQ ICPMS 1648a recovery acceptable? (5% HNO3 + 2 hour hot block digestion)	NO
Which MDL is lower	ICPMS
Other notes	OK with SF ICPMS



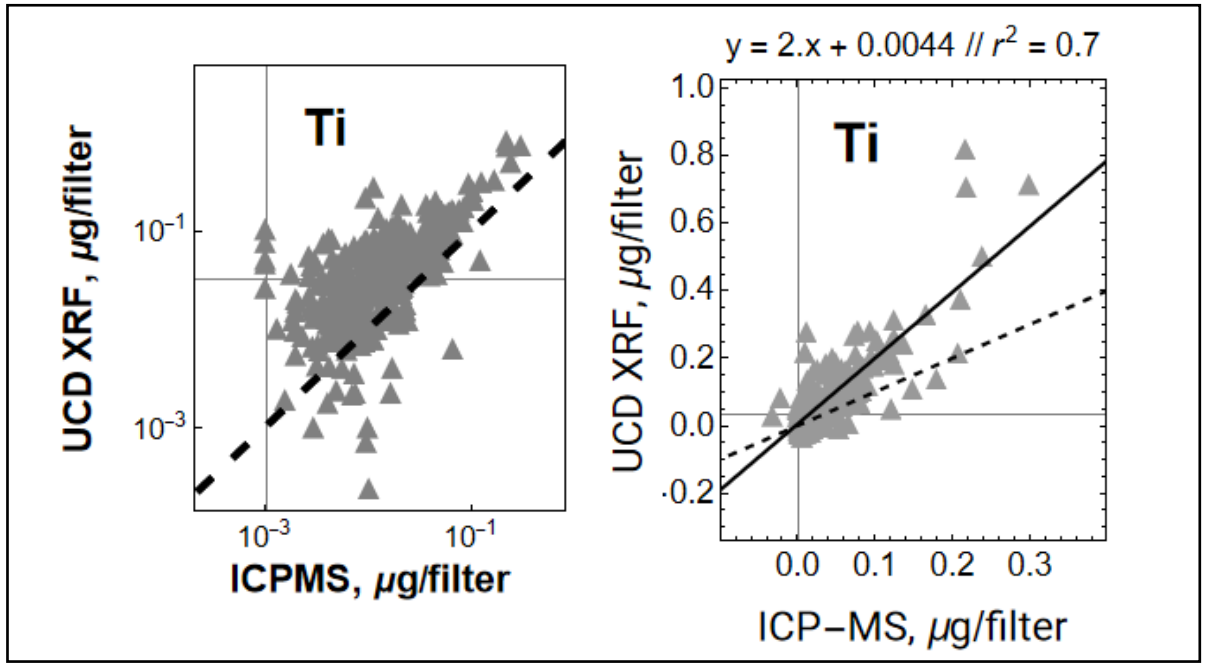


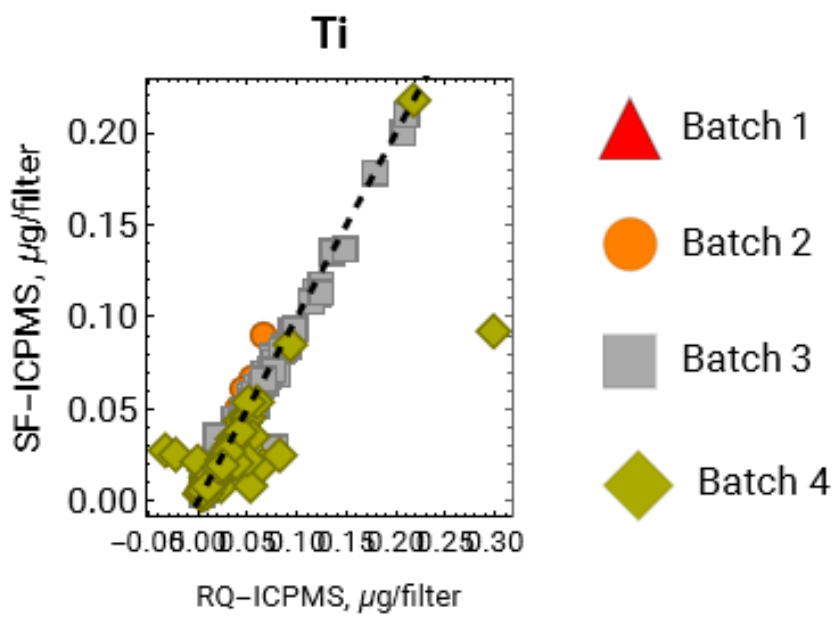


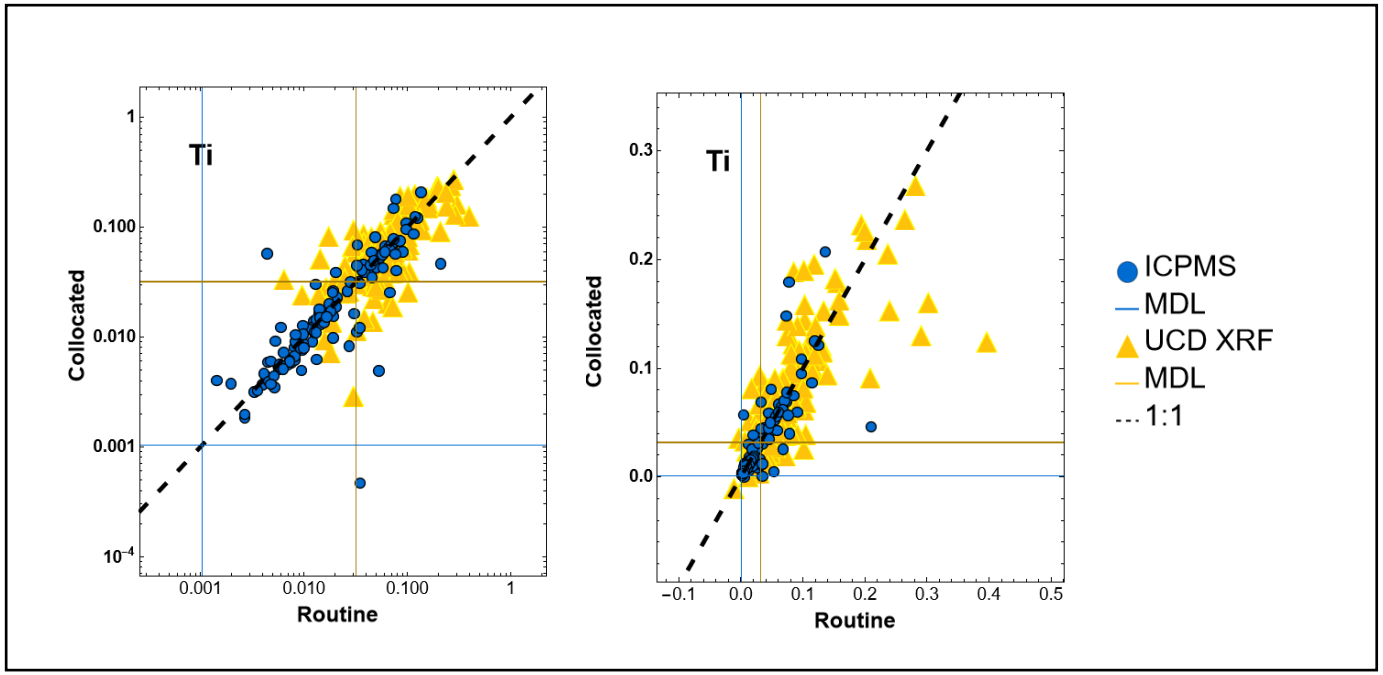


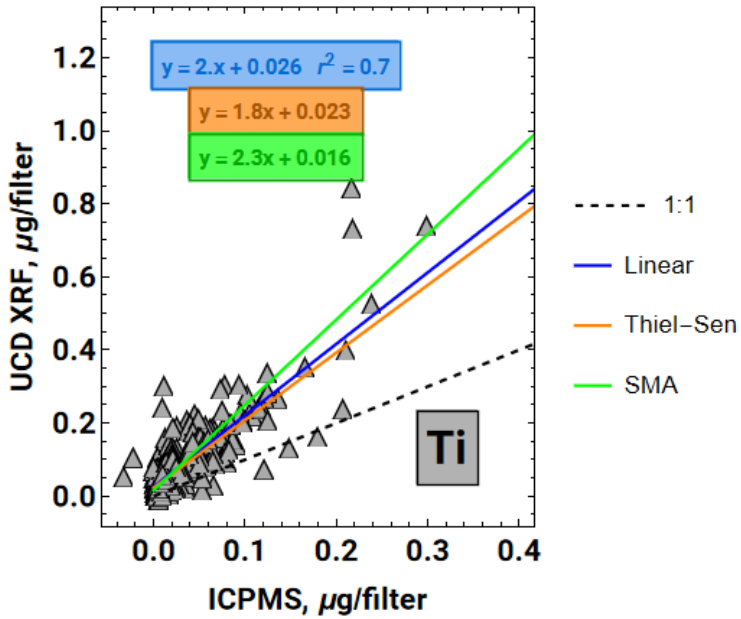
Ti

XRF > 10% MDL	YES
% above MDL	52%
RQ ICPMS > 10% MDL	YES
% above MDL	99%
RQ ICPMS 1648a recovery acceptable? (5% HNO3 + 2 hour hot block digestion)	NO
Which MDL is lower	ICPMS



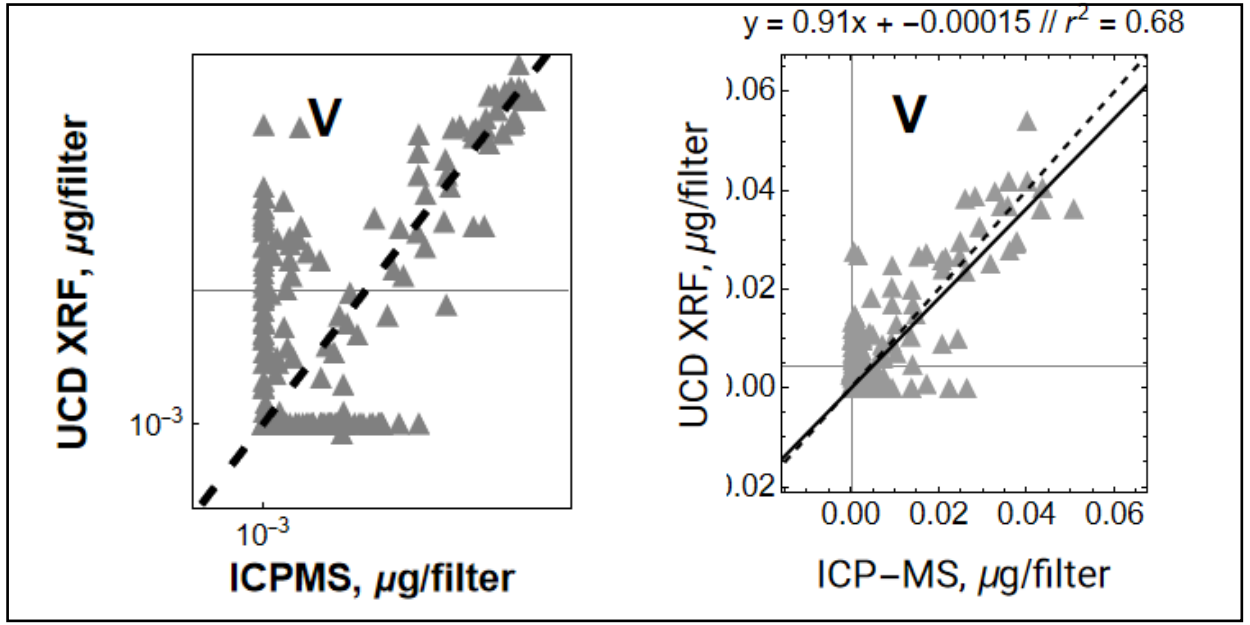


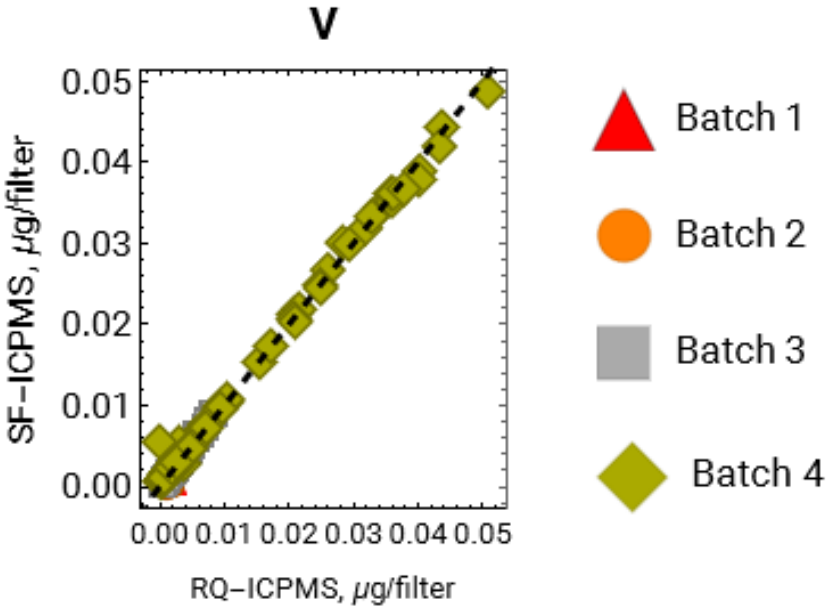


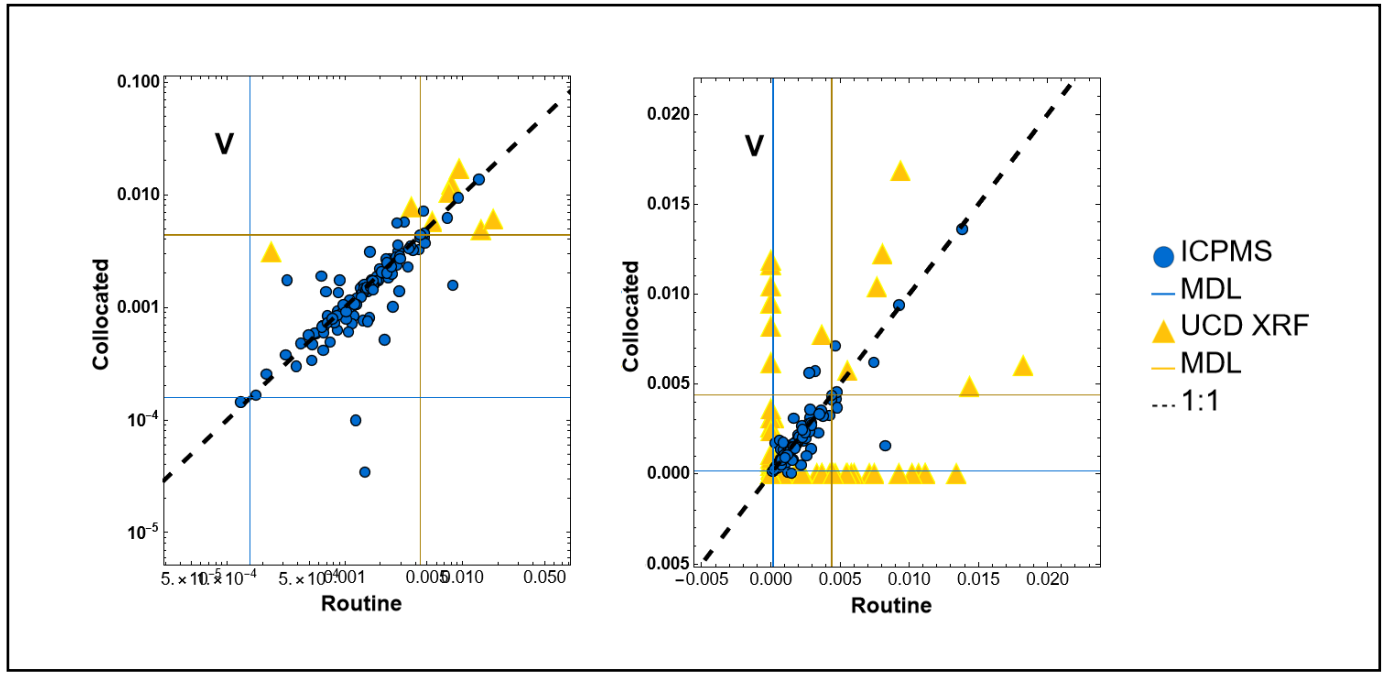


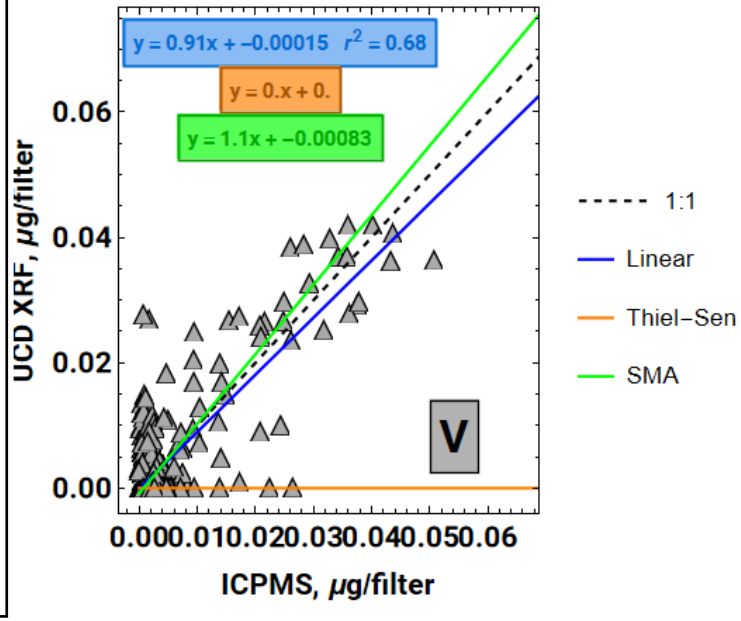
V

XRF > 10% MDL	YES
% above MDL	17%
RQ ICPMS >10% MDL	YES
% above MDL	99%
RQ ICPMS 1648a recovery acceptable? (5% HNO3 + 2 hour hot block digestion)	YES
Which MDL is lower	ICPMS



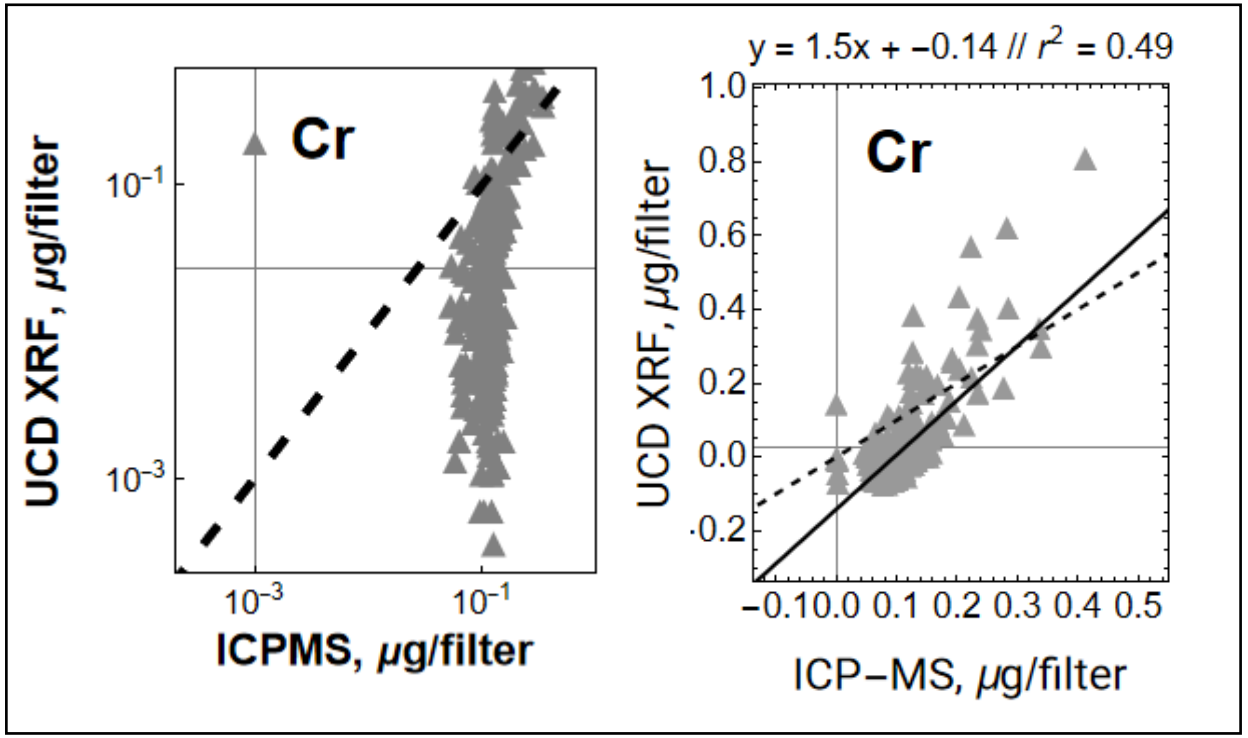


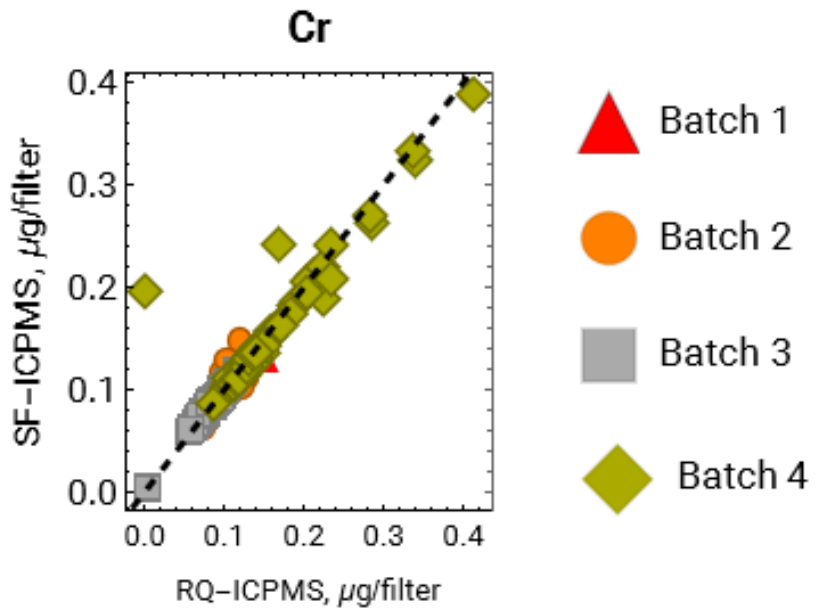


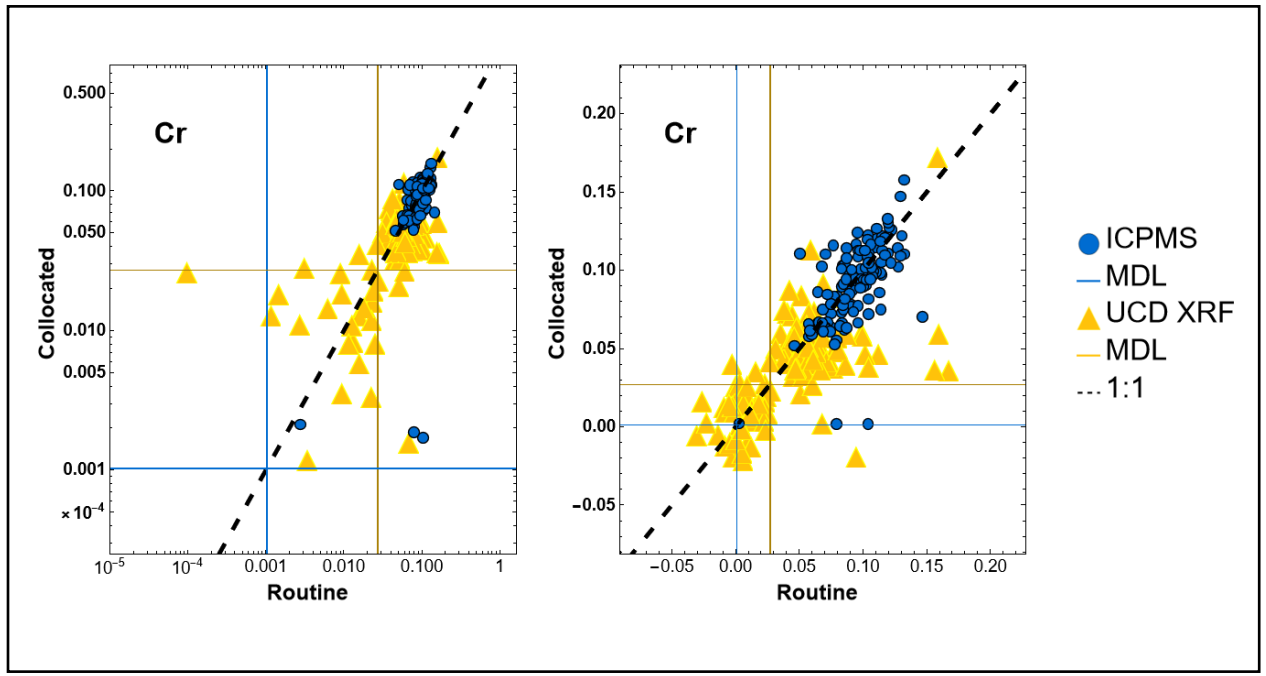


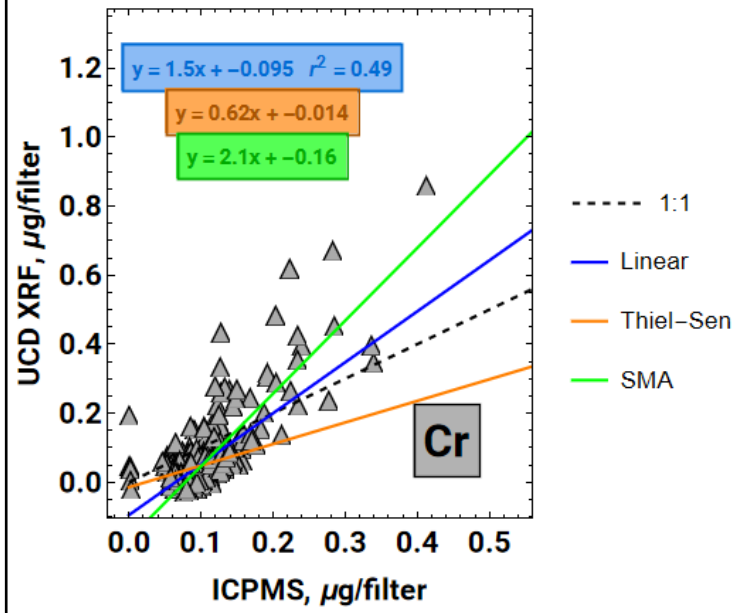
Cr

XRF > 10% MDL	YES
% above MDL	19%
RQ ICPMS >10% MDL	YES
% above MDL	100%
RQ ICPMS 1648a recovery acceptable? (5% HNO3 + 2 hour hot block digestion)	NO
Which MDL is lower	ICPMS
Other notes	• Cr is "noise" above MDL in XRF - ICPMS intercomparison • Cr is known to be better extracted with HF (+microwave digestion?)



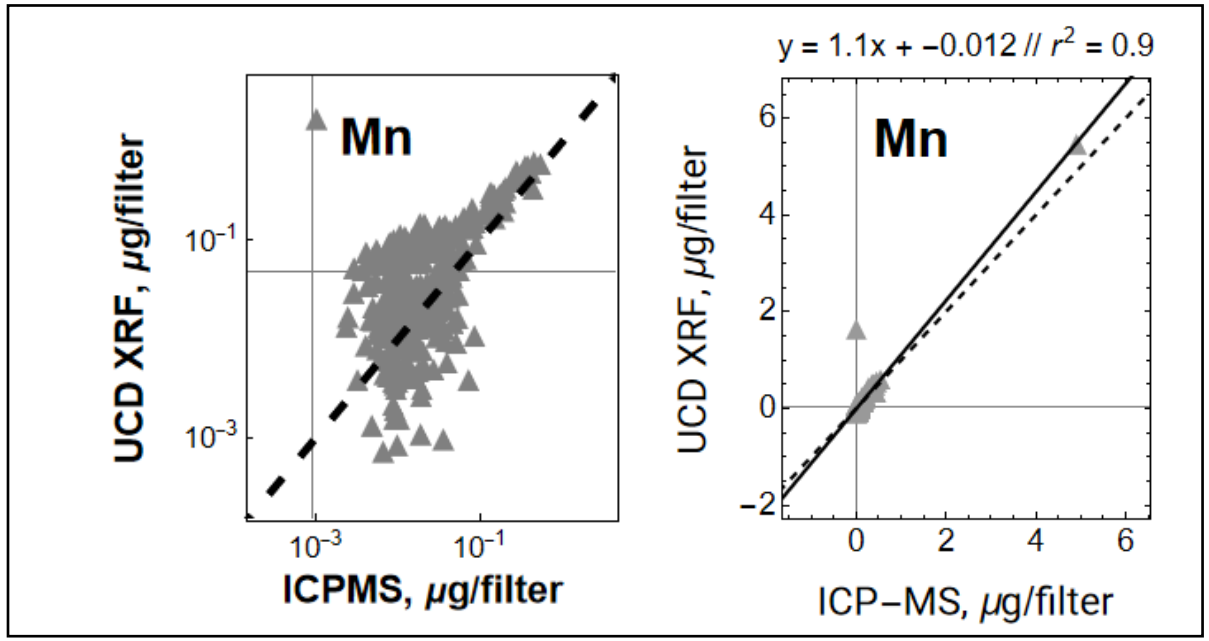


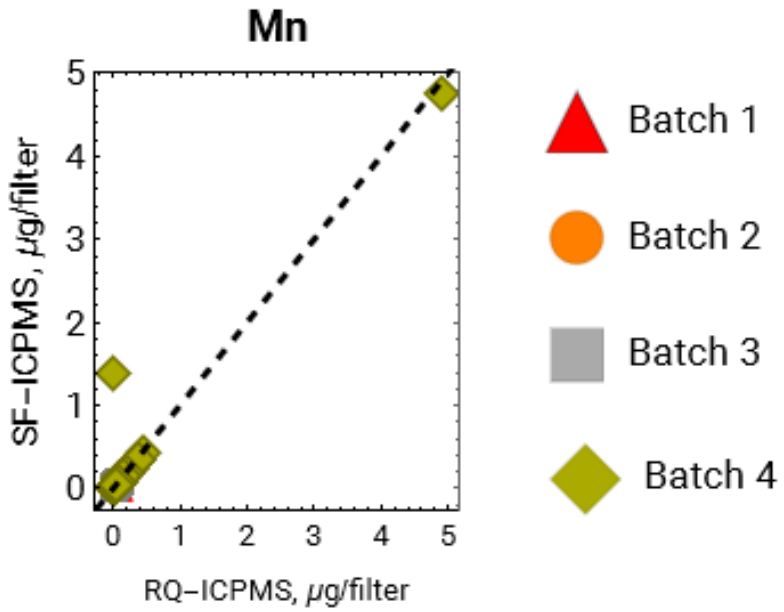


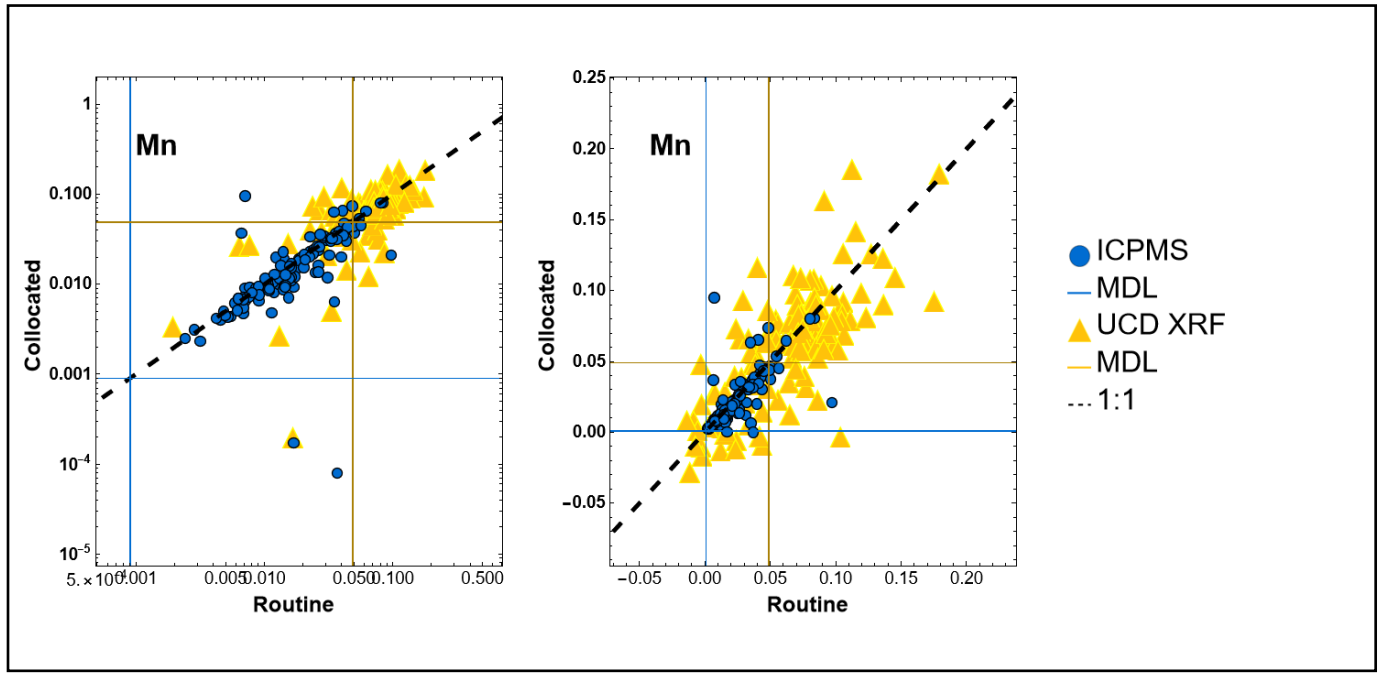


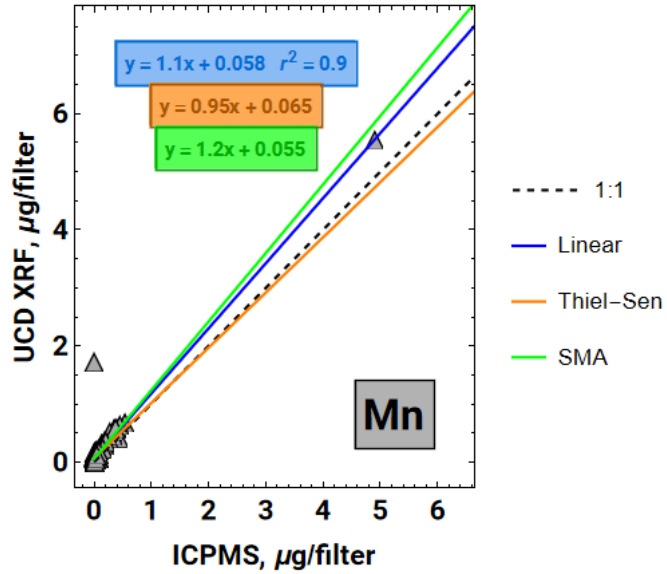
Mn

XRF > 10% MDL	YES
% above MDL	16%
RQ ICPMS >10% MDL	YES
% above MDL	99%
RQ ICPMS 1648a recovery acceptable? (5% HNO3 + 2 hour hot block digestion)	YES
Which MDL is lower	ICPMS



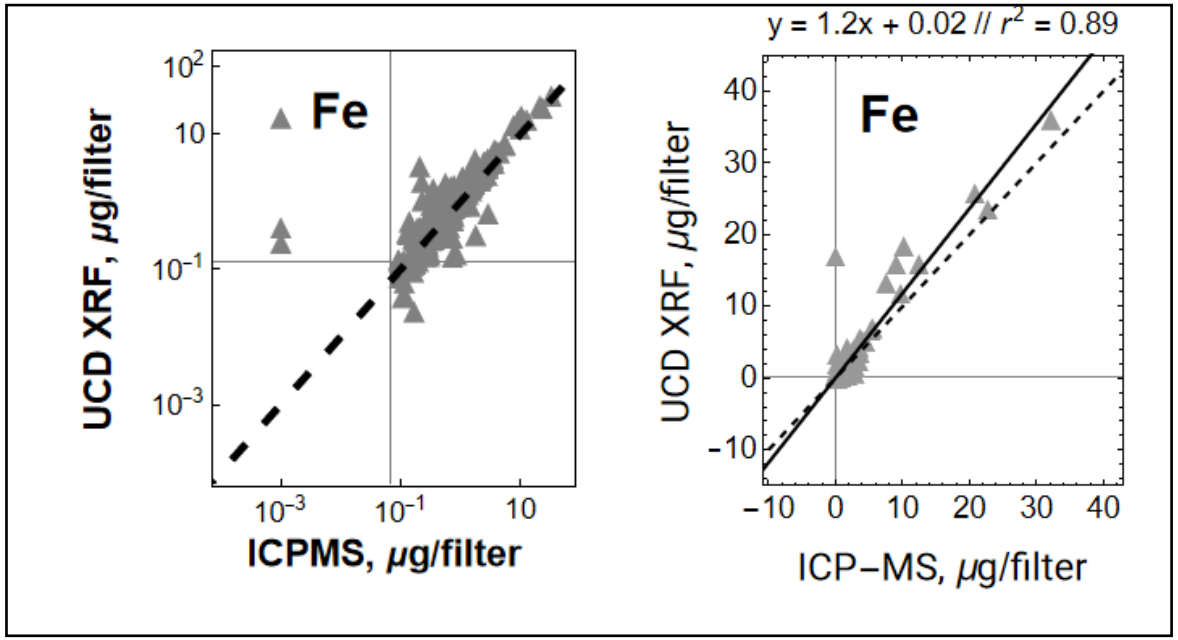


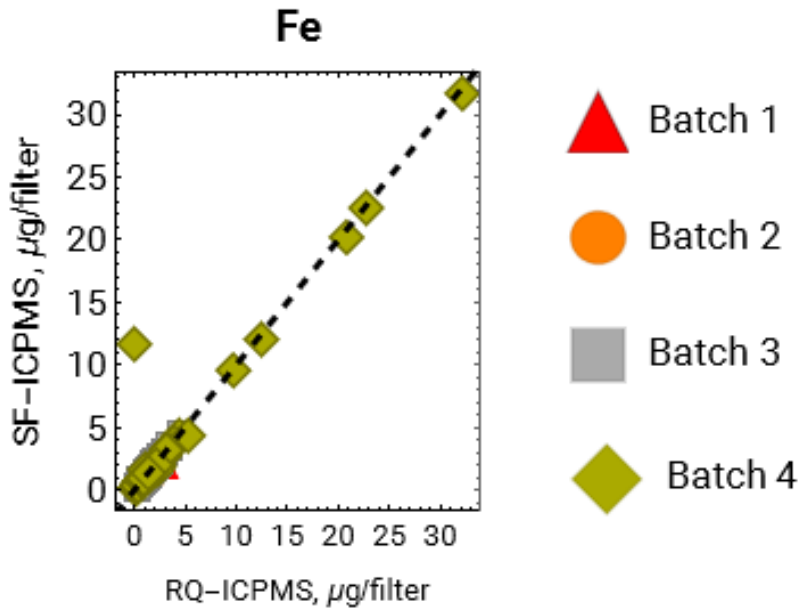


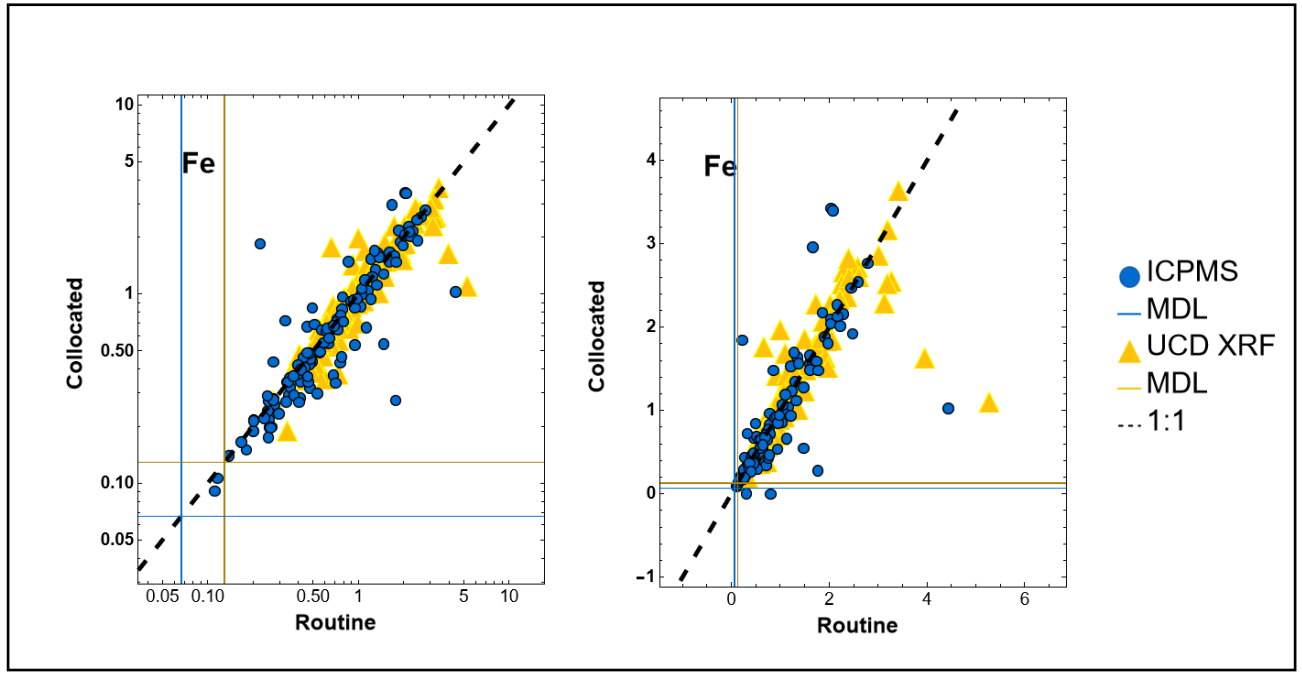


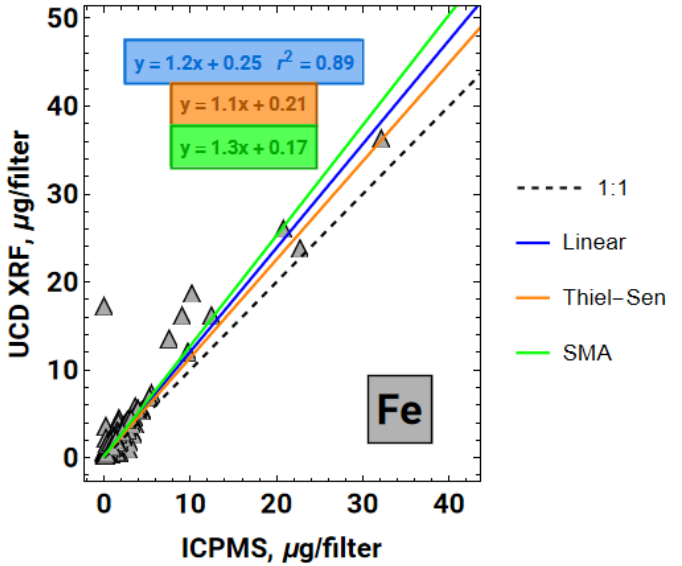
Fe

XRF > 10% MDL	YES
% above MDL	96%
RQ ICPMS > 10% MDL	YES
% above MDL	99%
RQ ICPMS 1648a recovery acceptable? (5% HNO3 + 2 hour hot block digestion)	NO
Which MDL is lower	ICPMS
Other notes	• OK MDL • OK XRF-ICPMS inter-method



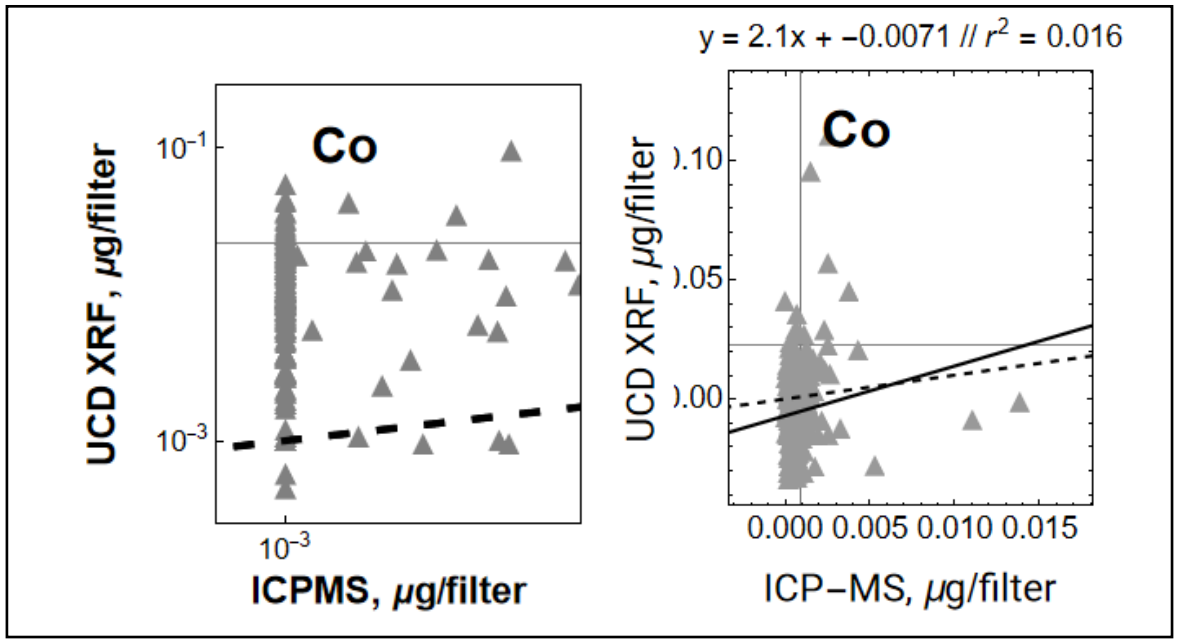


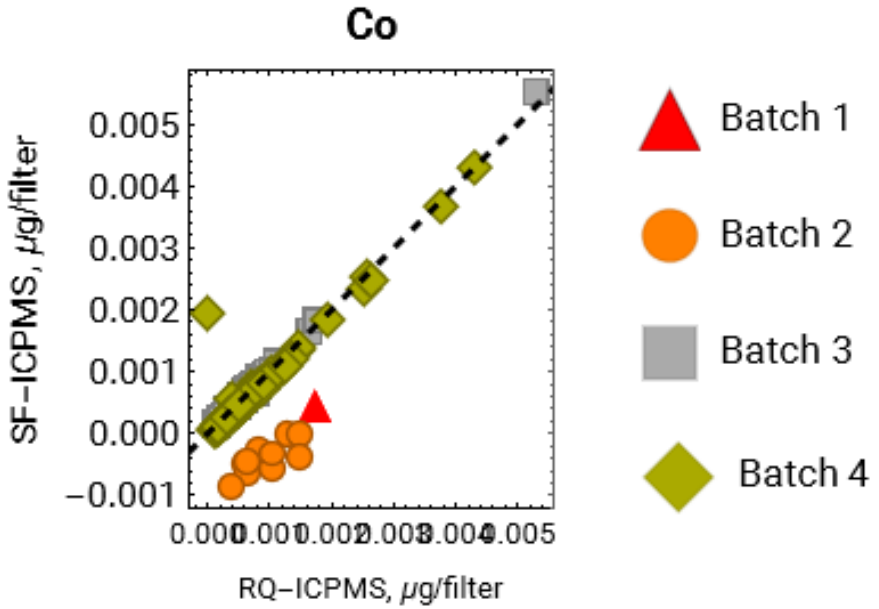


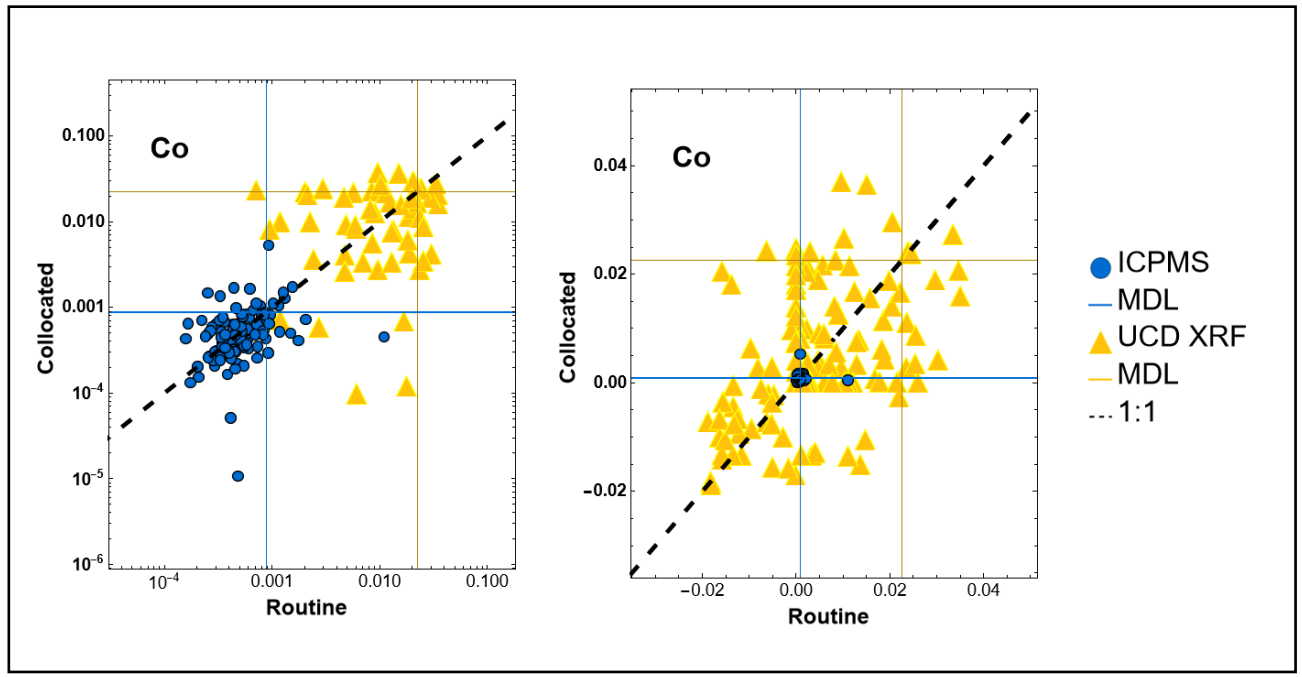


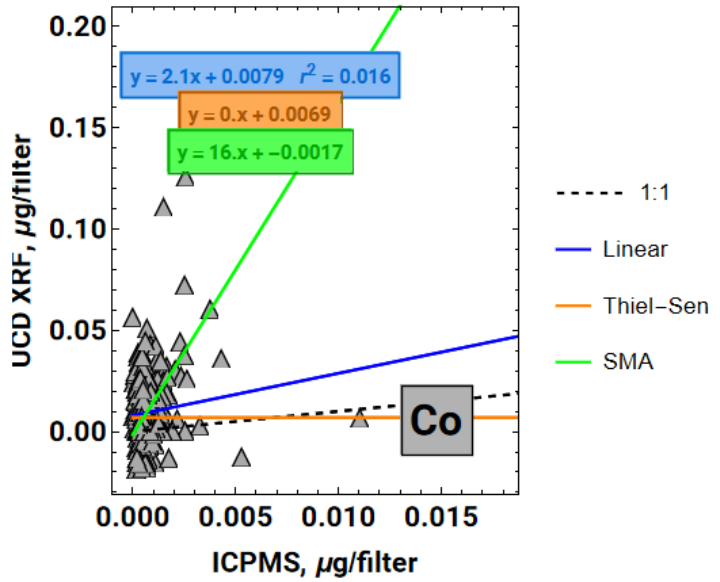
Co

XRF > 10% MDL	NO
% above MDL	2%
RQ ICPMS > 10% MDL	YES
% above MDL	15%
RQ ICPMS 1648a recovery acceptable? (5% HNO3 + 2 hour hot block digestion)	YES
Which MDL is lower	ICPMS



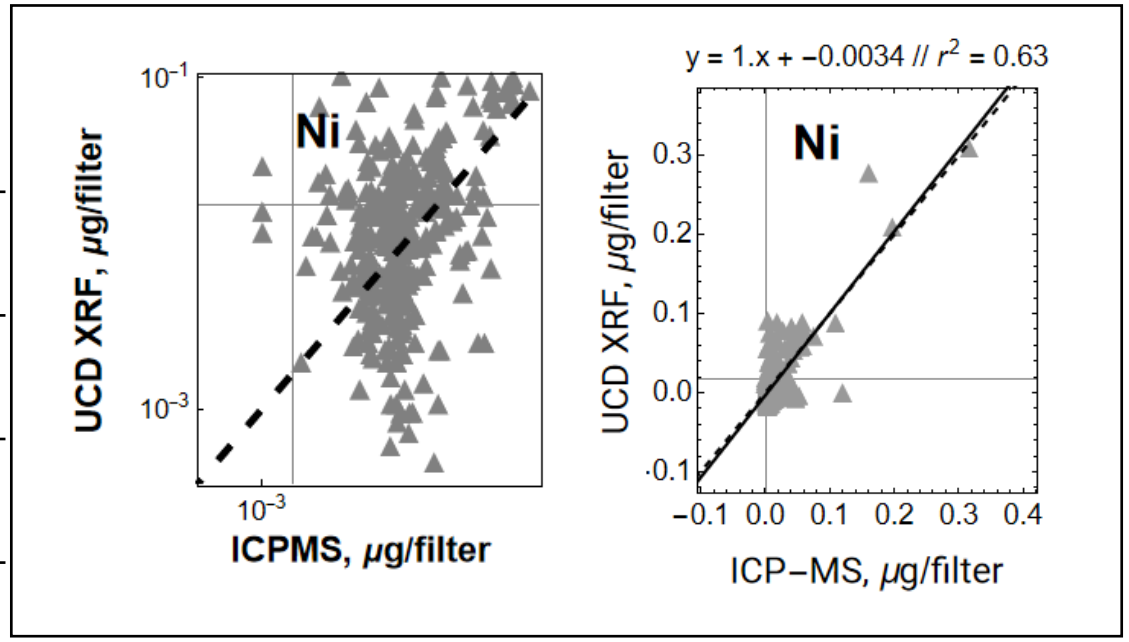


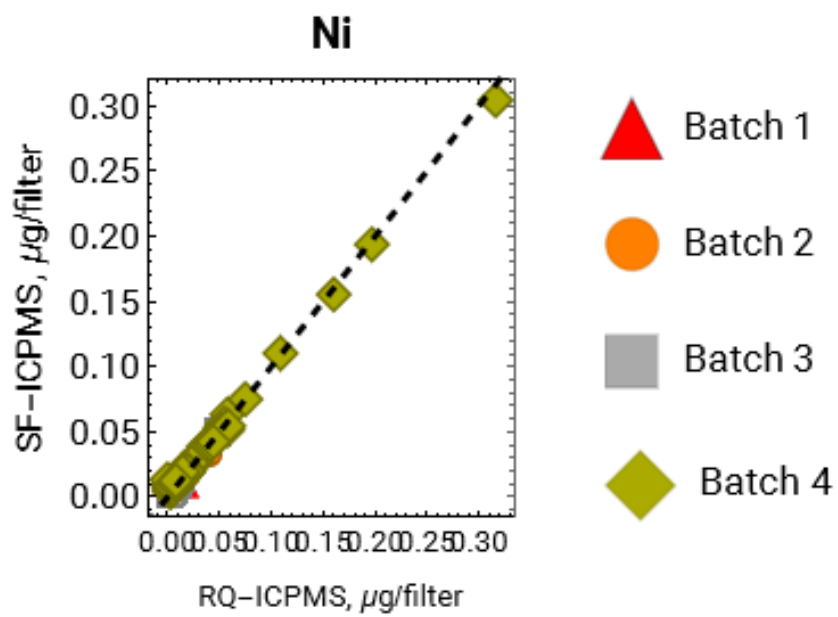


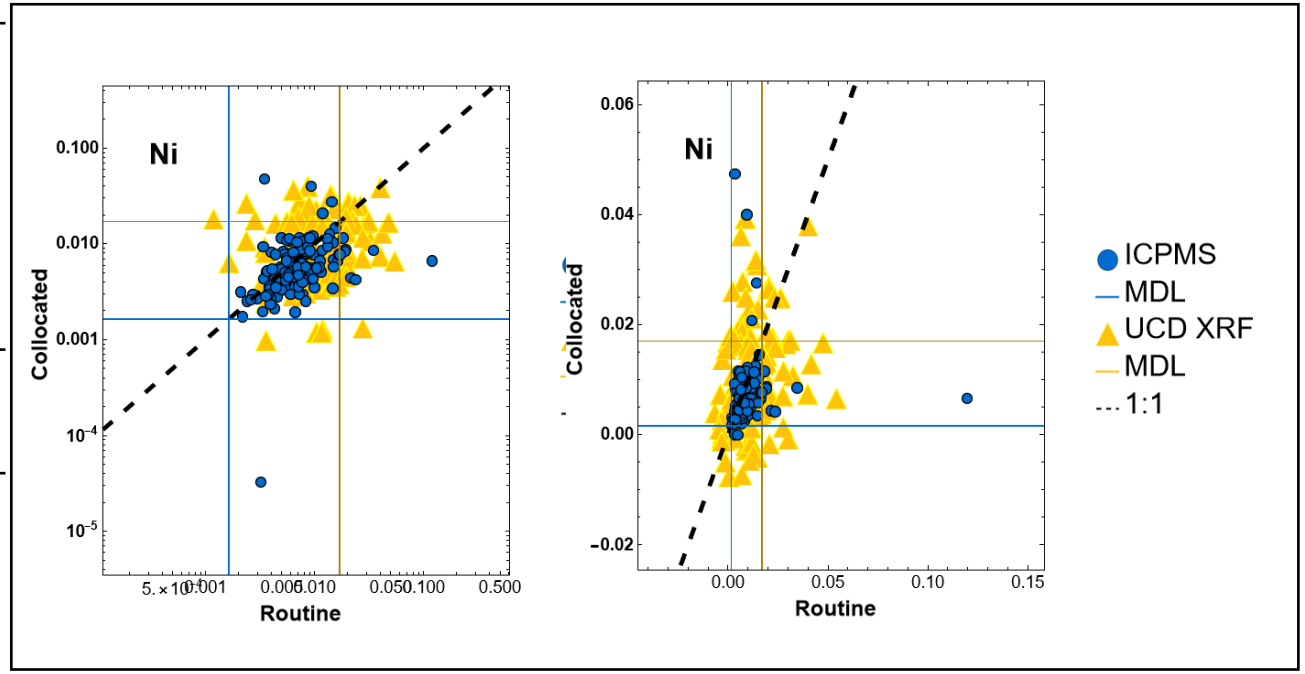


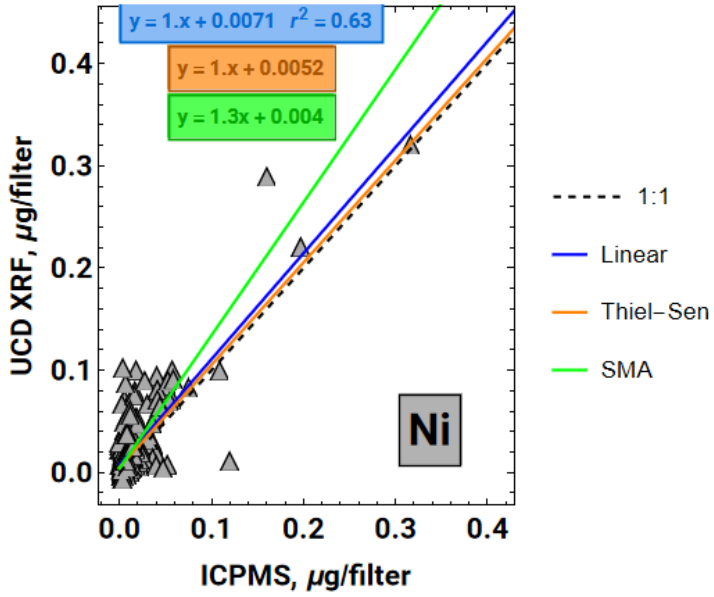
Ni

XRF > 10% MDL	YES
% above MDL	16%
RQ ICPMS > 10% MDL	YES
% above MDL	99%
RQ ICPMS 1648a recovery acceptable? (5% HNO3 + 2 hour hot block digestion)	NO
Which MDL is lower	ICPMS
Other Notes	Ni is known to be better extracted with HF (+ microwave digestion?)



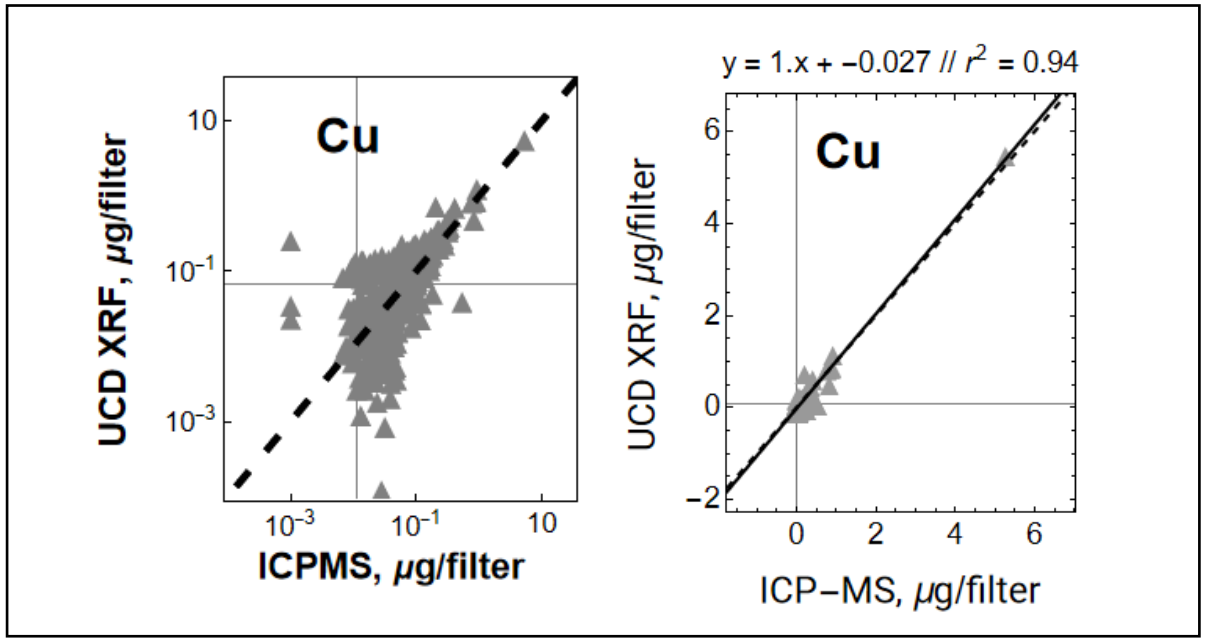


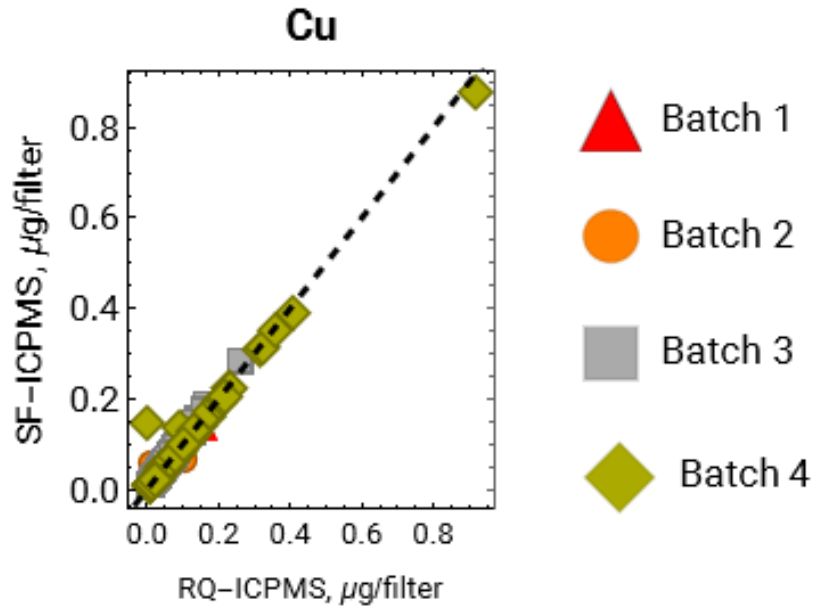


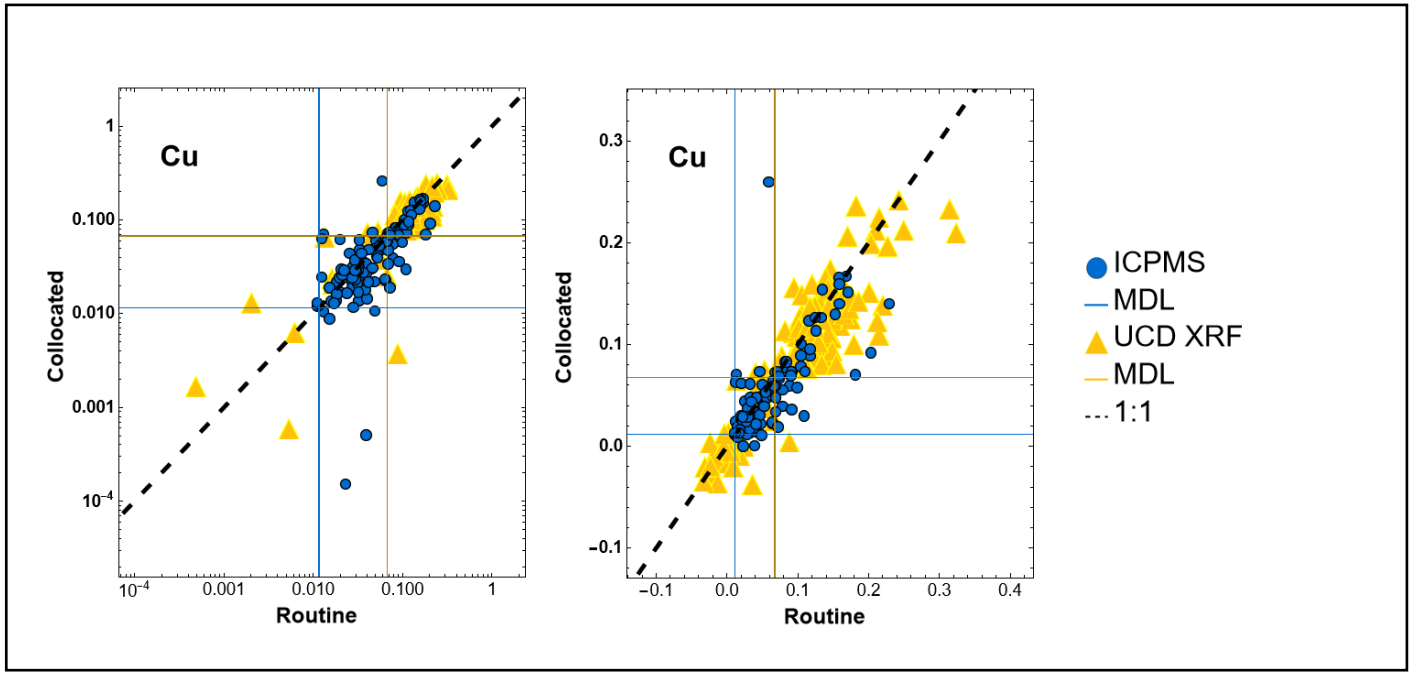


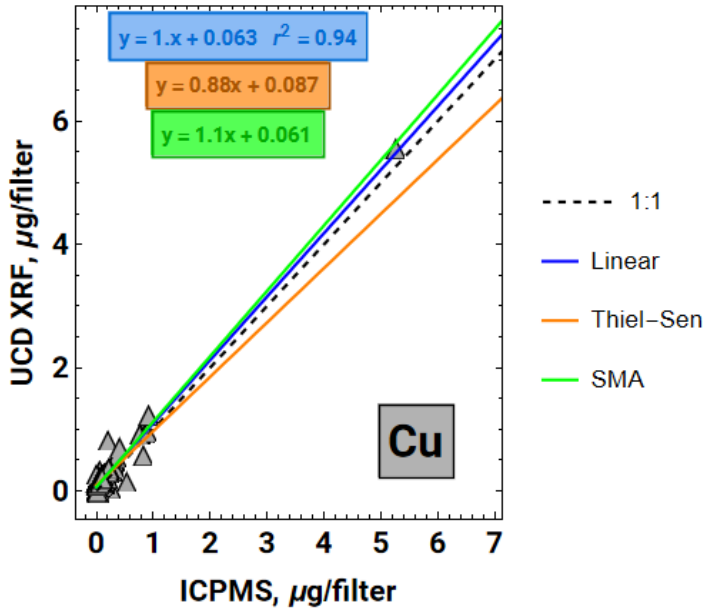
Cu

XRF > 10% MDL	YES
% above MDL	20%
RQ ICPMS >10% MDL	YES
% above MDL	95%
RQ ICPMS 1648a recovery acceptable ? (5% HNO3 + 2 hour hot block digestion)	YES
Which MDL is lower	ICPMS



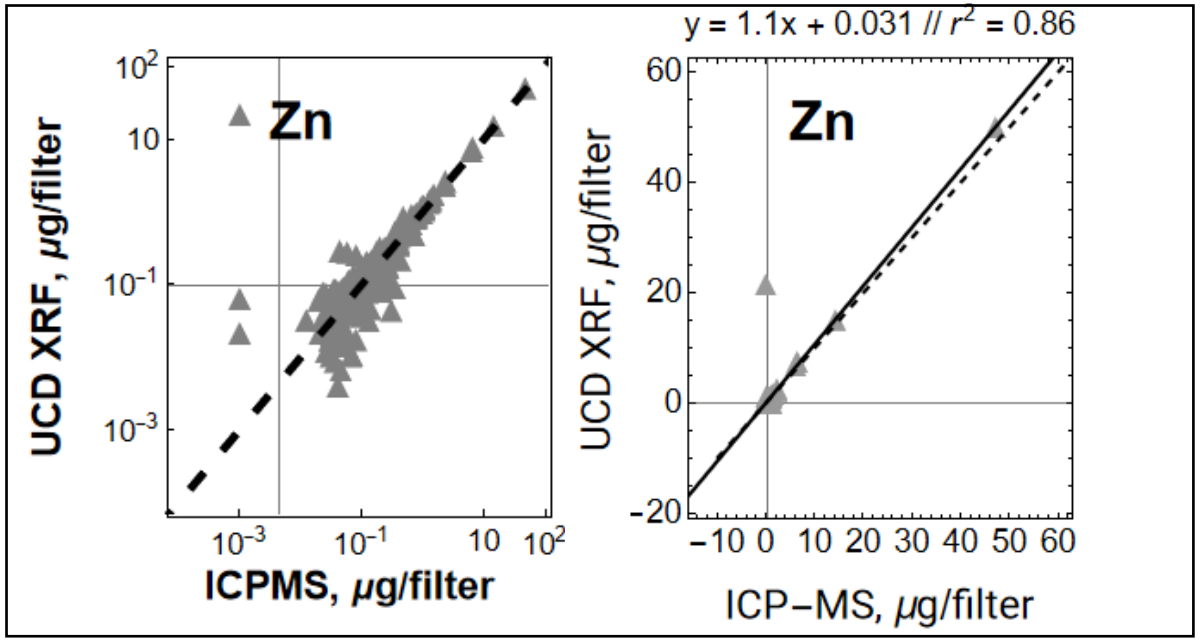


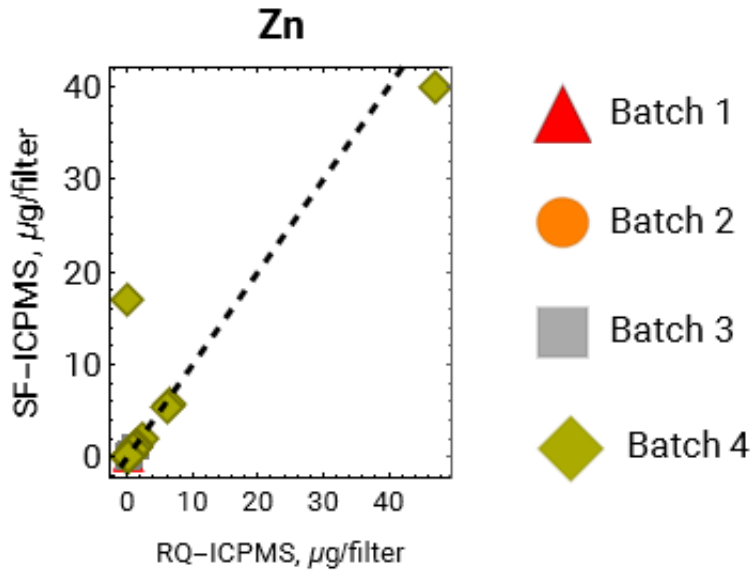


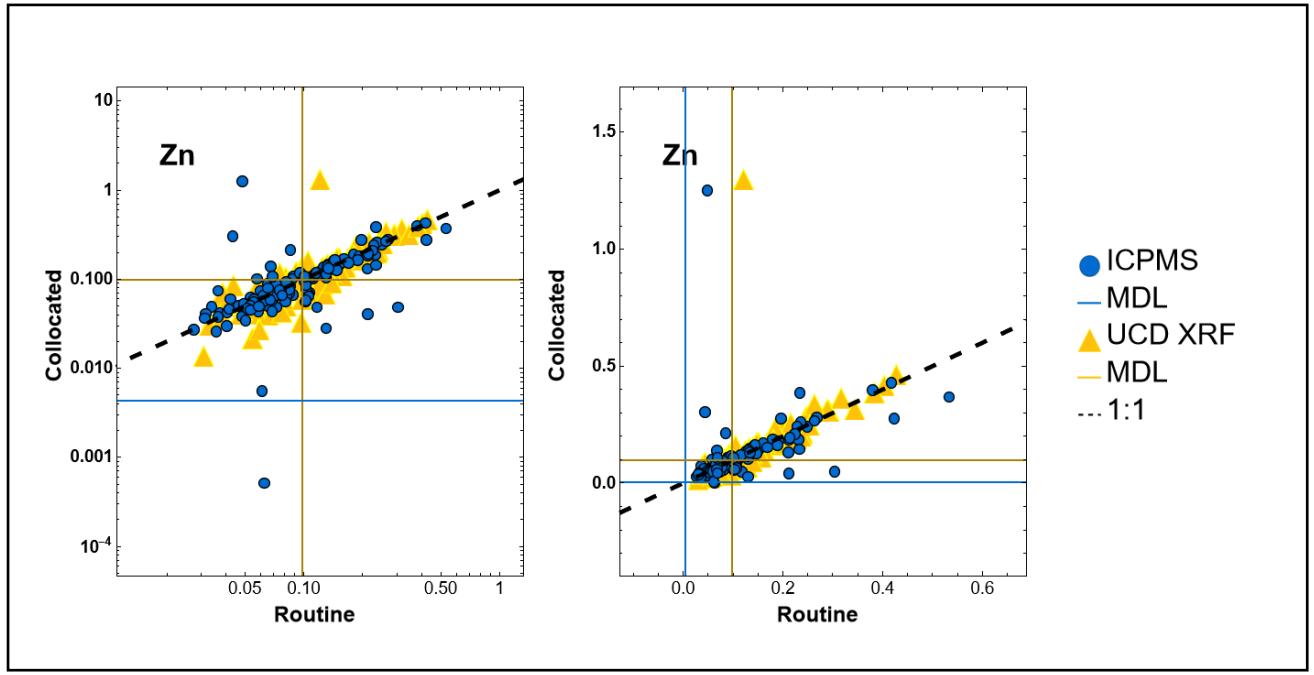


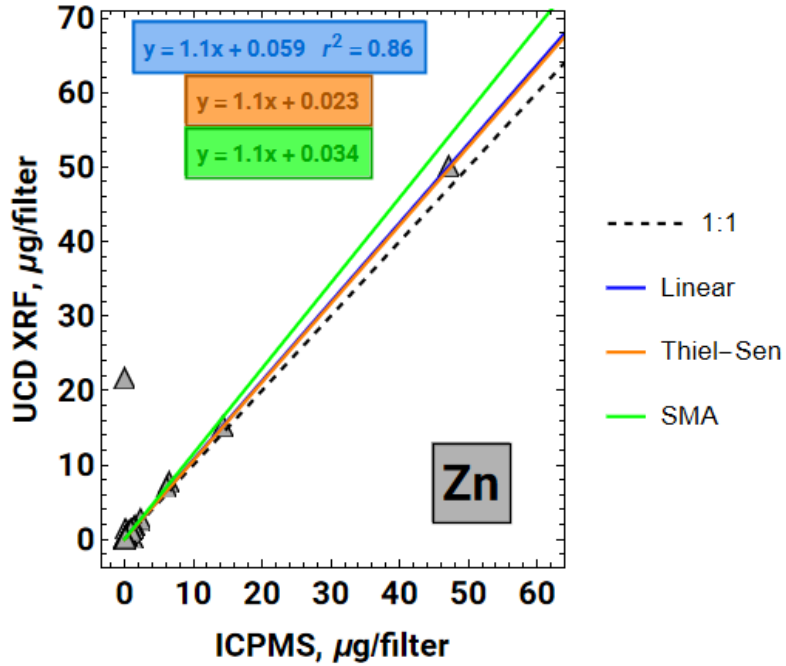
Zn

XRF > 10% MDL	YES
% above MDL	45%
RQ ICPMS >10% MDL	YES
% above MDL	99%
RQ ICPMS 1648a recovery acceptable? (5% HNO3 + 2 hour hot block digestion)	YES
Which MDL is lower	UCD XRF
Other notes	• OK MDL • OK XRF-ICPMS inter-method



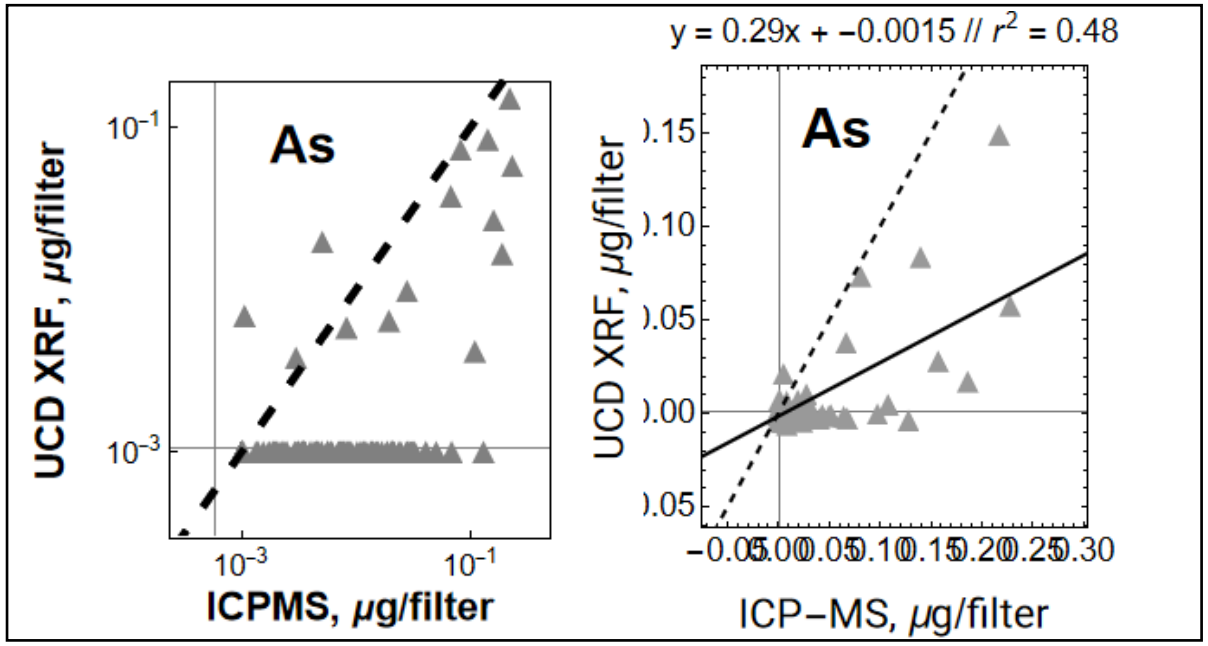


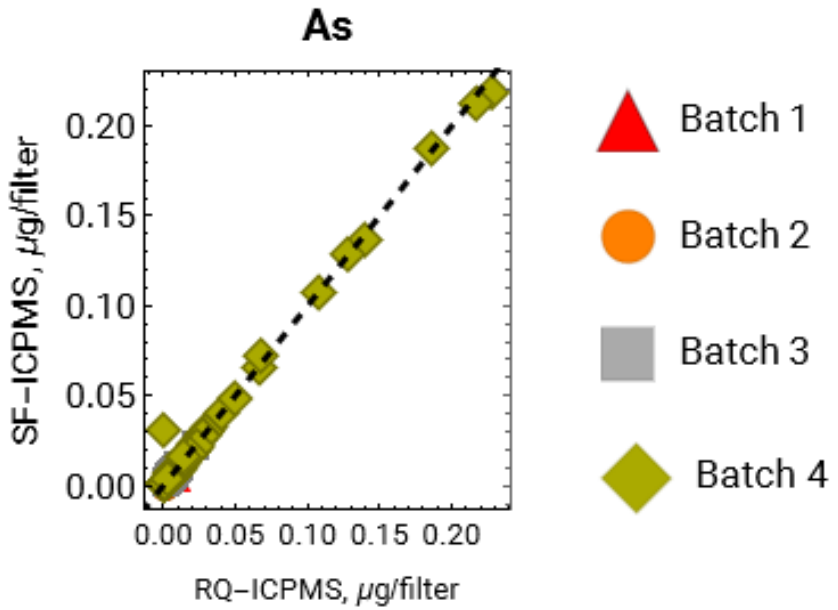


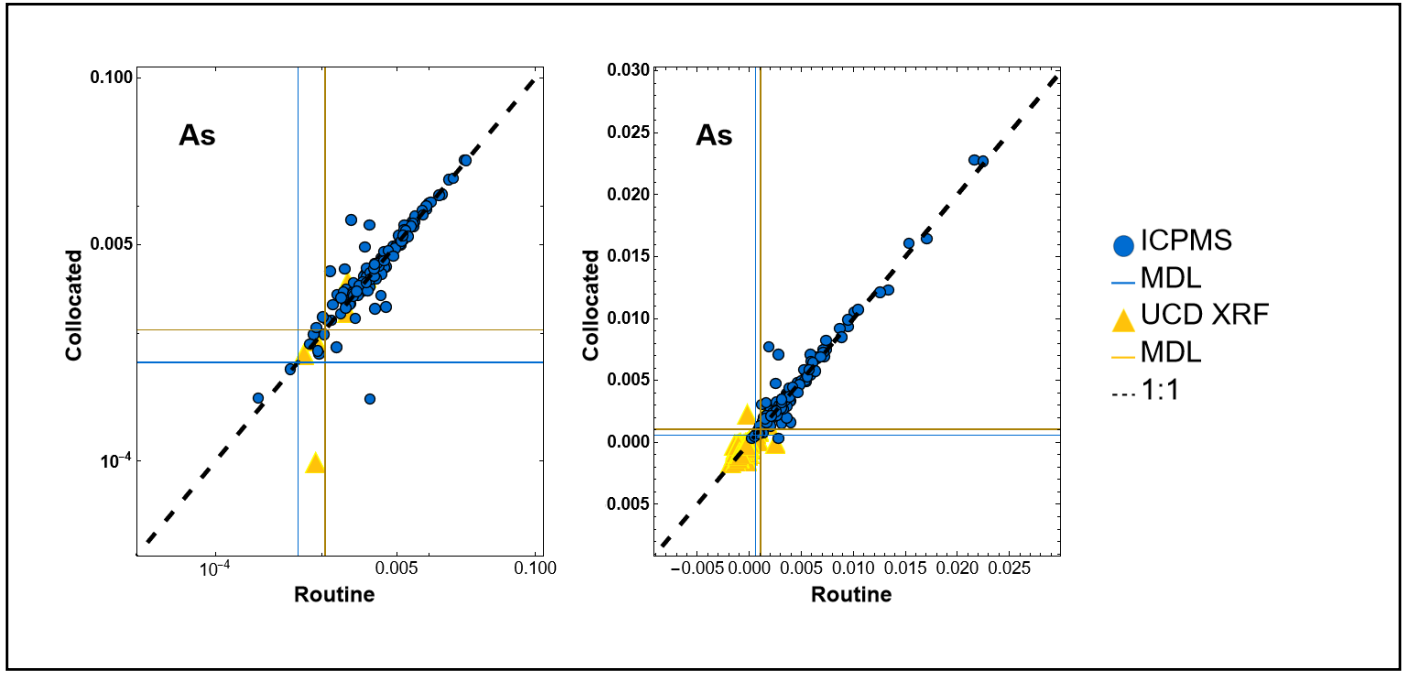


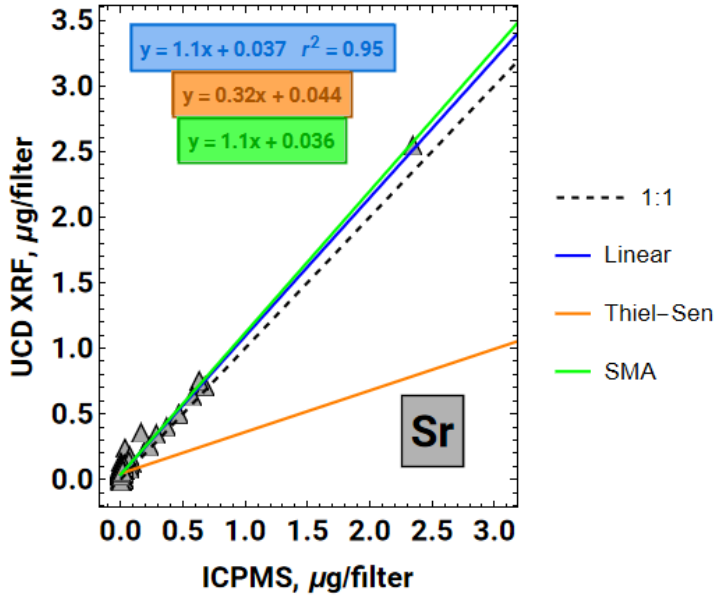
As

XRF > 10% MDL	NO
% above MDL	8%
RQ ICPMS >10% MDL	YES
% above MDL	98%
RQ ICPMS 1648a recovery acceptable? (5% HNO3 + 2 hour hot block digestion)	YES
Which MDL is lower	ICPMS



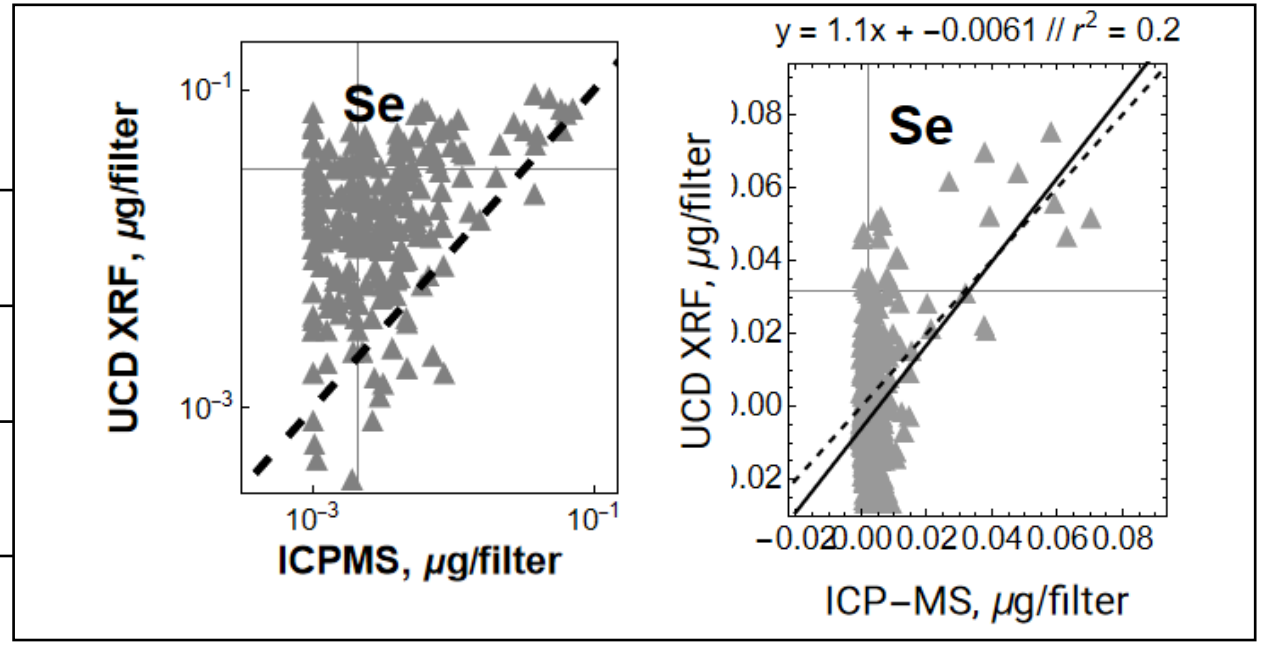


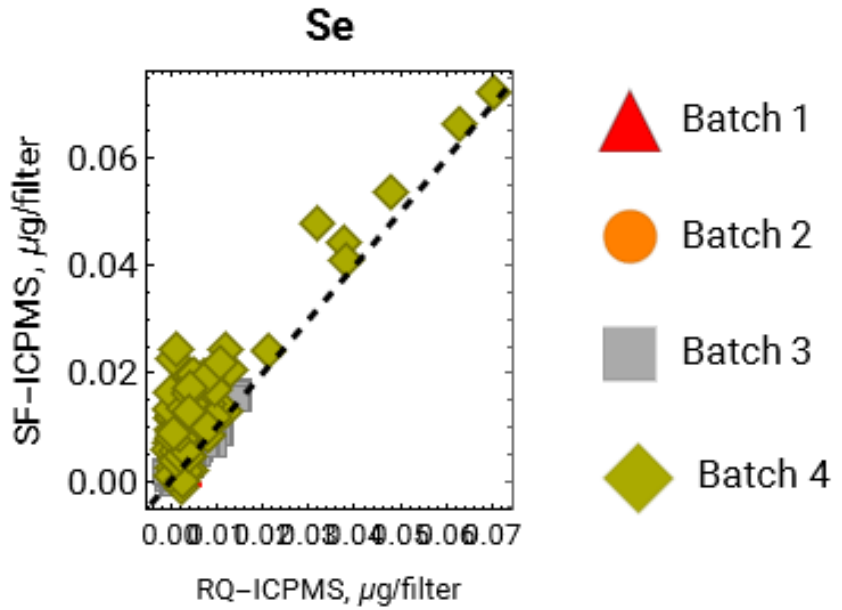


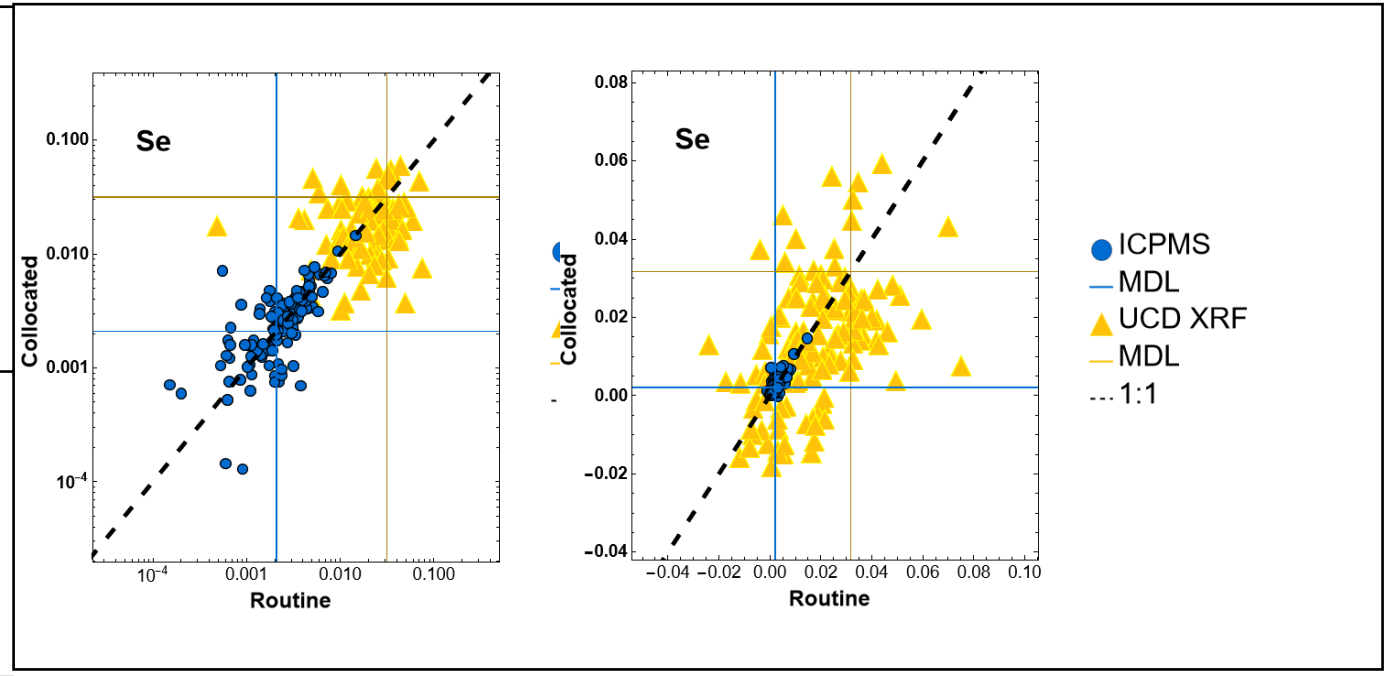


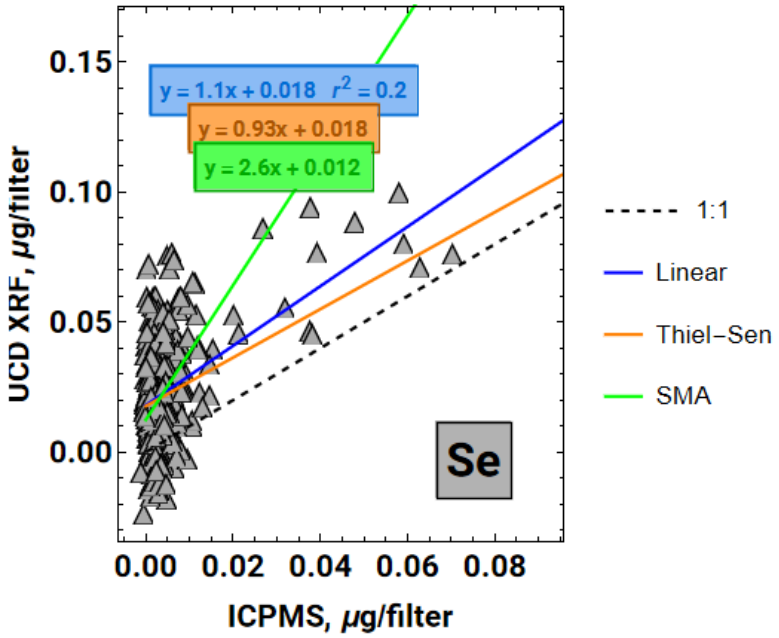
Se

XRF > 10% MDL	NO
% above MDL	5%
RQ ICPMS > 10% MDL	YES
% above MDL	58%
RQ ICPMS 1648a recovery acceptable ? (5% HNO3 + 2 hour hot block digestion)	YES
Which MDL is lower	ICPMS



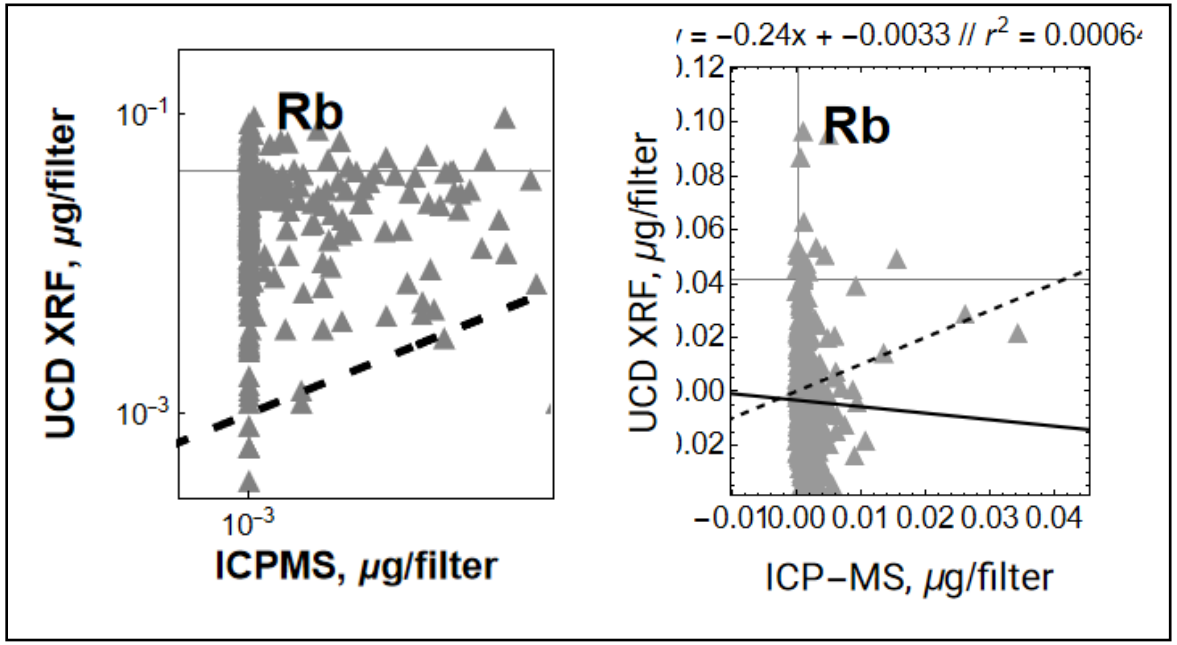


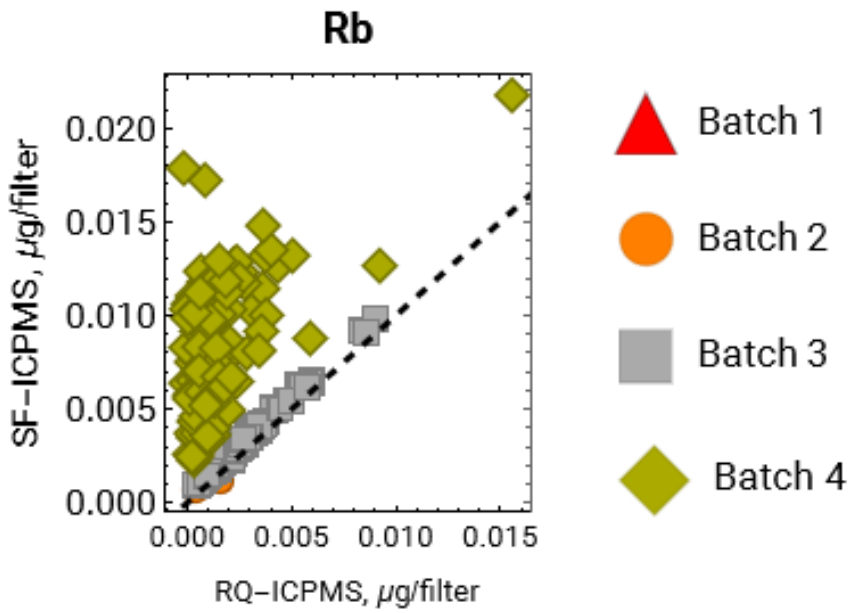


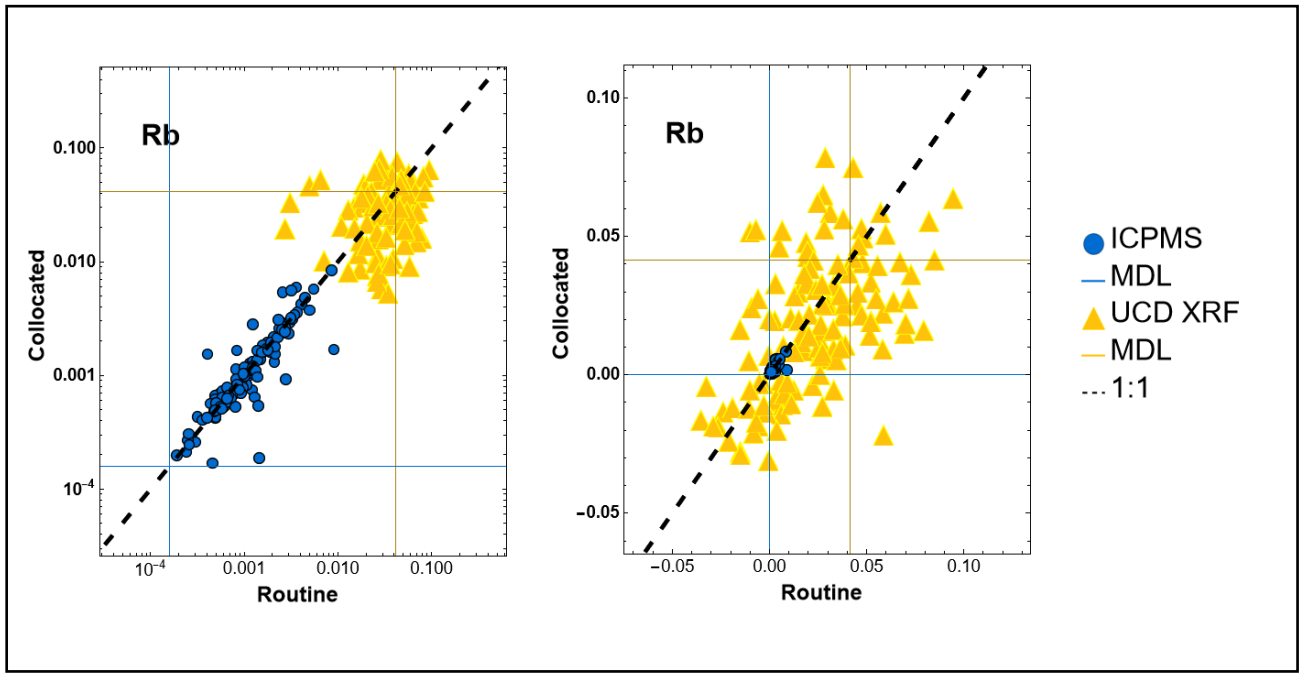


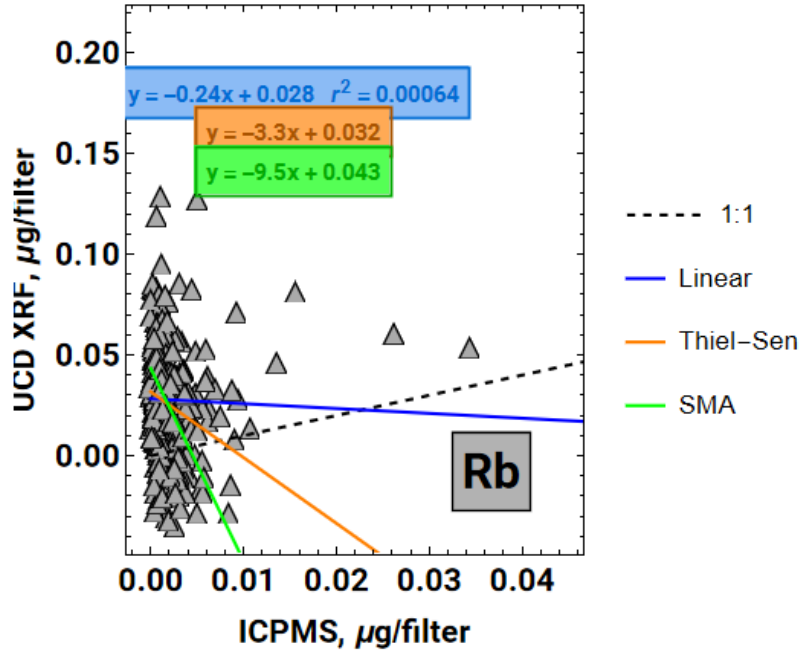
Rb

XRF > 10% MDL	NO
% above MDL	3%
RQ ICPMS >10% MDL	YES
% above MDL	98%
RQ ICPMS 1648a recovery acceptable ? (5% HNO3 + 2 hour hot block digestion)	NO
Which MDL is lower	ICPMS



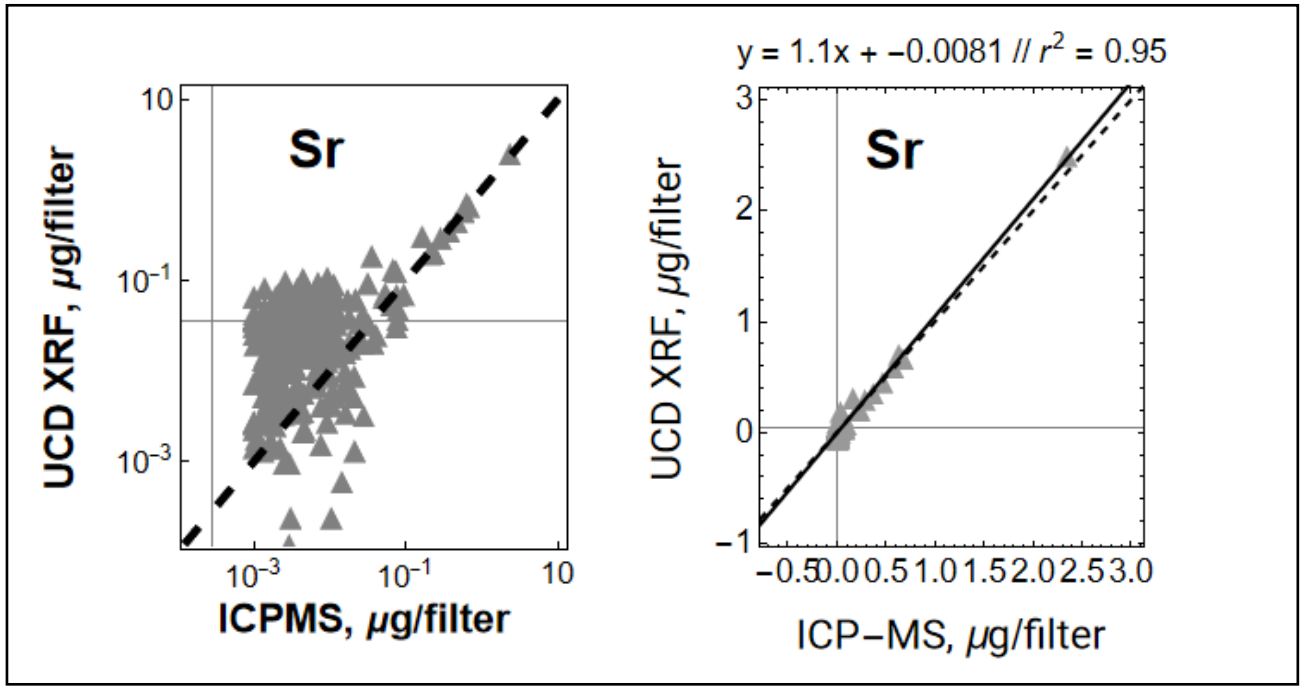


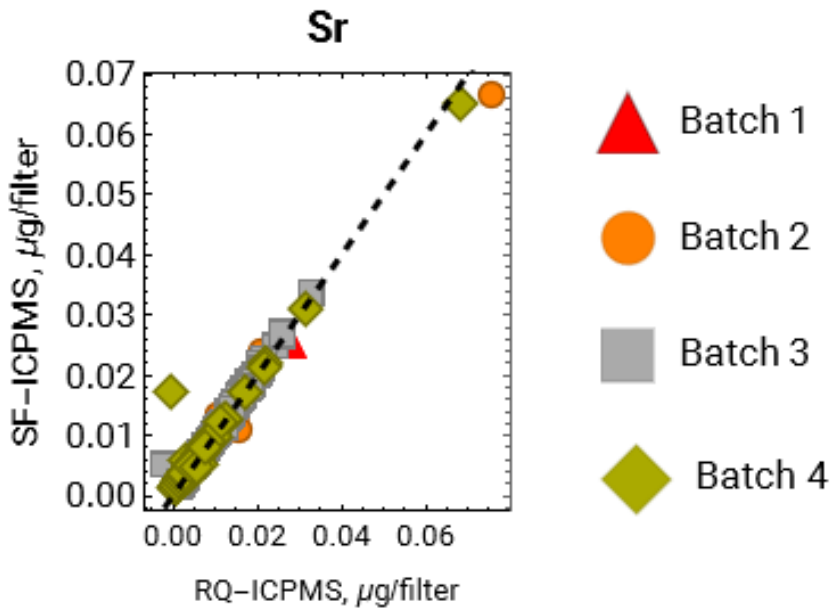


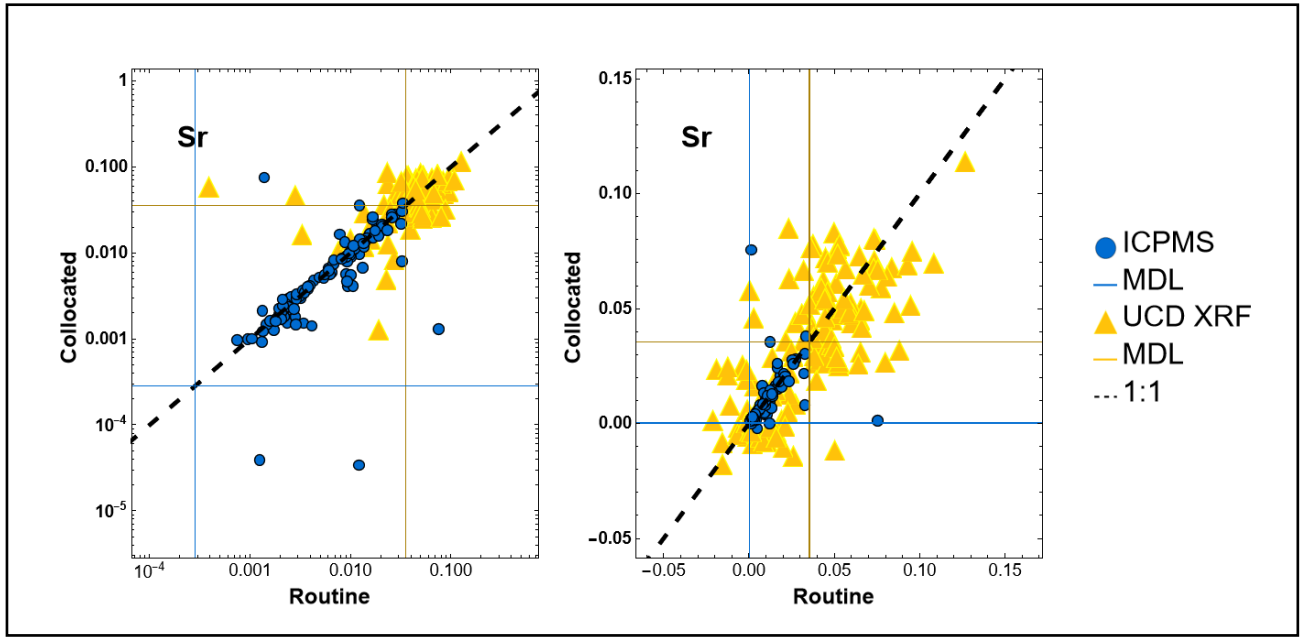


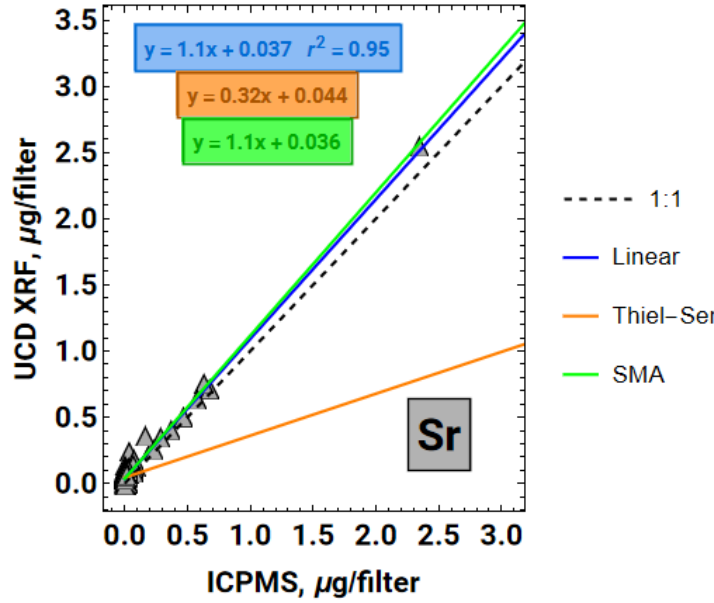
Sr

XRF > 10% MDL	NO
% above MDL	9%
RQ ICPMS > 10% MDL	YES
% above MDL	99%
RQ ICPMS 1648a recovery acceptable? (5% HNO3 + 2 hour hot block digestion)	NO
Which MDL is lower	ICPMS



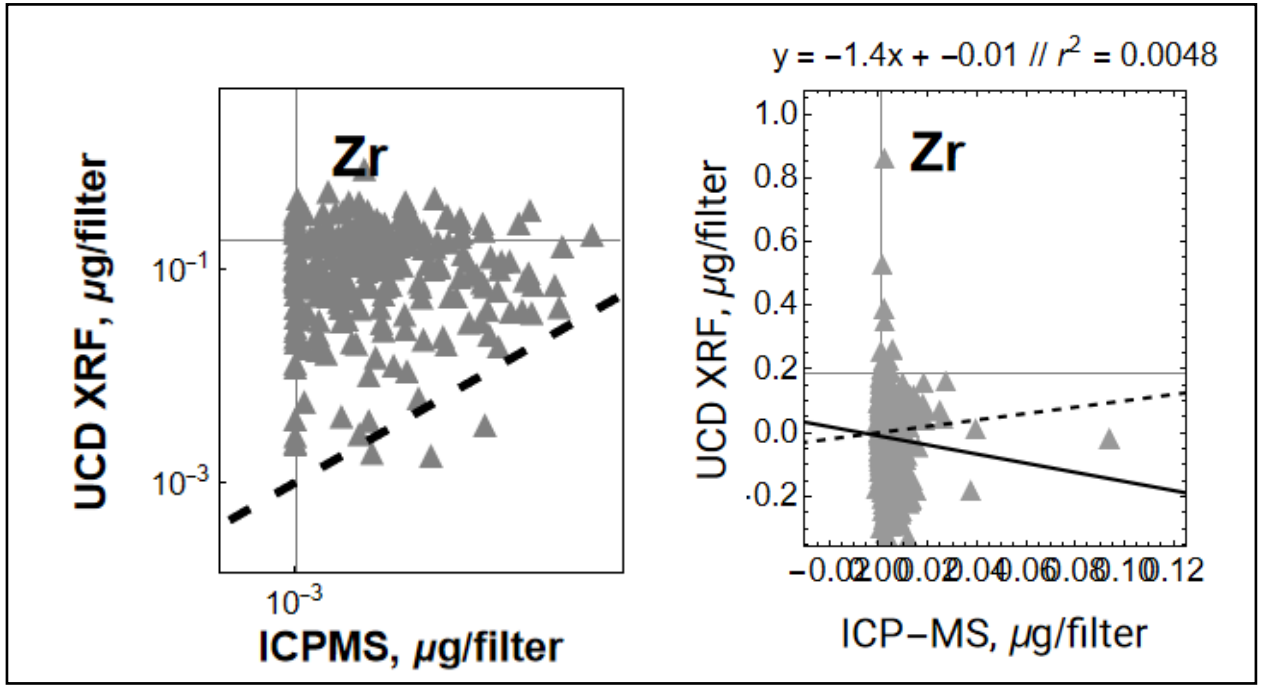


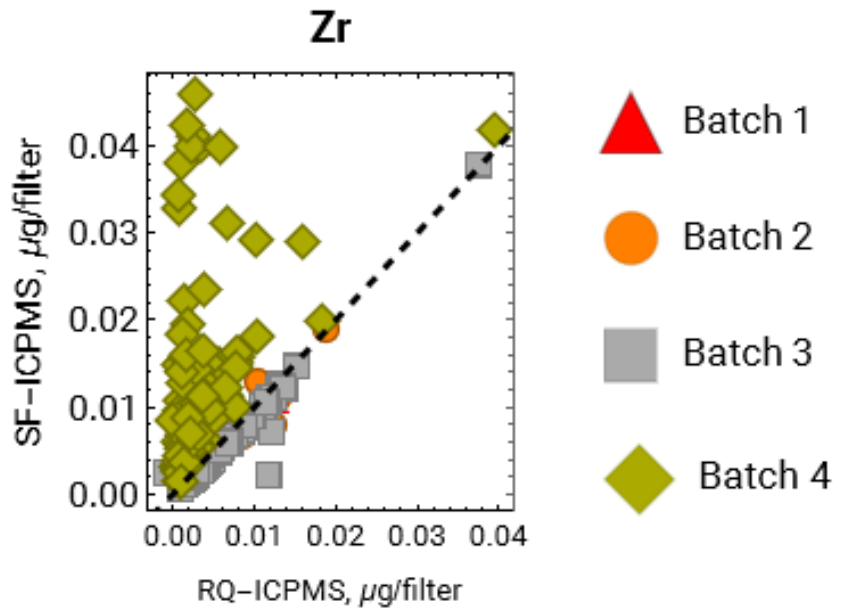


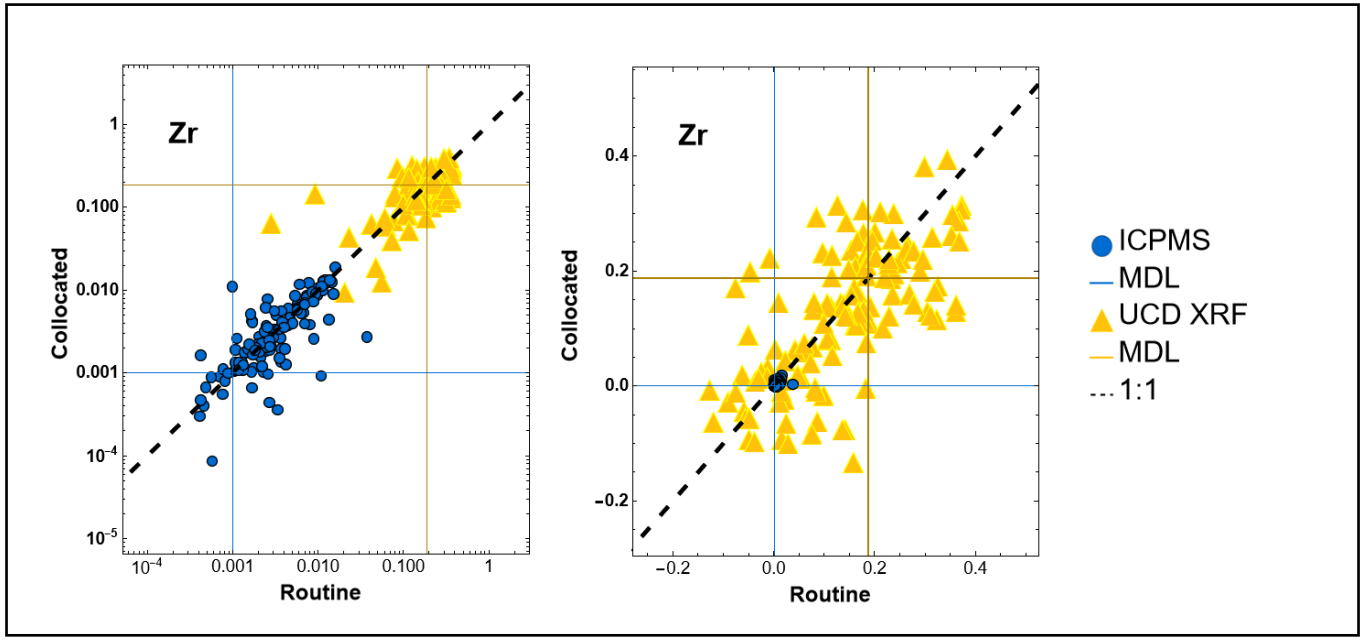


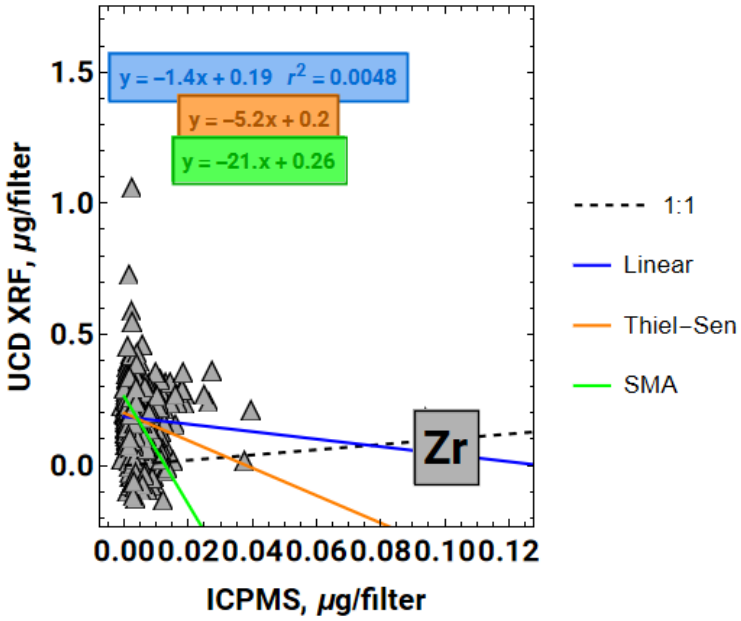
Zr

XRF > 10% MDL	NO
% above MDL	3%
RQ ICPMS >10% MDL	YES
% above MDL	84%
RQ ICPMS 1648a recovery acceptable ? (5% HNO3 + 2 hour hot block digestion)	Not evaluated
Which MDL is lower	ICPMS



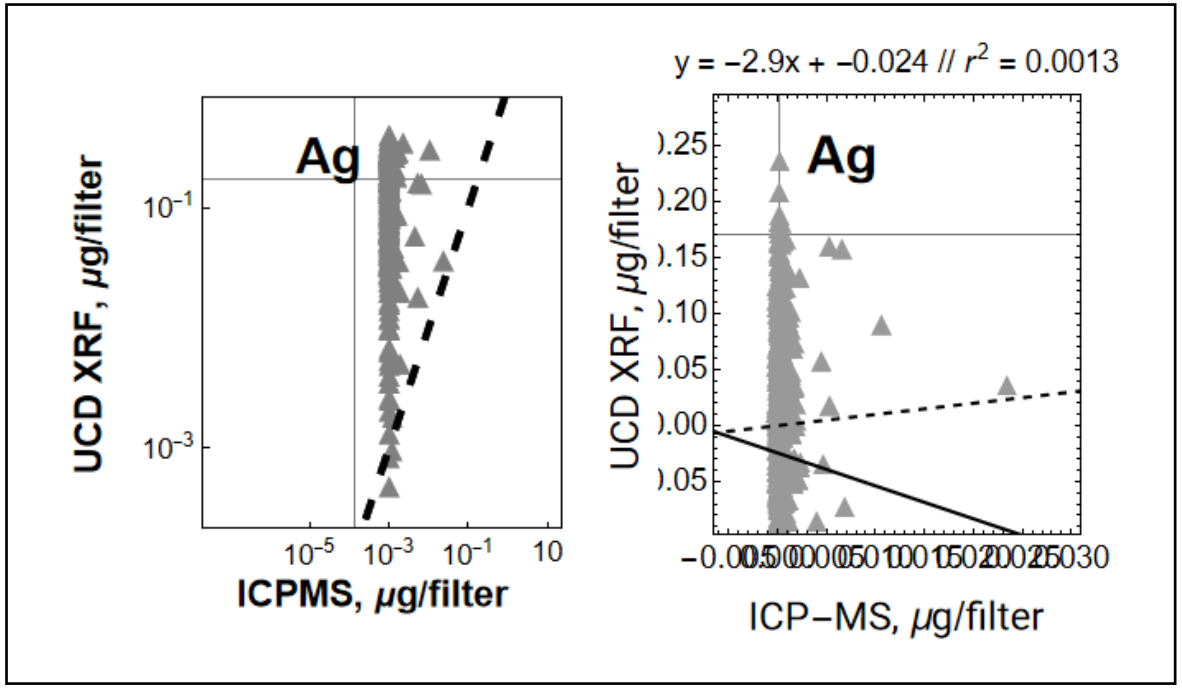


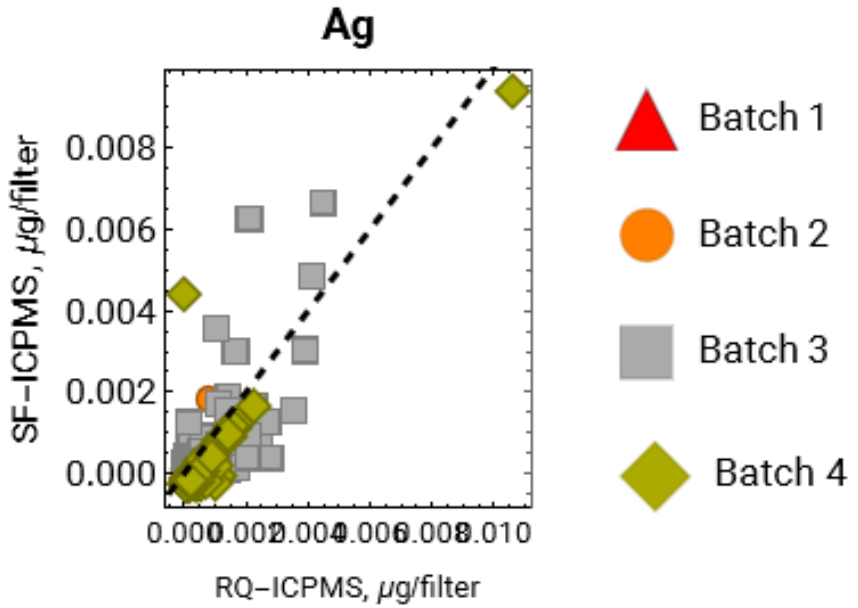


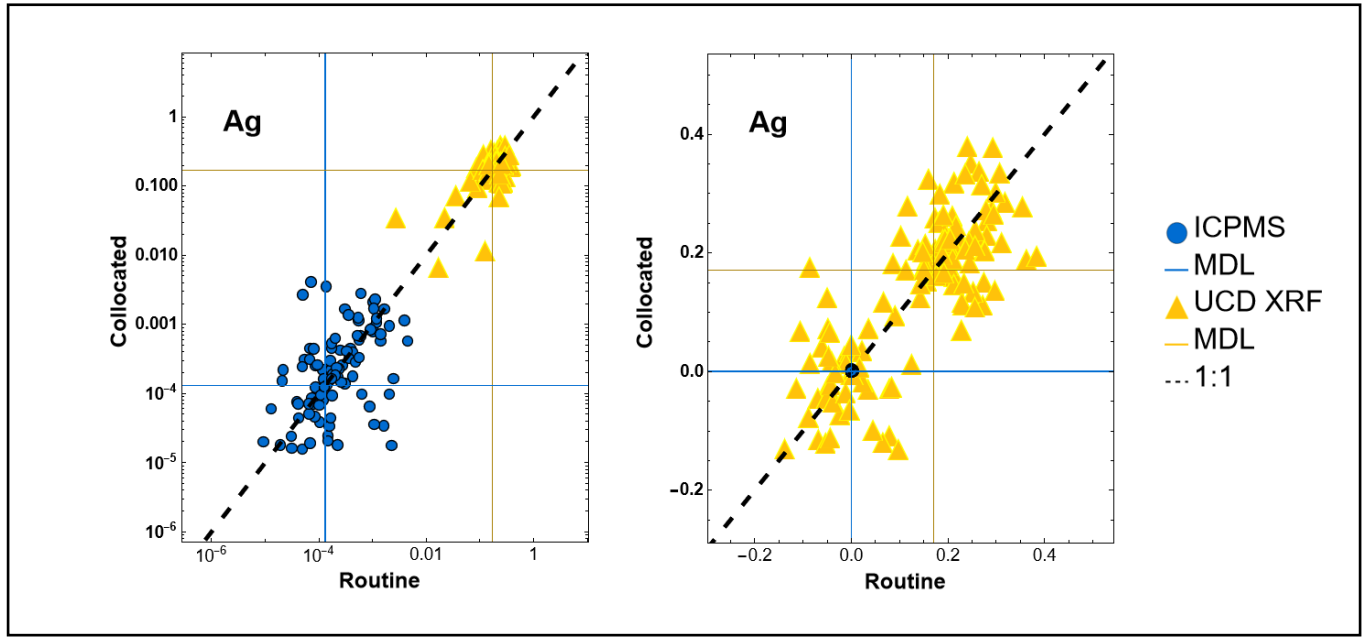


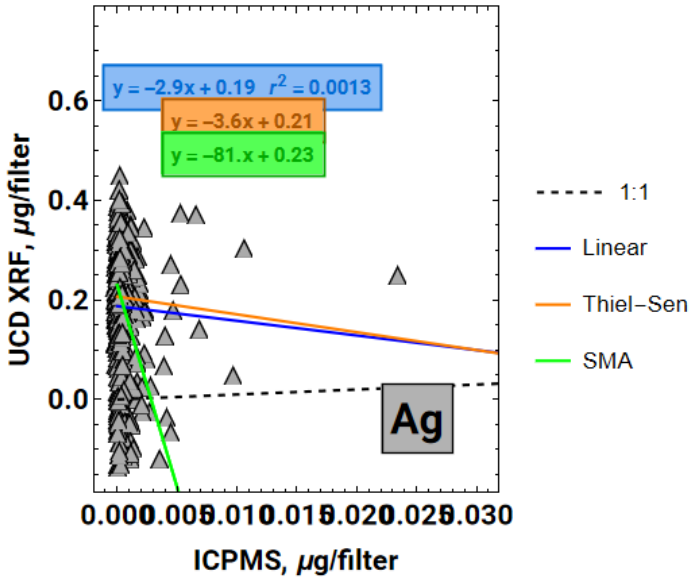
Ag

XRF > 10% MDL	NO
% above MDL	1%
RQ ICPMS >10% MDL	YES
% above MDL	65%
RQ ICPMS 1648a recovery acceptable ? (5% HNO3 + 2 hour hot block digestion)	YES
Which MDL is lower	ICPMS



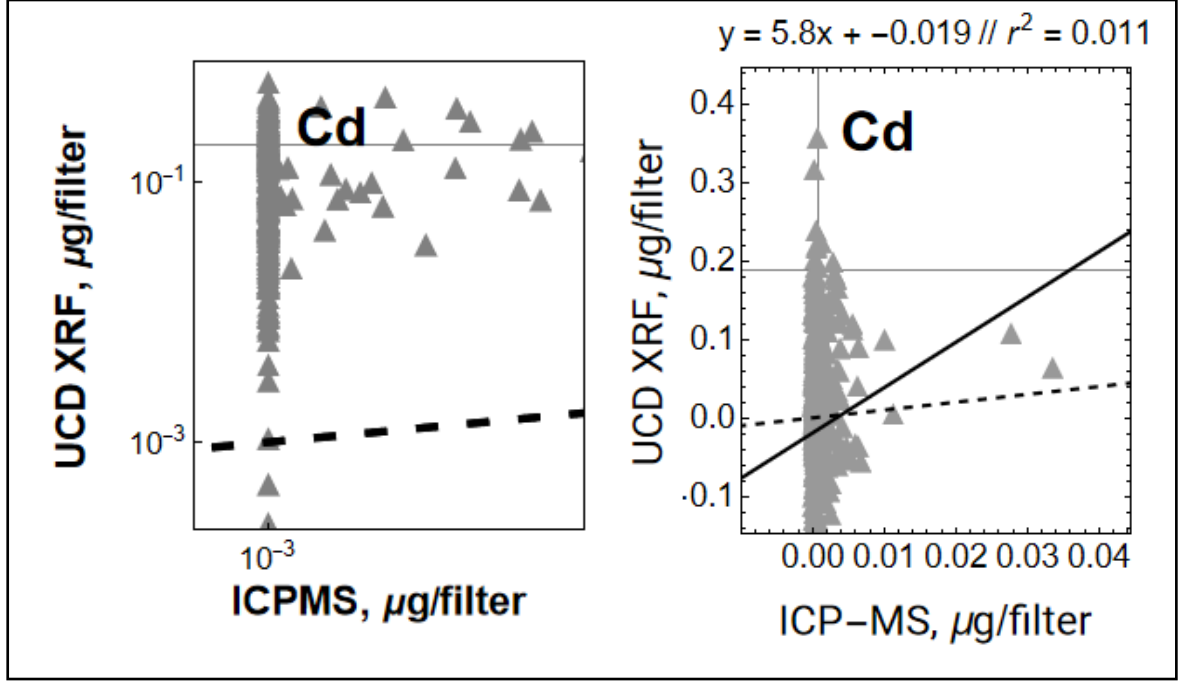


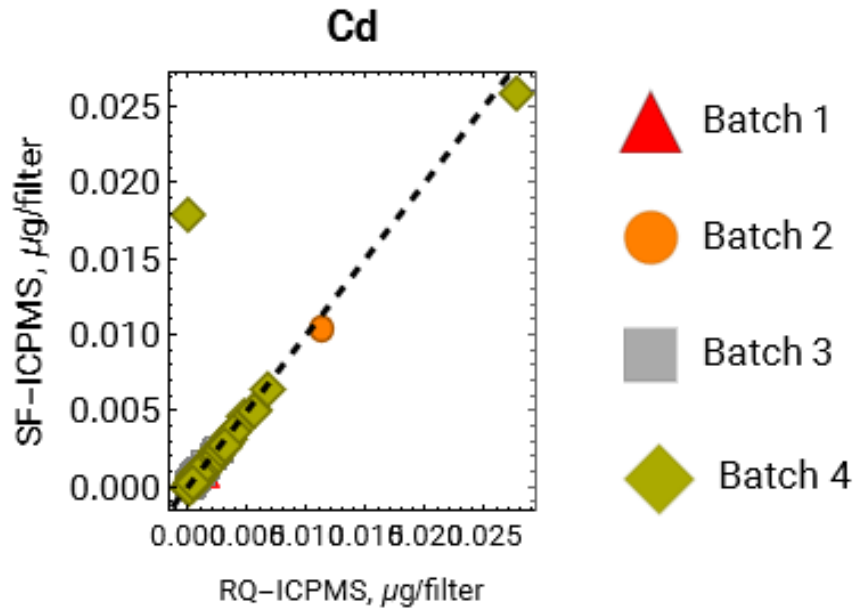


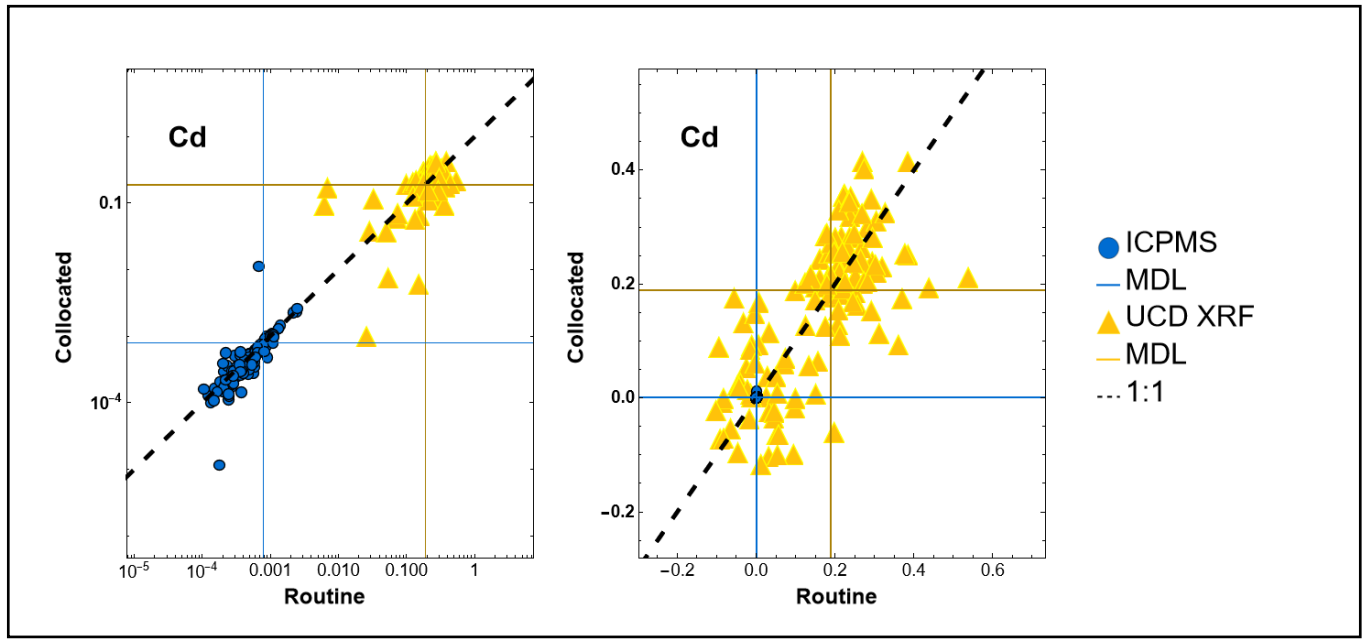


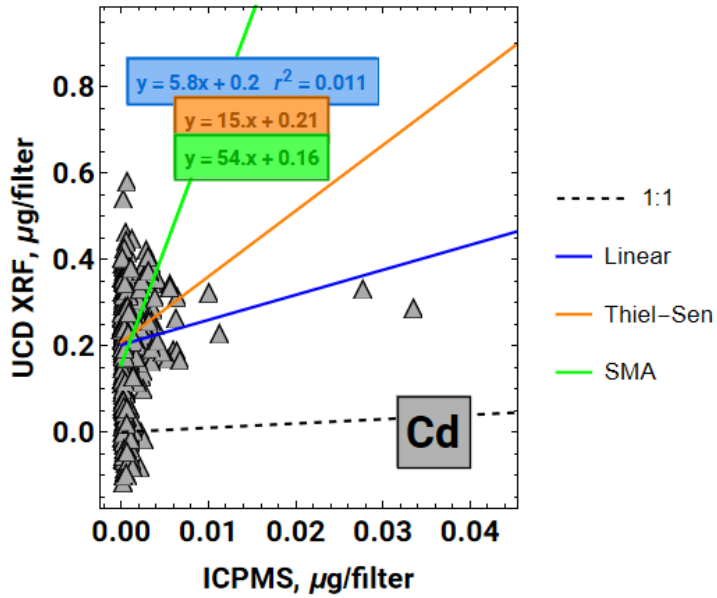
Cd

XRF > 10% MDL	NO
% above MDL	2%
RQ ICPMS >10% MDL	YES
% above MDL	27%
RQ ICPMS 1648a recovery acceptable ? (5% HNO3 + 2 hour hot block digestion)	YES
Which MDL is lower	ICPMS



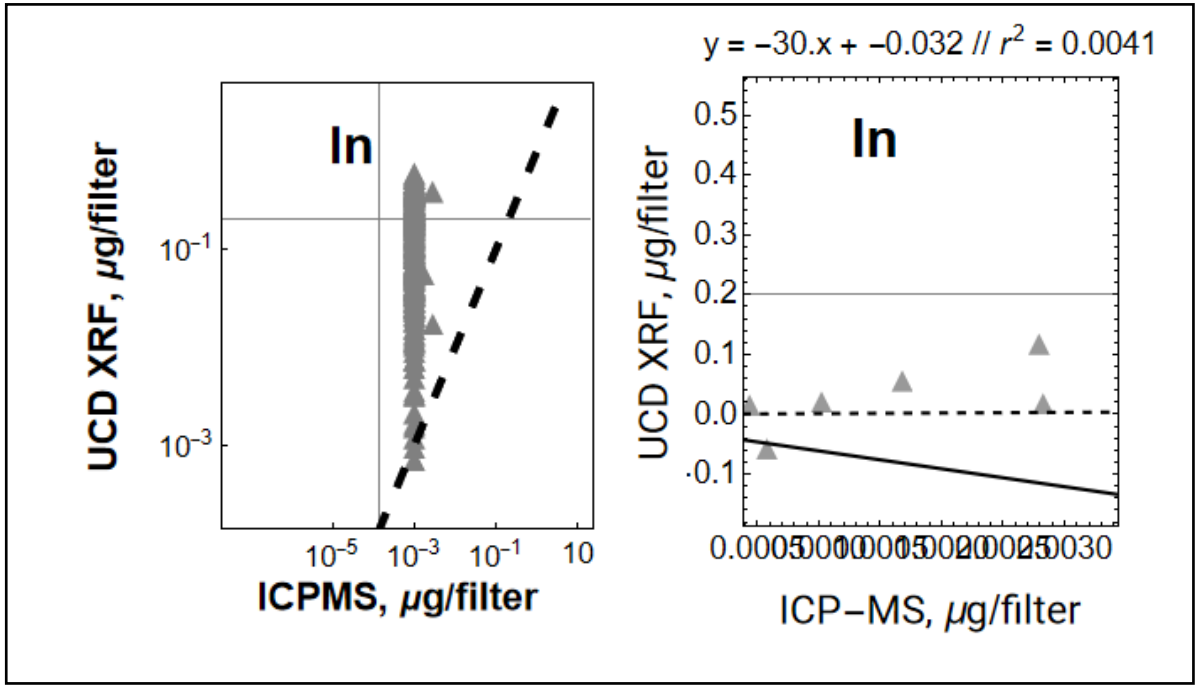


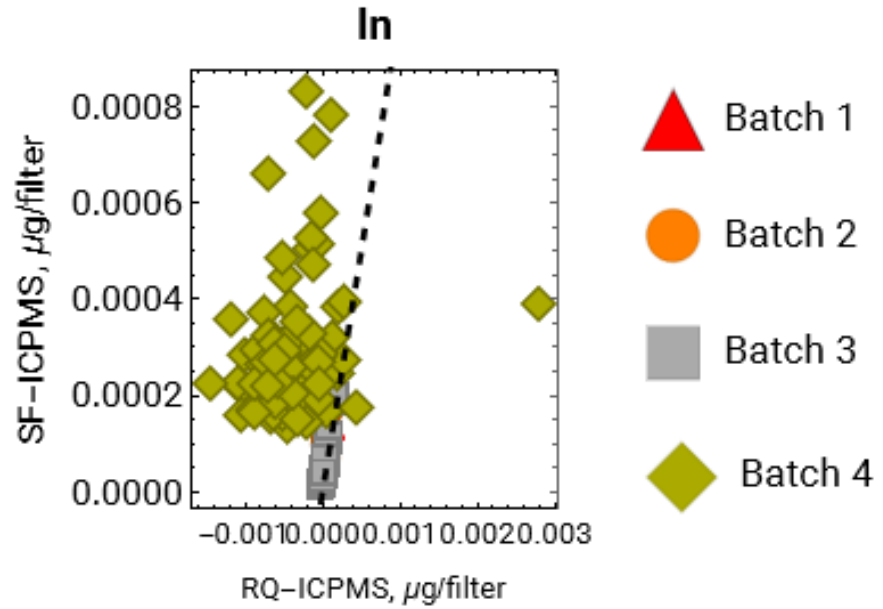


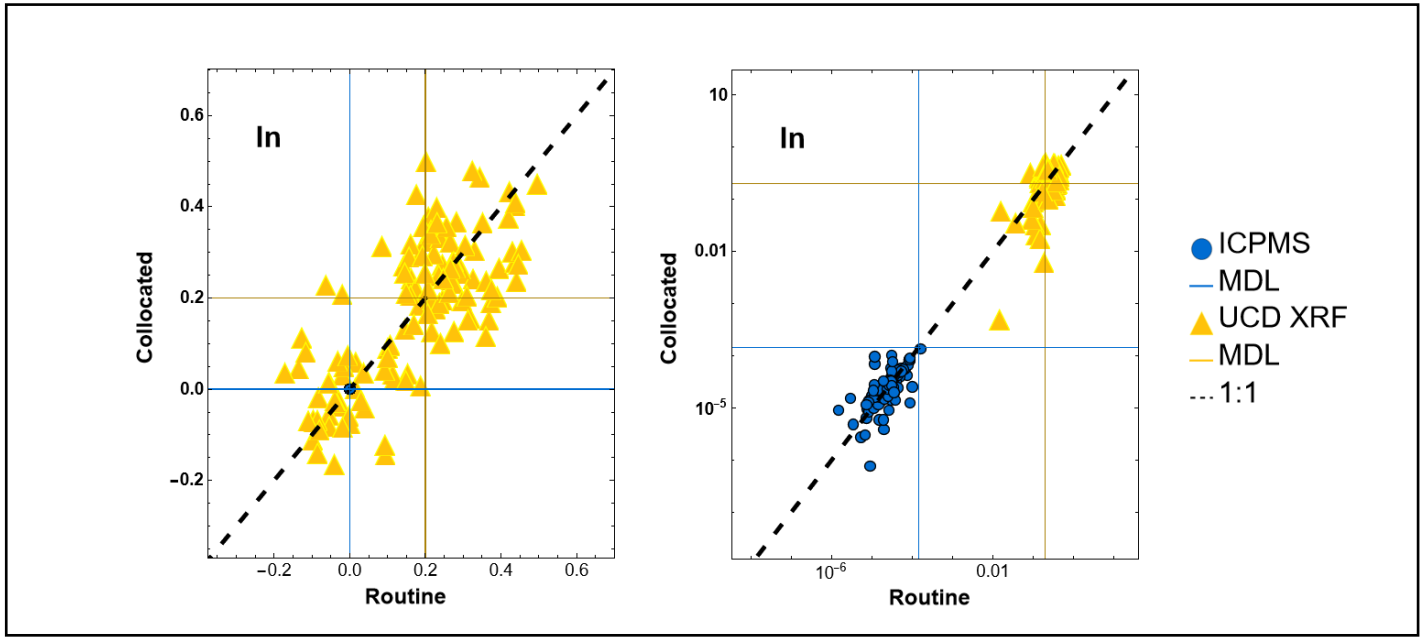


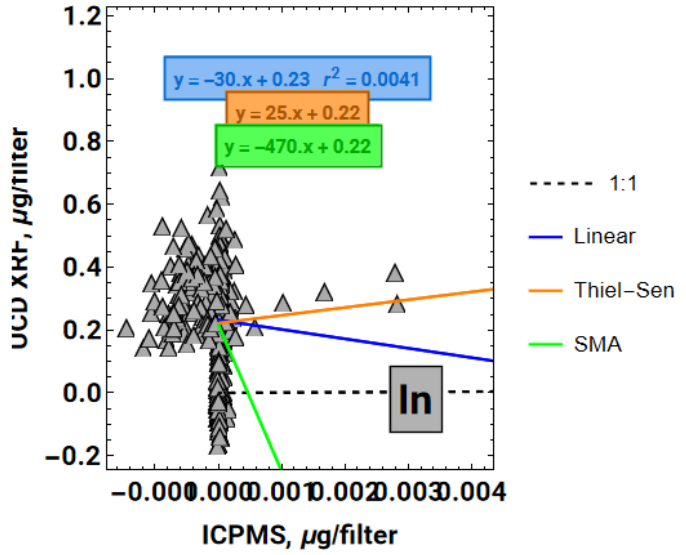
In

XRF > 10% MDL	NO
% above MDL	4%
RQ ICPMS > 10% MDL	NO
% above MDL	4%
RQ ICPMS 1648a recovery acceptable ? (5% HNO3 + 2 hour hot block digestion)	Not evaluated
Which MDL is lower	ICPMS



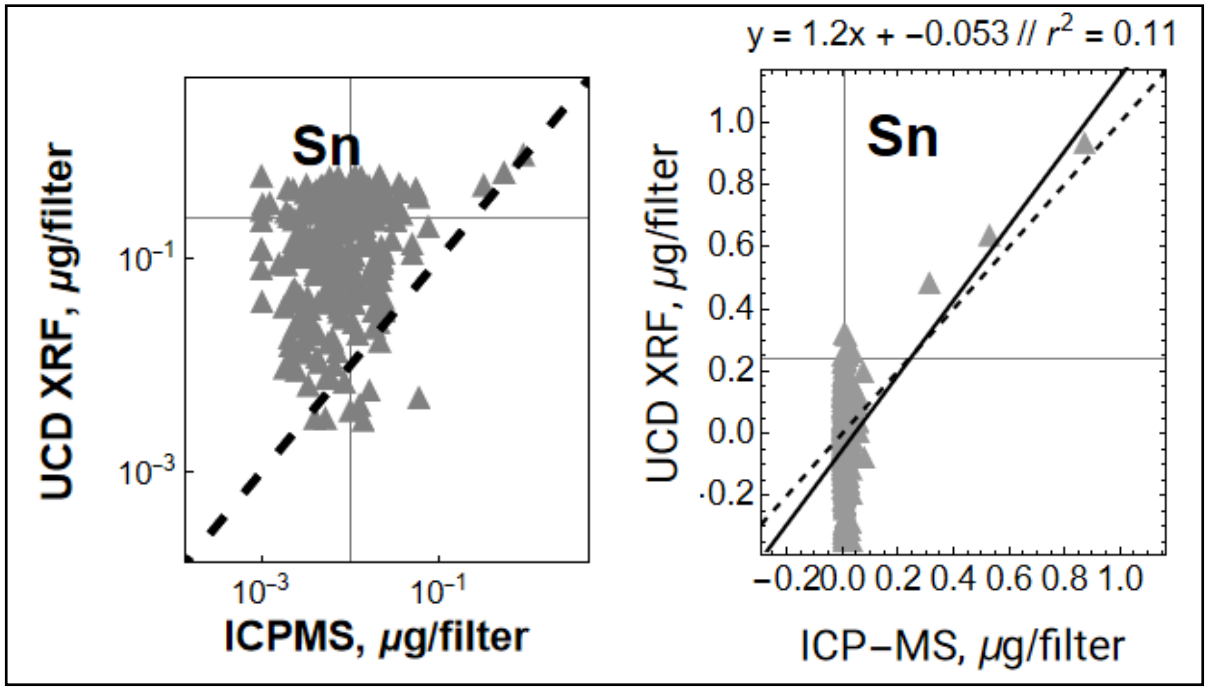


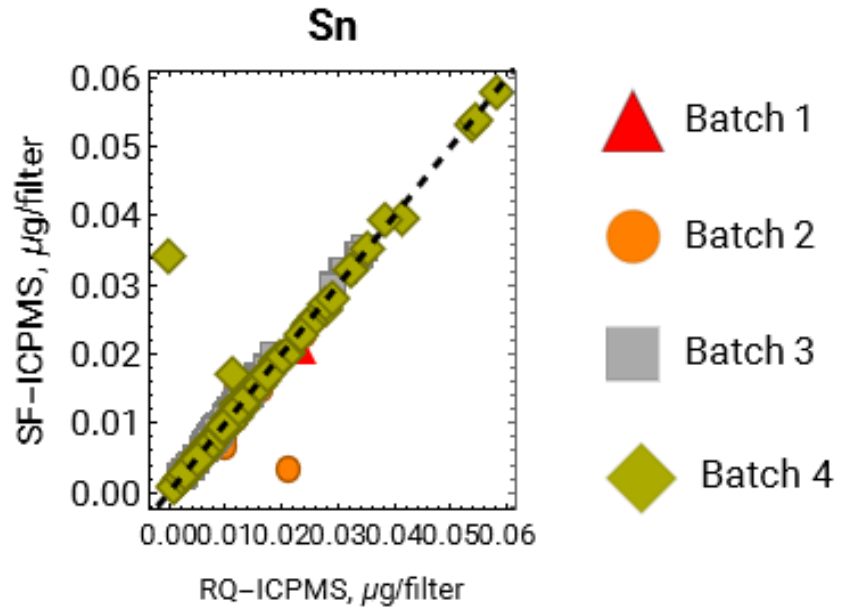


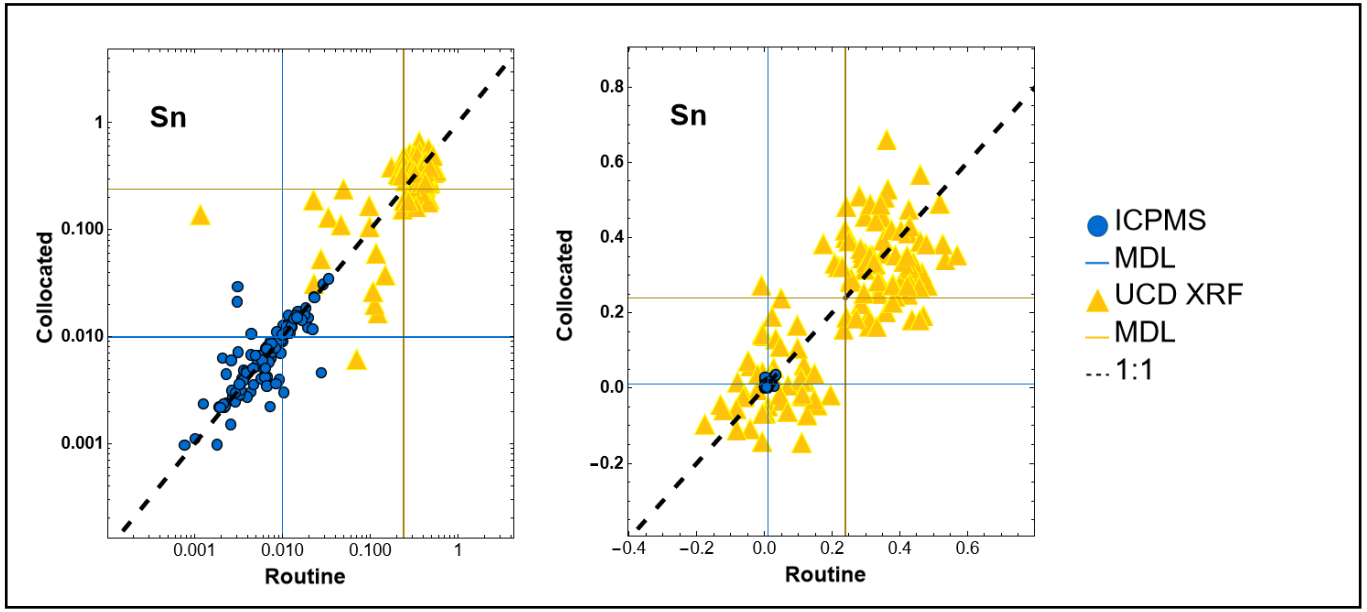


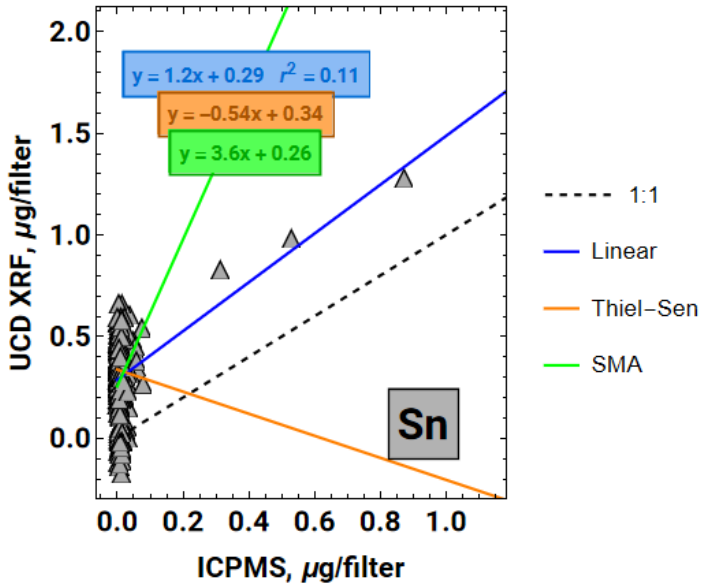
Sn

XRF > 10% MDL	NO
% above MDL	2%
RQ ICPMS > 10% MDL	YES
% above MDL	35%
RQ ICPMS 1648a recovery acceptable ? (5% HNO3 + 2 hour hot block digestion)	Not evaluated
Which MDL is lower	ICPMS



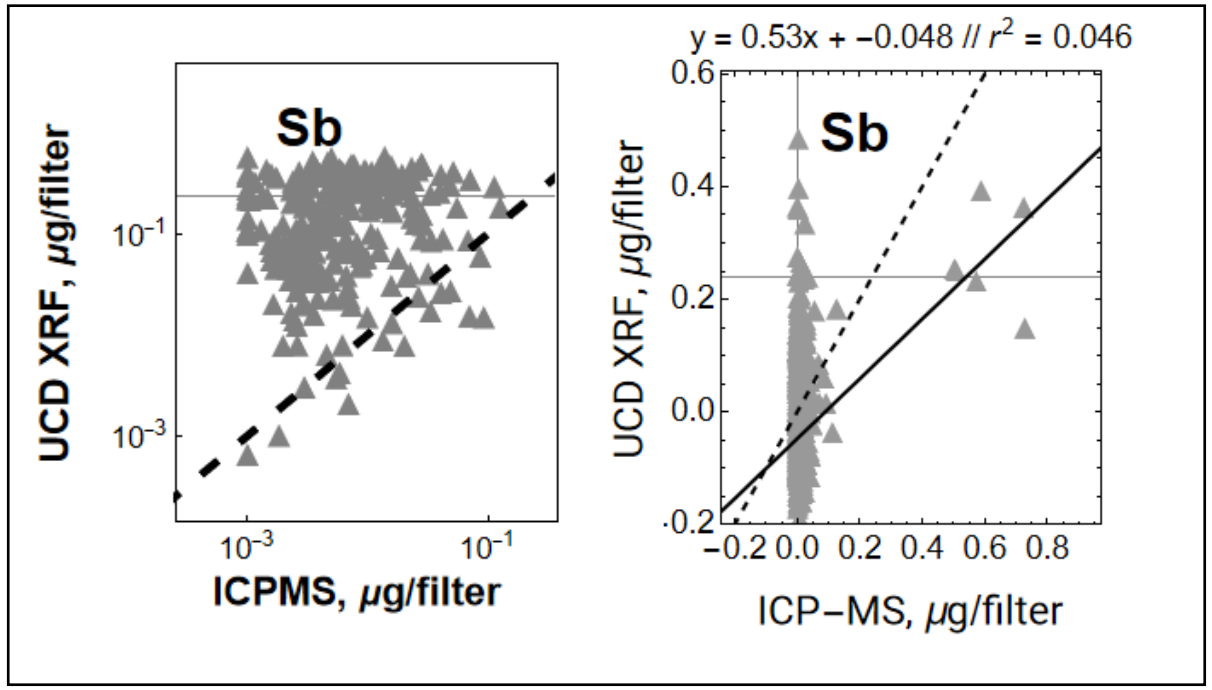


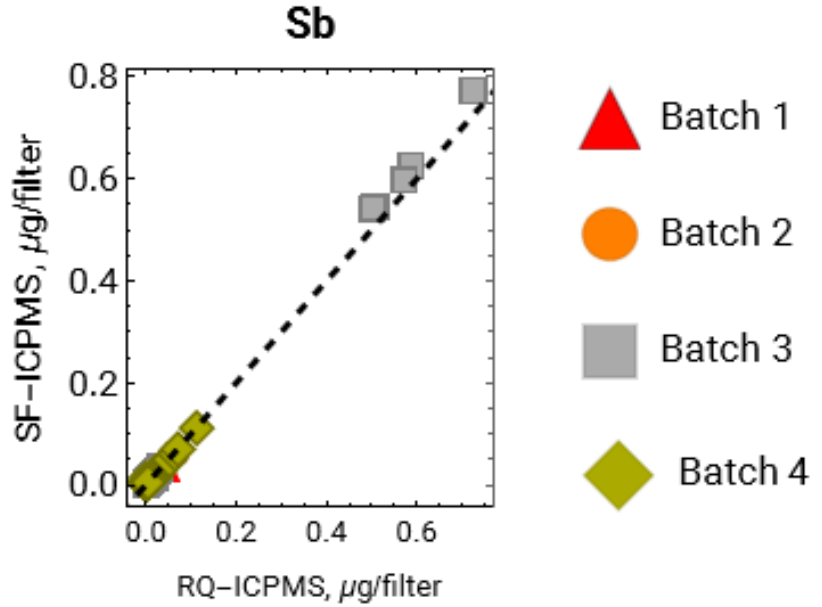


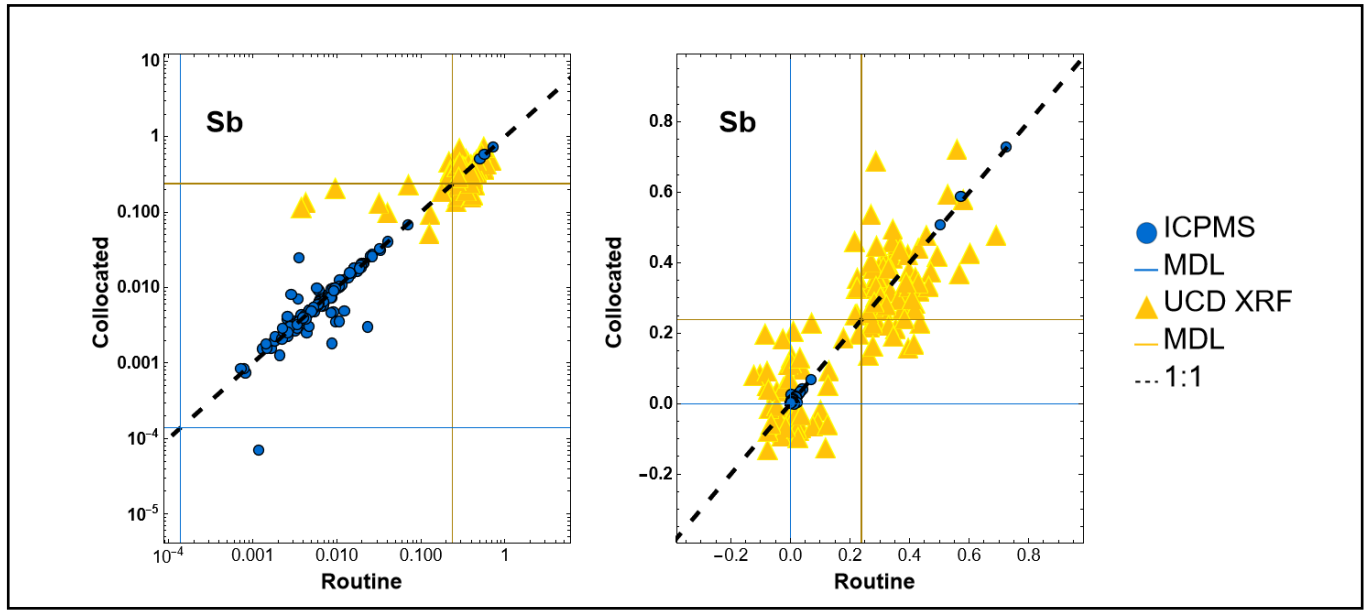


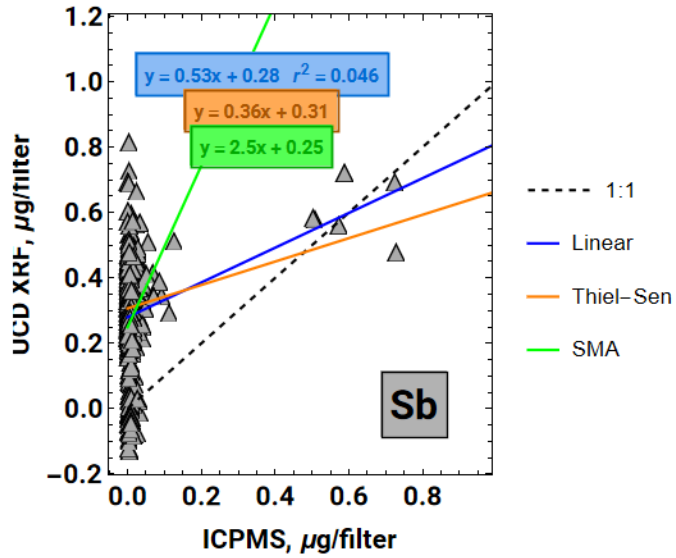
Sb

XRF > 10% MDL	NO
% above MDL	3%
RQ ICPMS >10% MDL	YES
% above MDL	99%
RQ ICPMS 1648a recovery acceptable? (5% HNO3 + 2 hour hot block digestion)	Not evaluated
Which MDL is lower	ICPMS



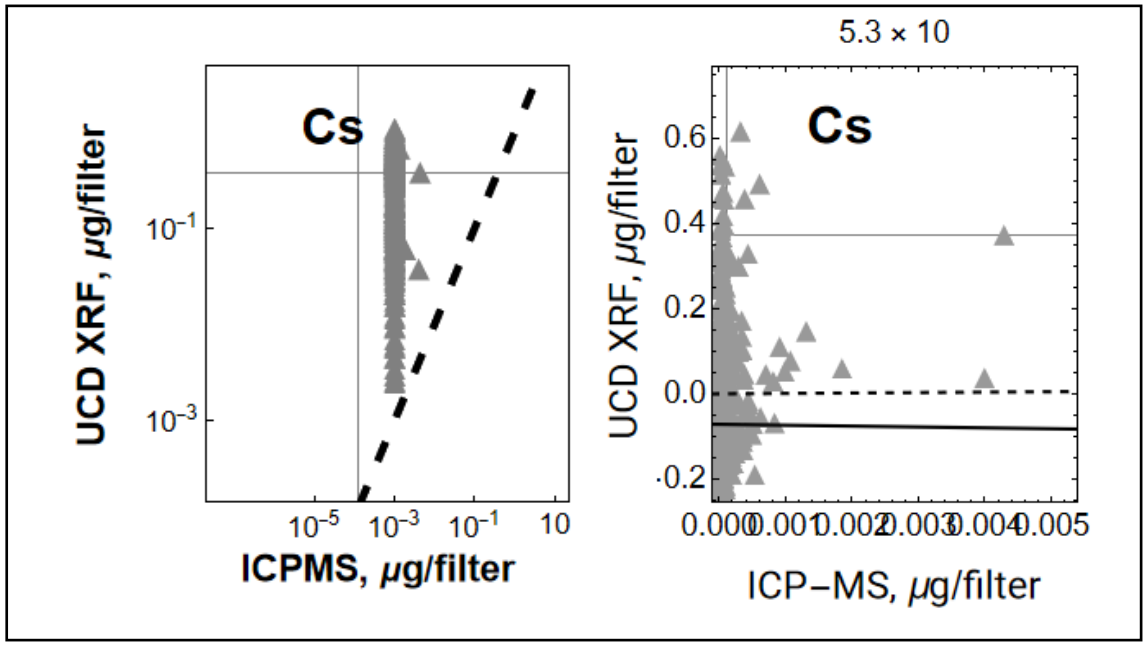


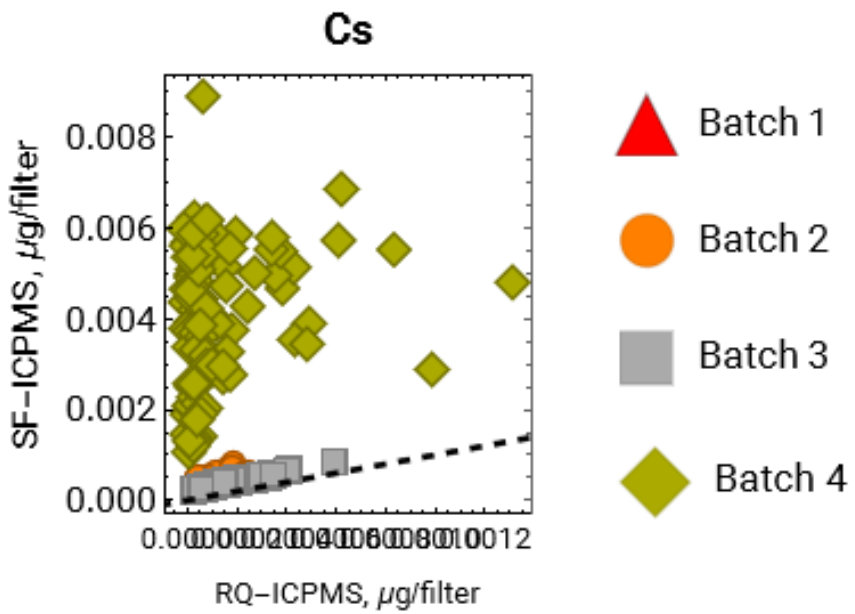


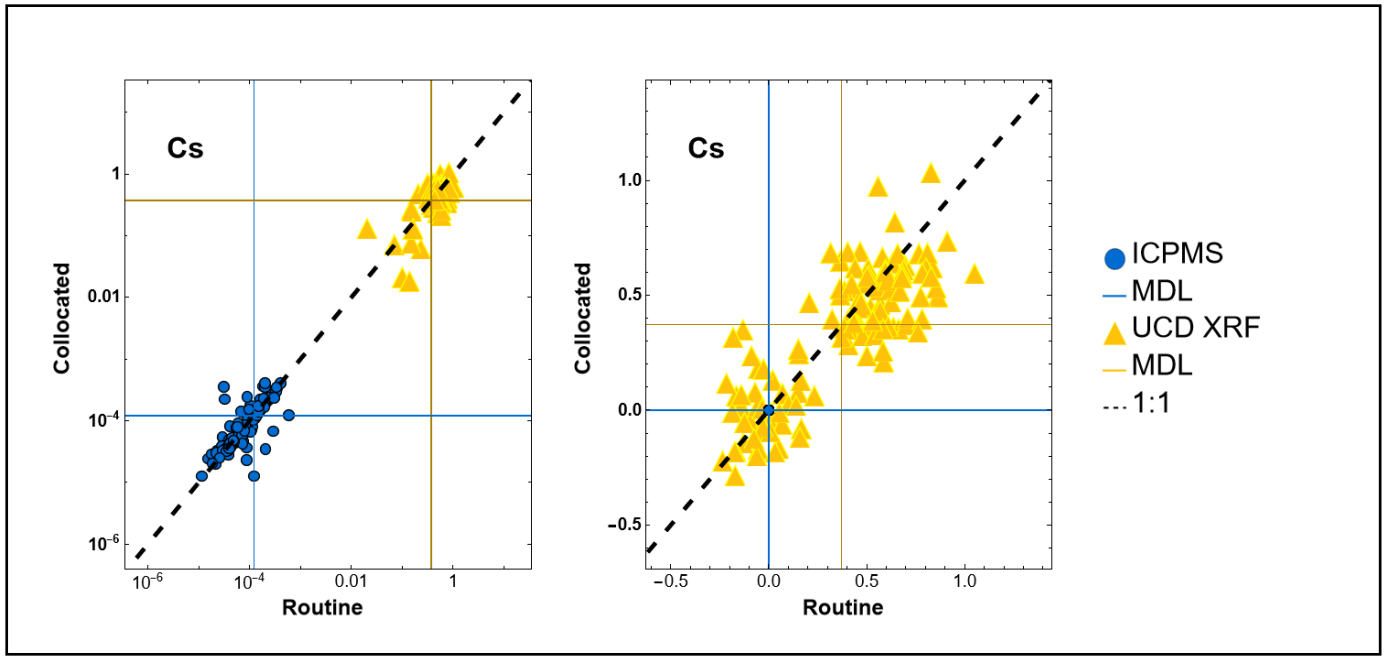


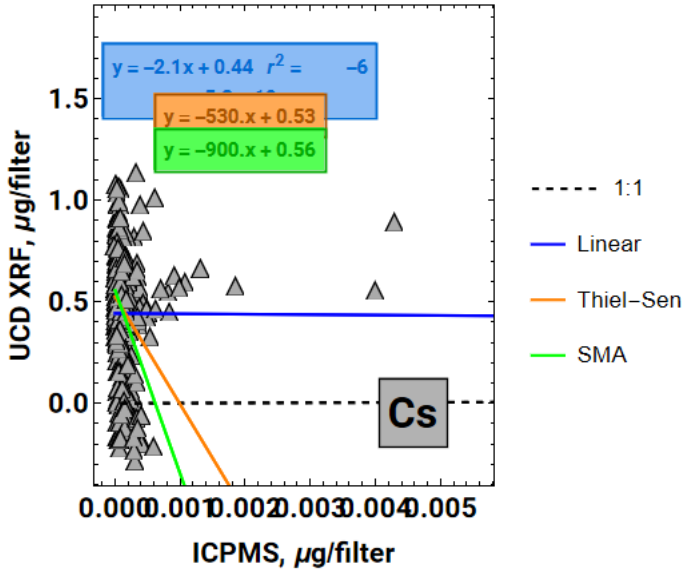
Cs

XRF > 10% MDL	NO
% above MDL	3%
RQ ICPMS >10% MDL	YES
% above MDL	28%
RQ ICPMS 1648a recovery acceptable? (5% HNO3 + 2 hour hot block digestion)	NO
Which MDL is lower	ICPMS



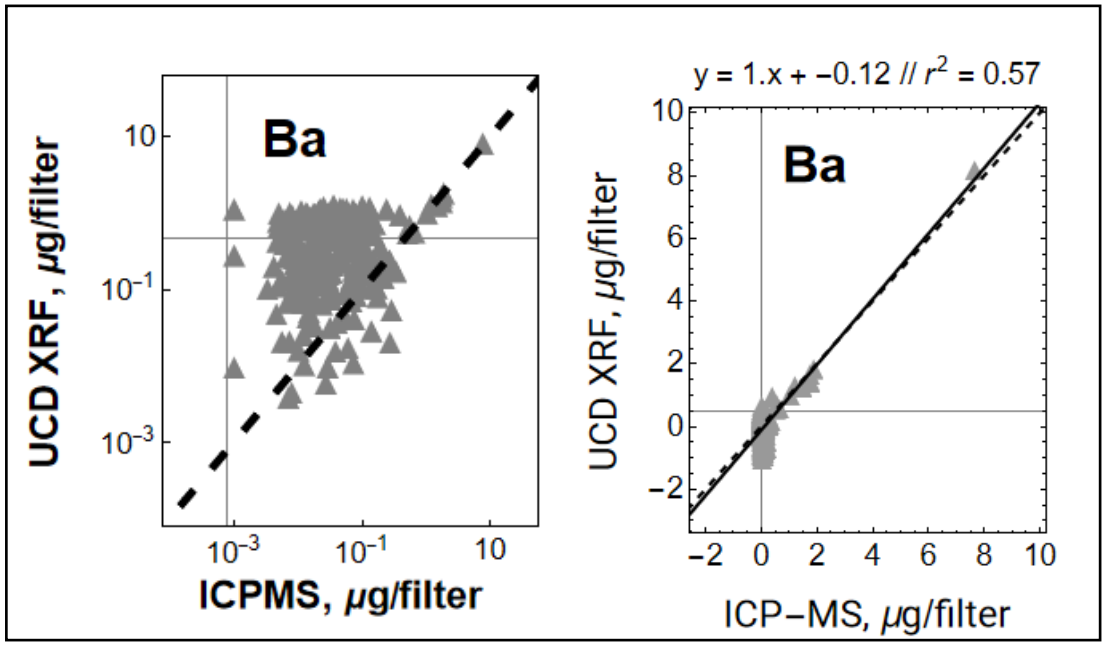


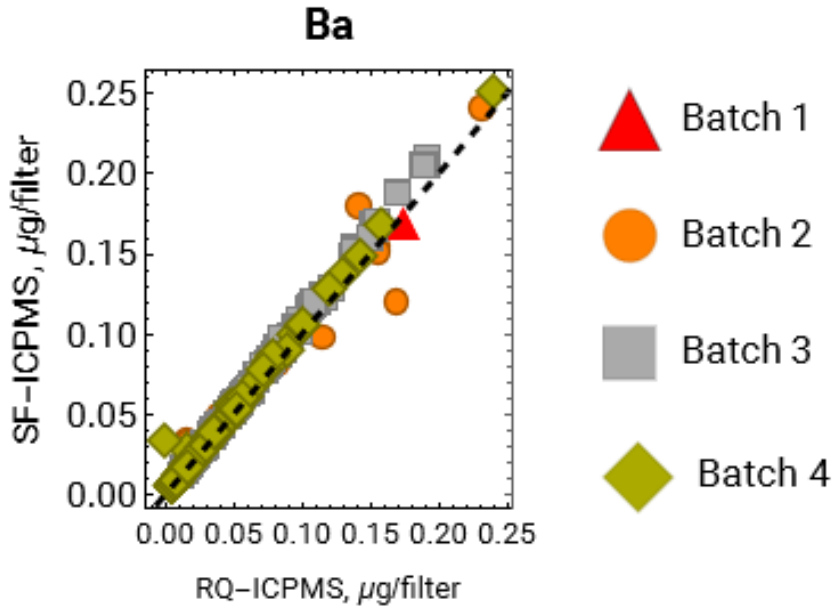


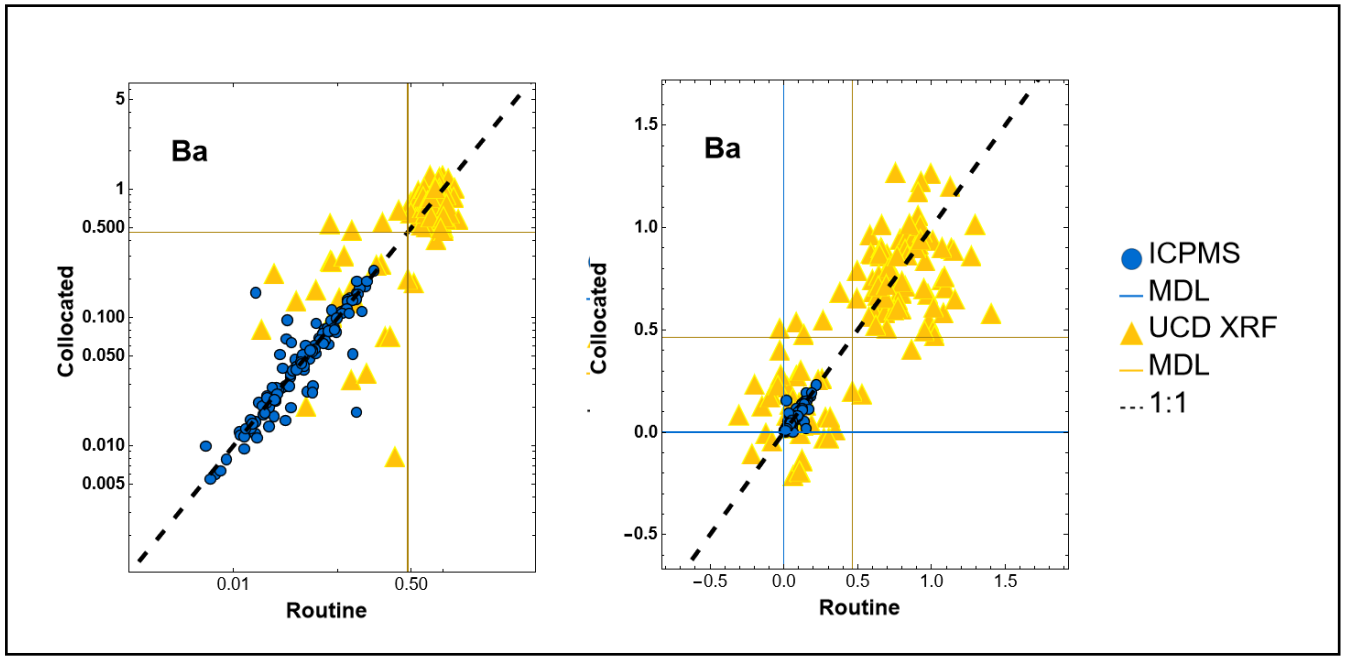


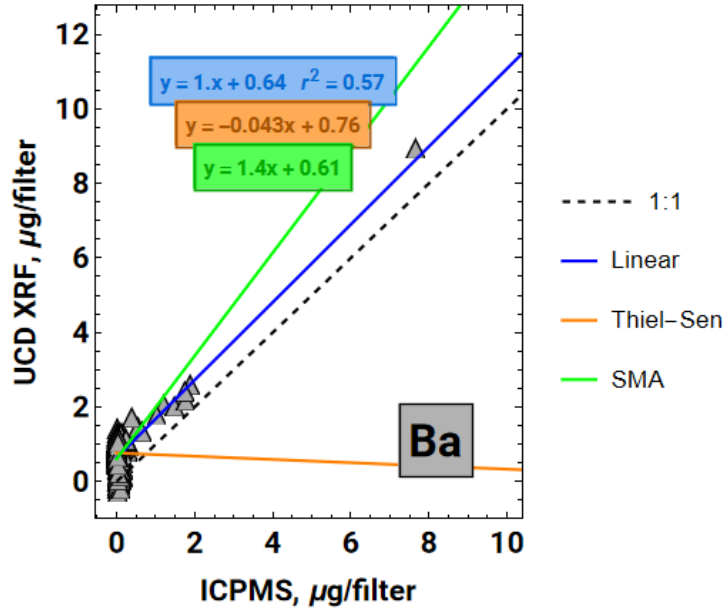
Ba

XRF > 10% MDL	NO
% above MDL	4%
RQ ICPMS >10% MDL	YES
% above MDL	99%
RQ ICPMS 1648a recovery acceptable? (5% HNO3 + 2 hour hot block digestion)	Not evaluated
Which MDL is lower	ICPMS



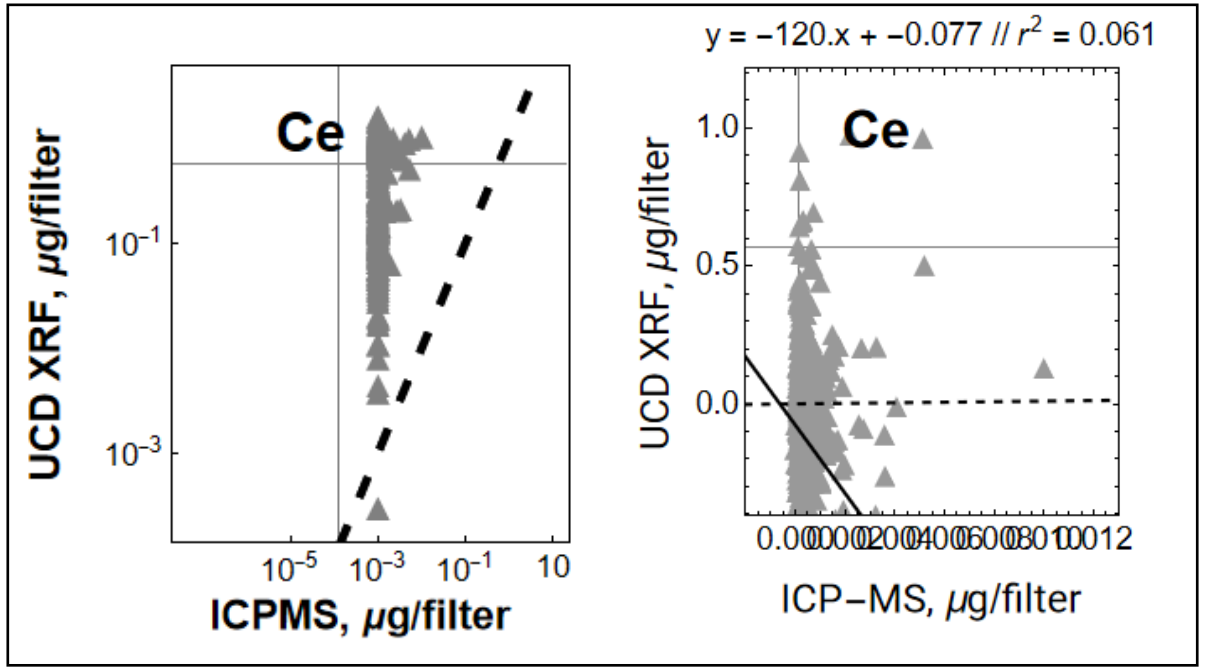


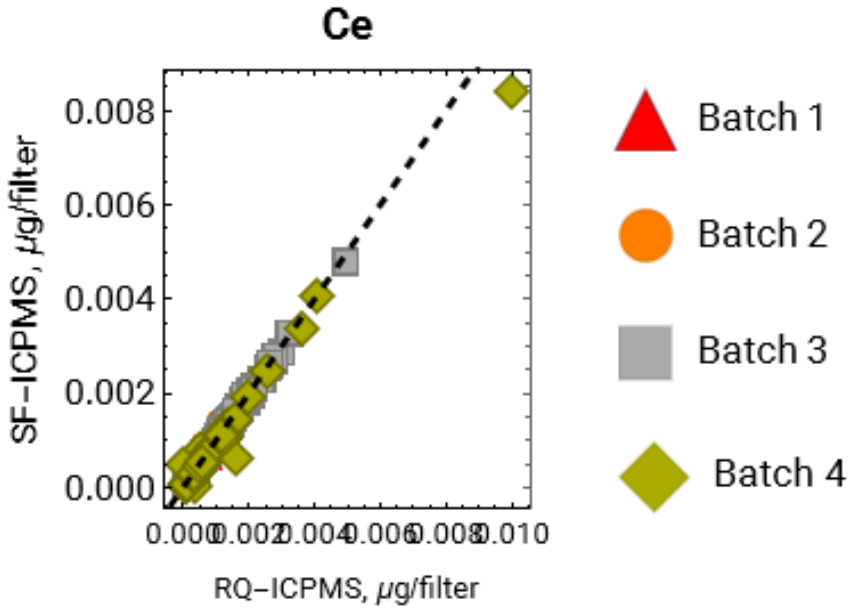


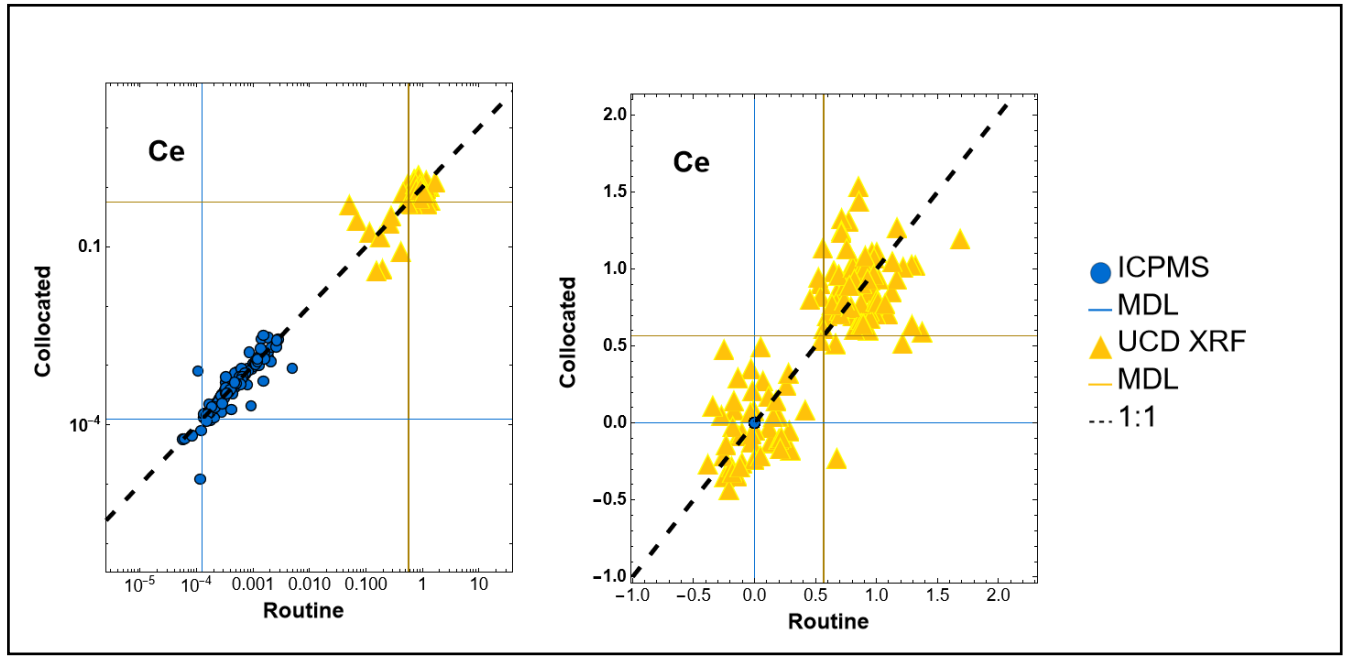


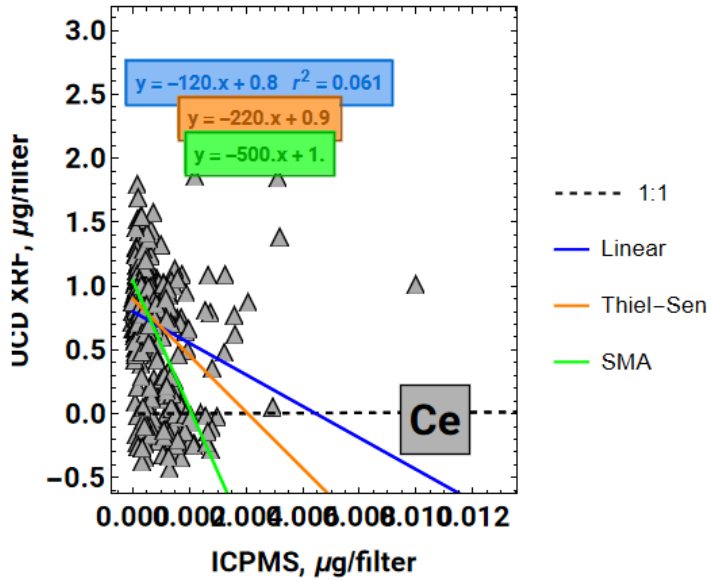
Ce

XRF > 10% MDL	NO
% above MDL	2%
RQ ICPMS >10% MDL	YES
% above MDL	91%
RQ ICPMS 1648a recovery acceptable? (5% HNO3 + 2 hour hot block digestion)	NO
Which MDL is lower	ICPMS



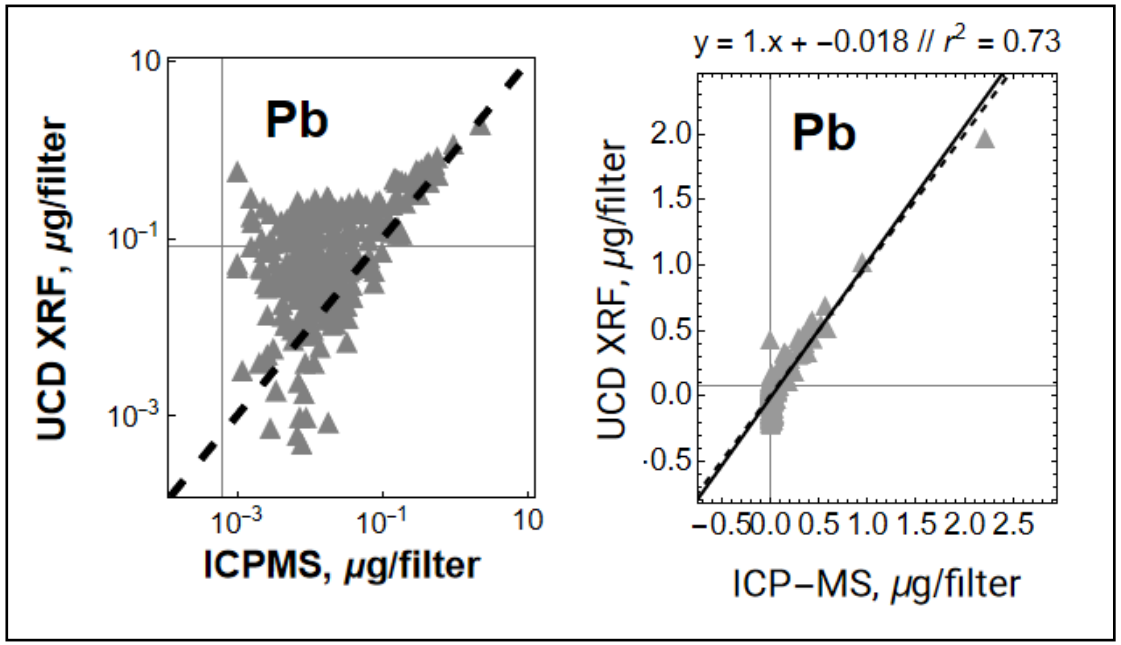


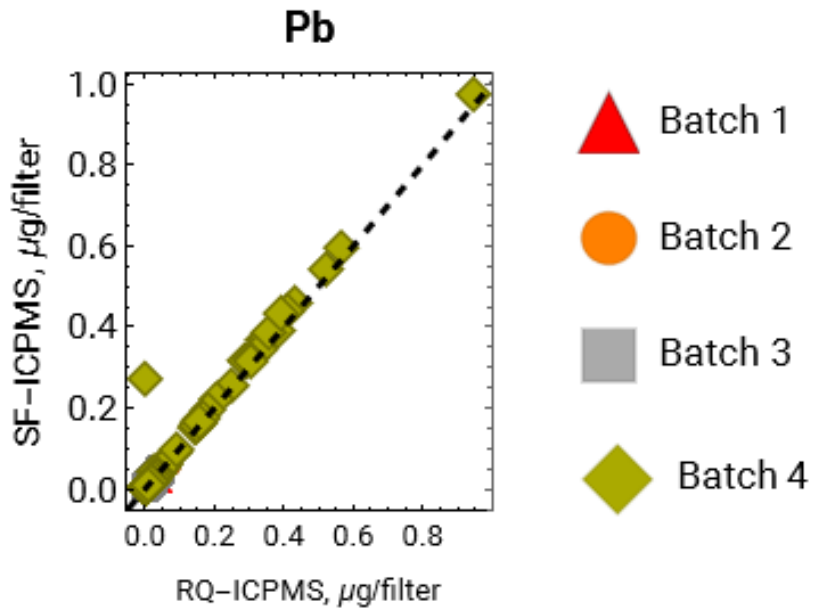


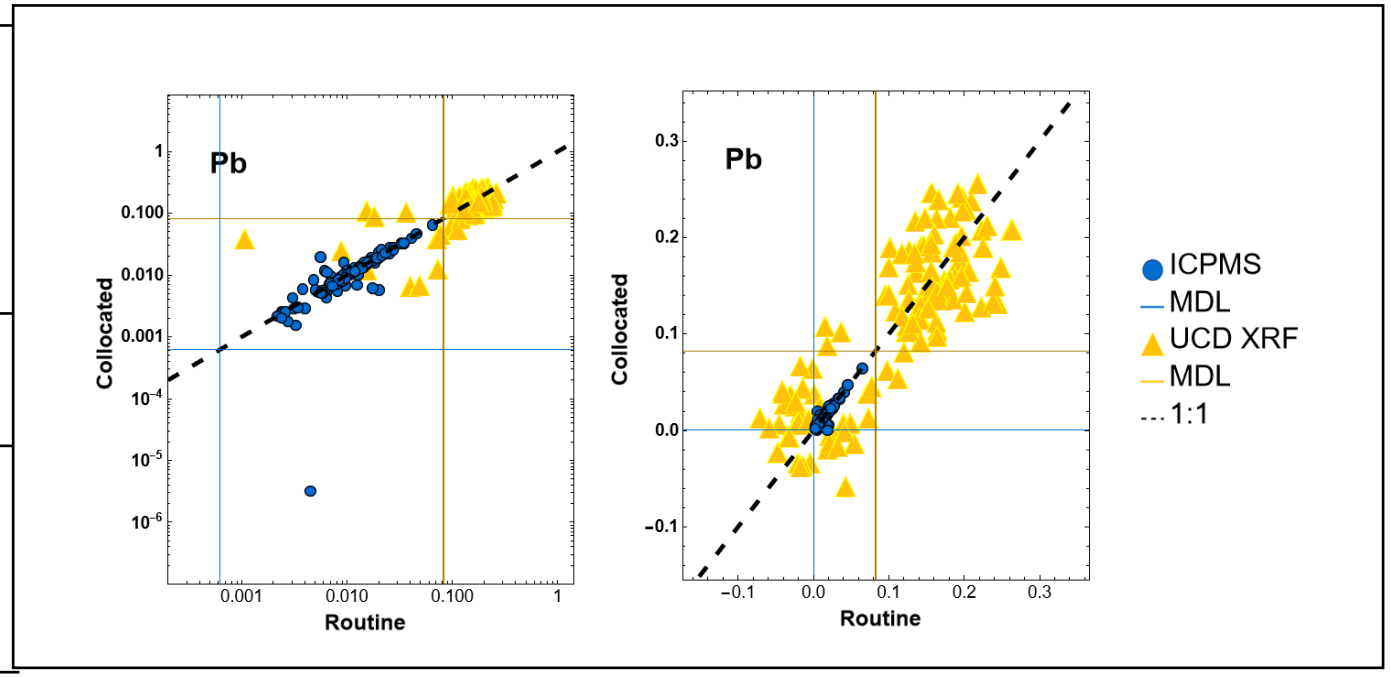


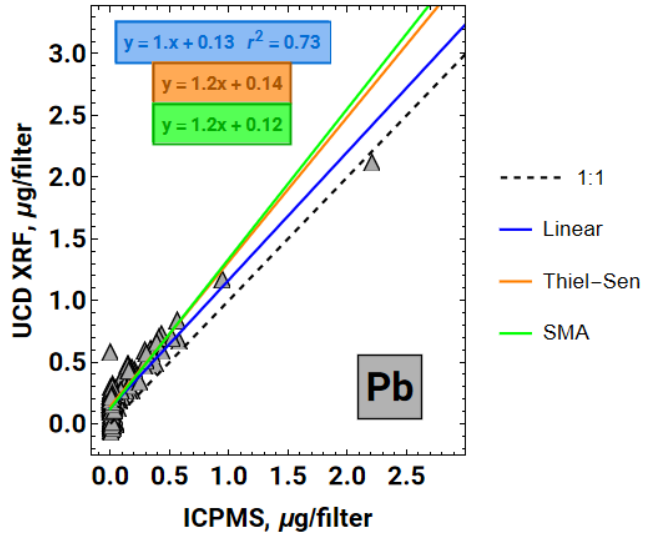
Pb

XRF > 10% MDL	YES
% above MDL	15%
RQ ICPMS > 10% MDL	YES
% above MDL	99%
RQ ICPMS 1648a recovery acceptable? (5% HNO3 + 2 hour hot block digestion)	YES
Which MDL is lower	ICPMS
Other notes	Pb is "noise" above MDL in XRF - ICPMS intercomparison





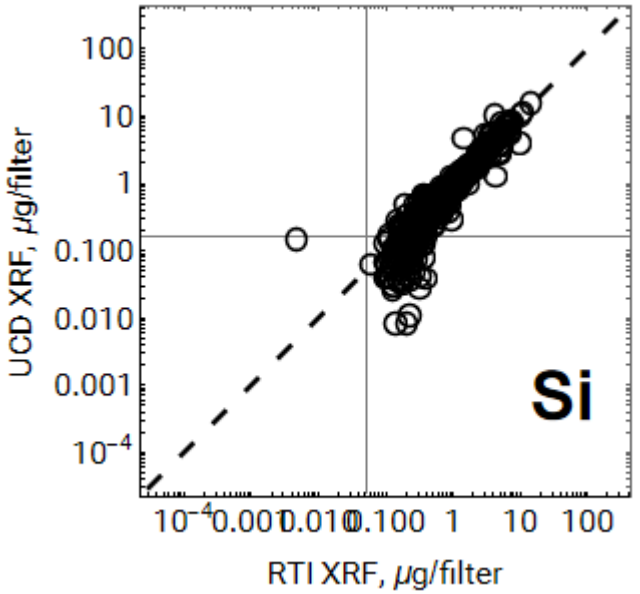


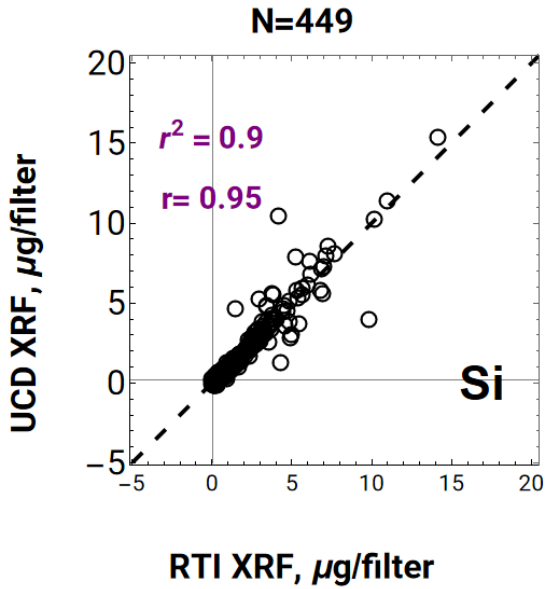


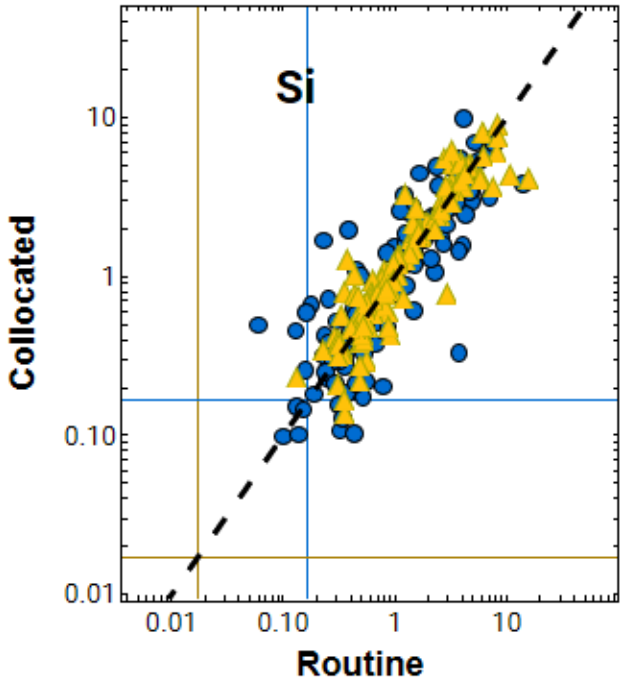
XRF-Only elements

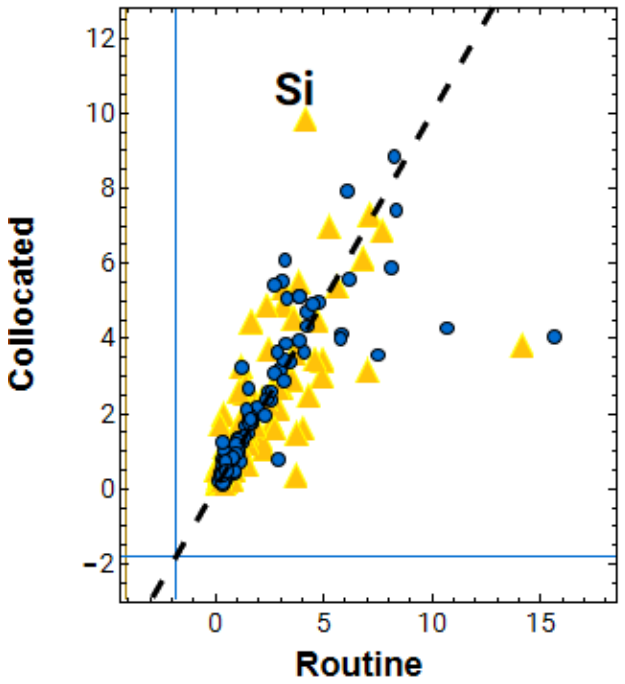
Si

XRF > 10% MDL	YES
% above MDL	78%
RQ ICPMS > 10% MDL	NO (not measured)
RQ ICPMS 1648a recovery acceptable? (5% HNO3 + 2 hour hot block digestion)	NO (not measured)





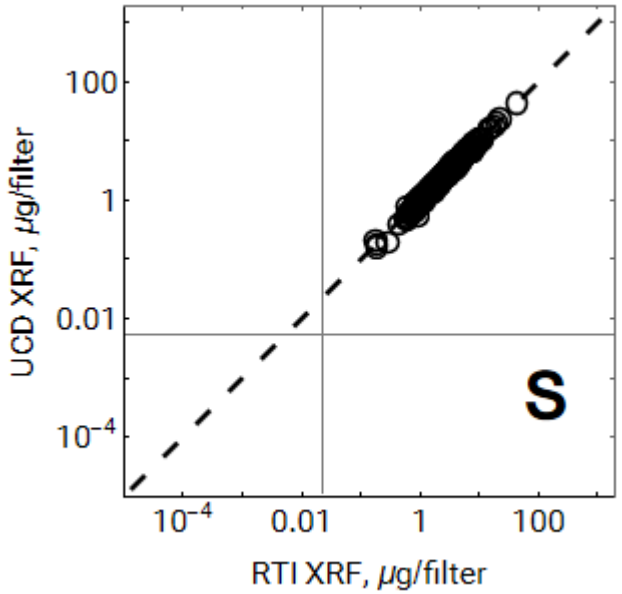


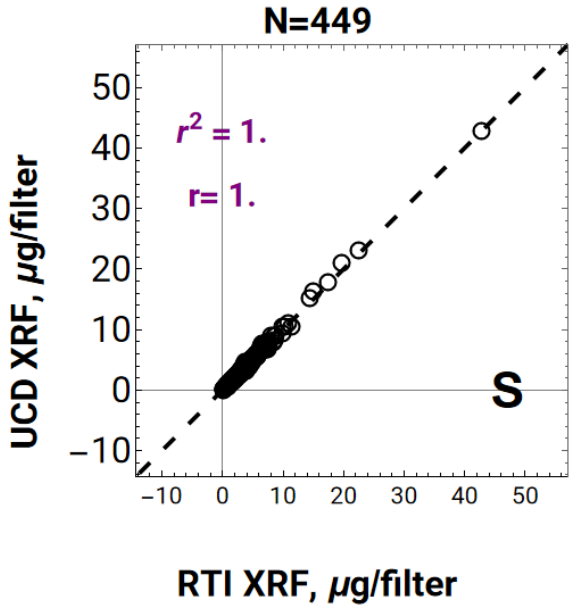


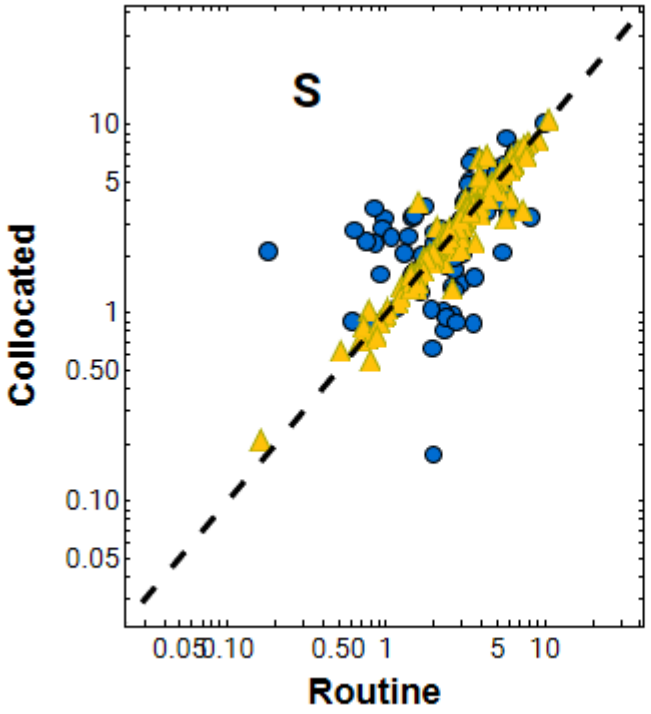
UCD XRF
MDL
RTI XRF
MDL
1:1

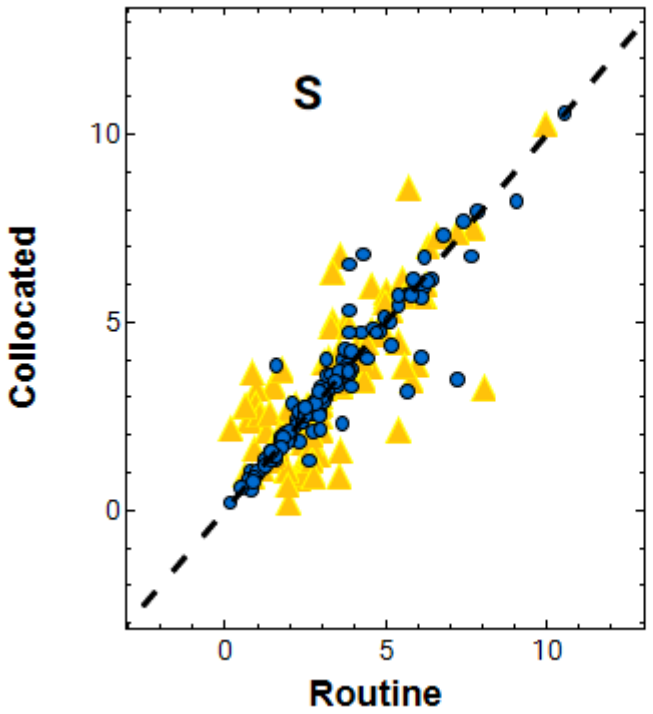
S

XRF > 10% MDL	YES
% above MDL	100%
RQ ICPMS > 10% MDL	No (not measured
RQ ICPMS 1648a recovery acceptable? (5% HNO3 + 2 hour hot block digestion)	Not evaluated





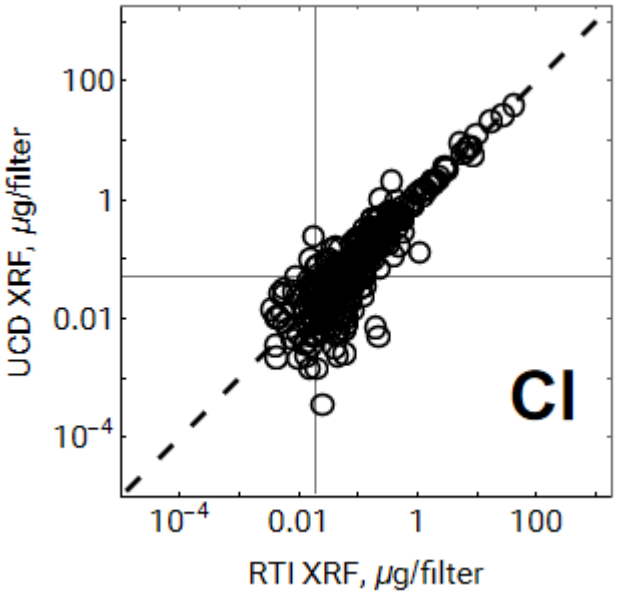


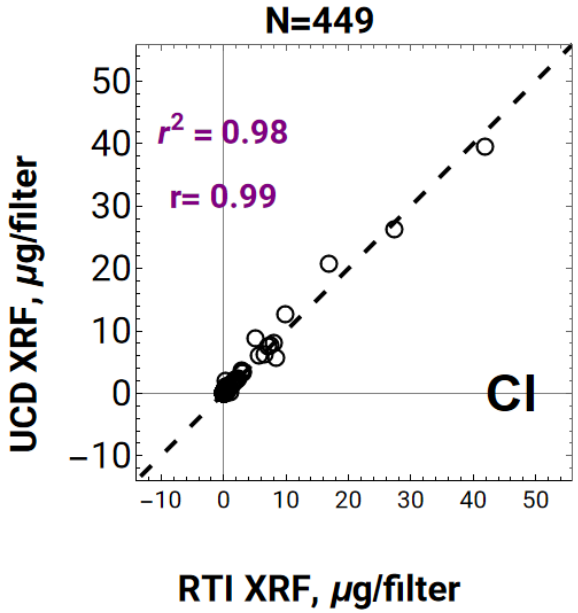


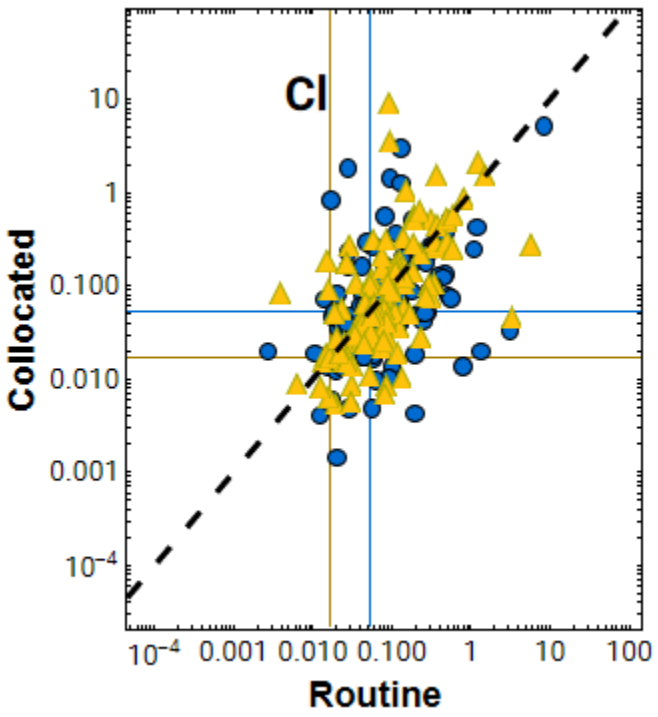
UCD XRF
MDL
RTI XRF
MDL
1:1

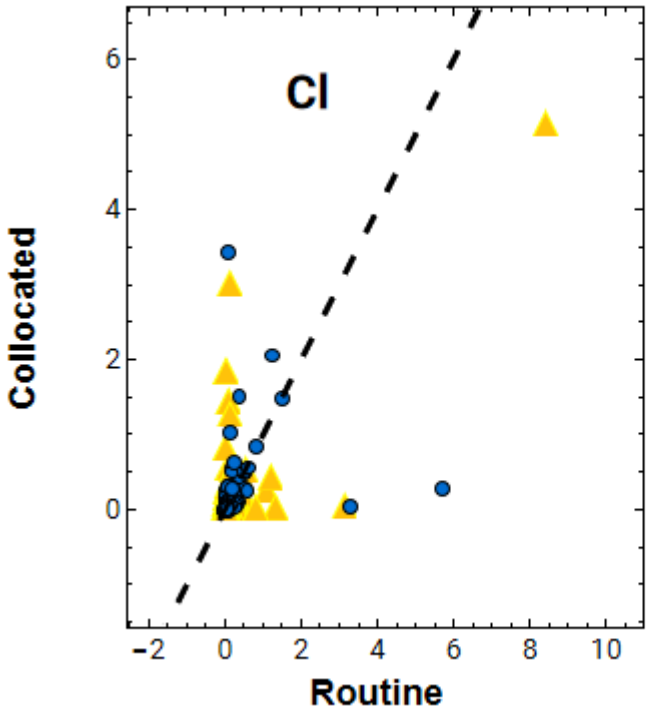
Cl

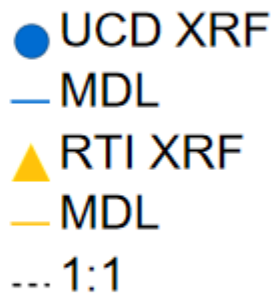
XRF > 10% MDL	YES
% above MDL	50%
RQ ICPMS > 10% MDL	No (not measured
RQ ICPMS 1648a recovery acceptable? (5% HNO3 + 2 hour hot block digestion)	Not evaluated





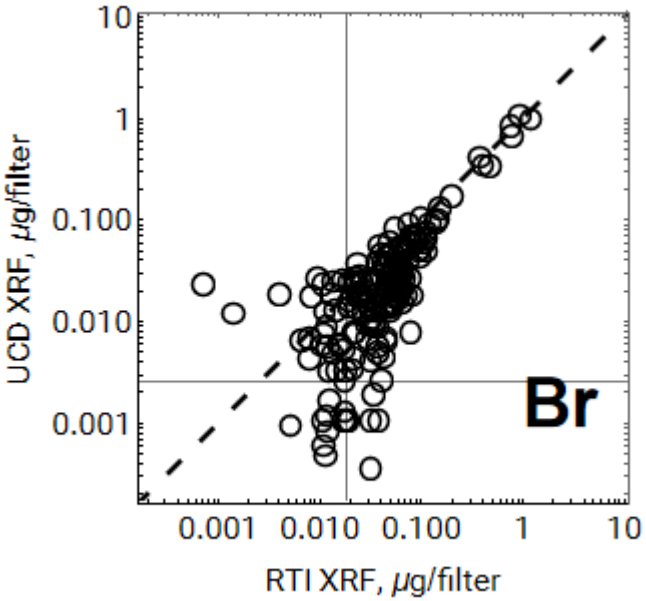


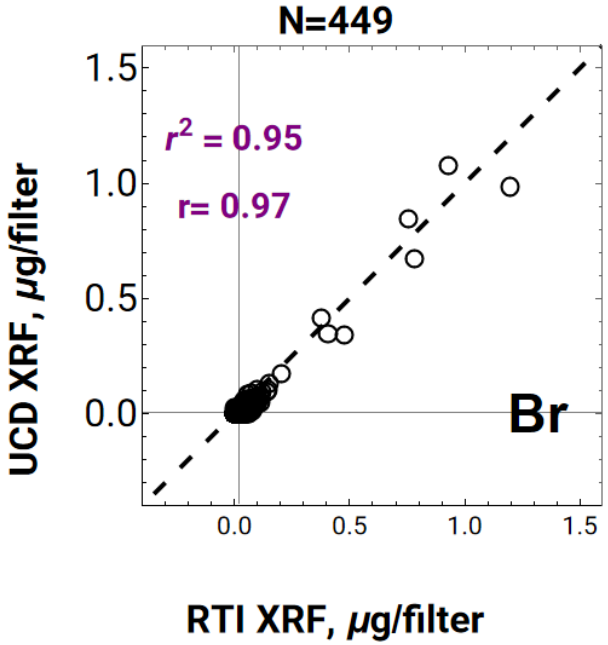


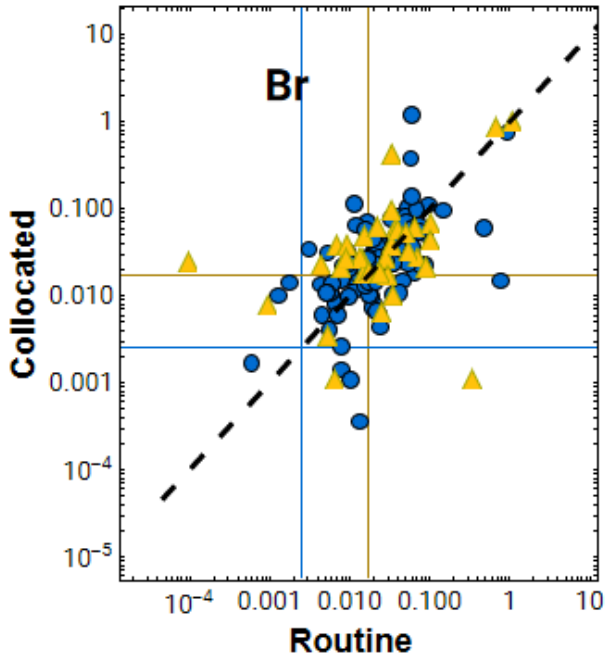


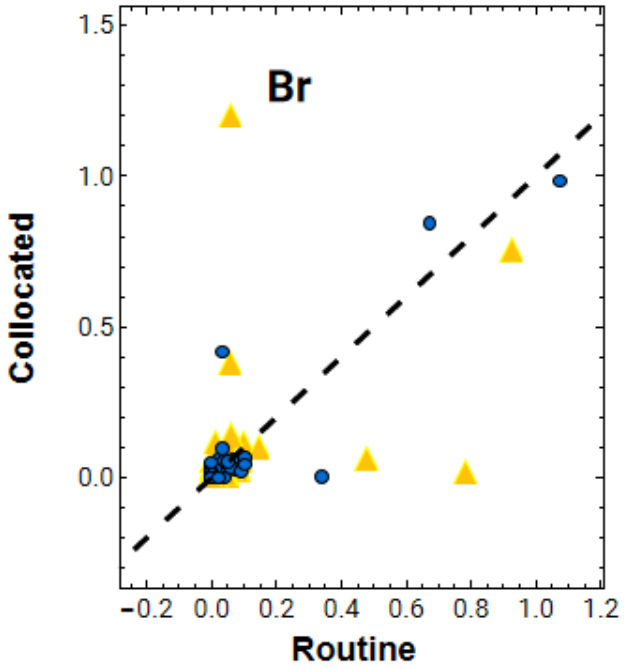
Br

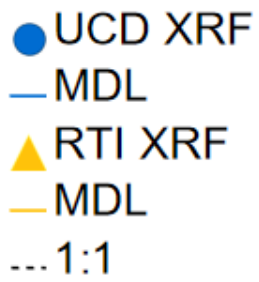
XRF > 10% MDL	YES
% above MDL	37%
RQ ICPMS > 10% MDL	NO
RQ ICPMS 1648a recovery acceptable? (5% HNO3 + 2 hour hot block digestion)	Not evaluated







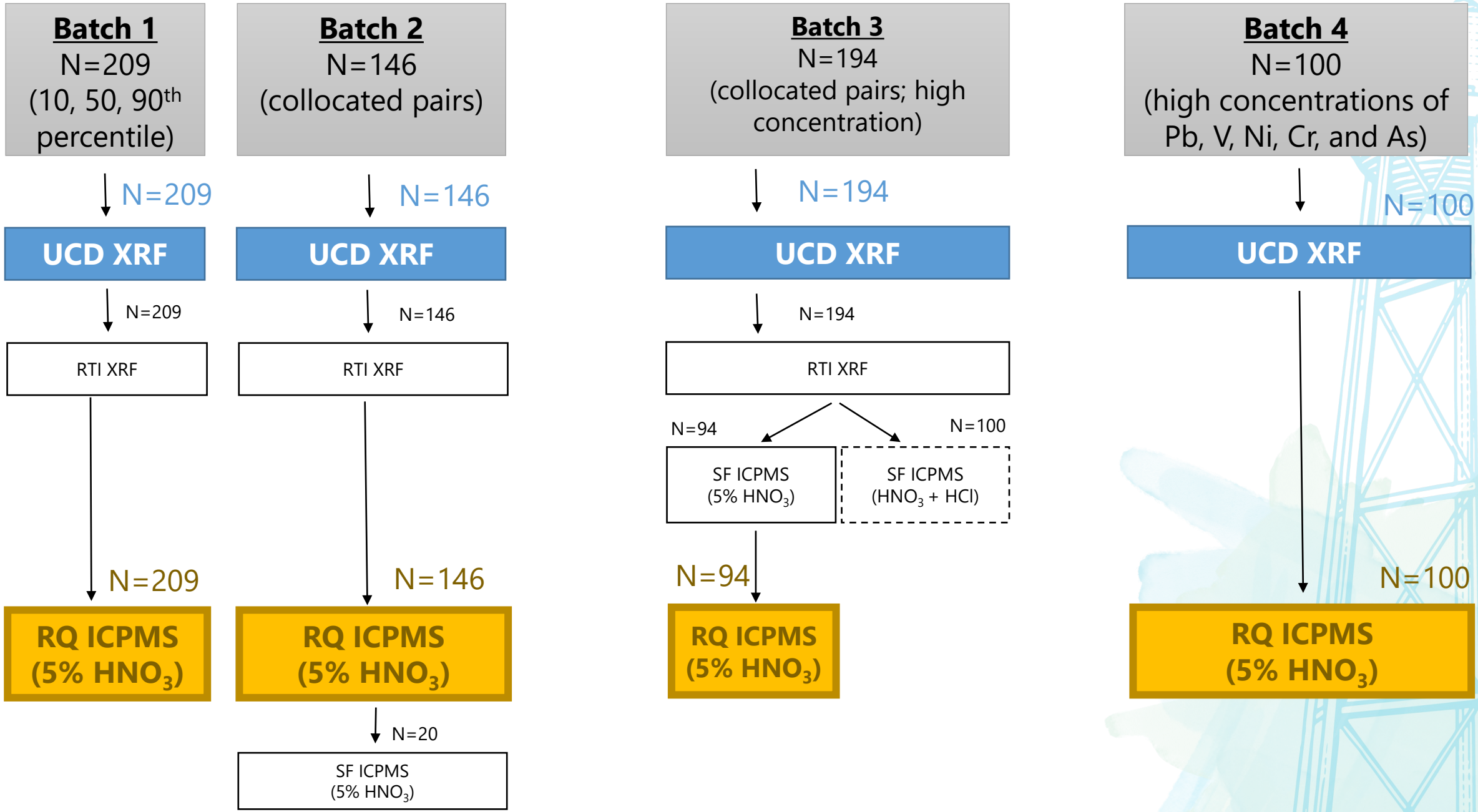




CSN samples

- *N* = 549
- January 2019 – June 2022
- 10^{th}, 50^{th}, and 90^{th} percentiles in the network for each element
- High concentrations of Pb, V, Ni, Cr, and As

- Routine-collocated sample pairs for sample precision estimates
  - Rutgers, NJ
  - Dudley Square, Boston, MA
  - Rubidoux, Riverside, CA
  - Bakersfield, CA
  - G.T. Craig, OH
  - Deer Park, Houston, TX



5% HNO_3 + graphite block (90 mins 95°C)

10% HNO_3 + 3% HCl + 2 mL H_2O_2 (60 mins 95°C, 30 mins 95°C)

Considerations:

- **Were the elements detected?**

  Intra-method: Method detection limits

- **Are the reported concentrations reliable?**

  Inter-method: XRF-ICPMS intercomparison

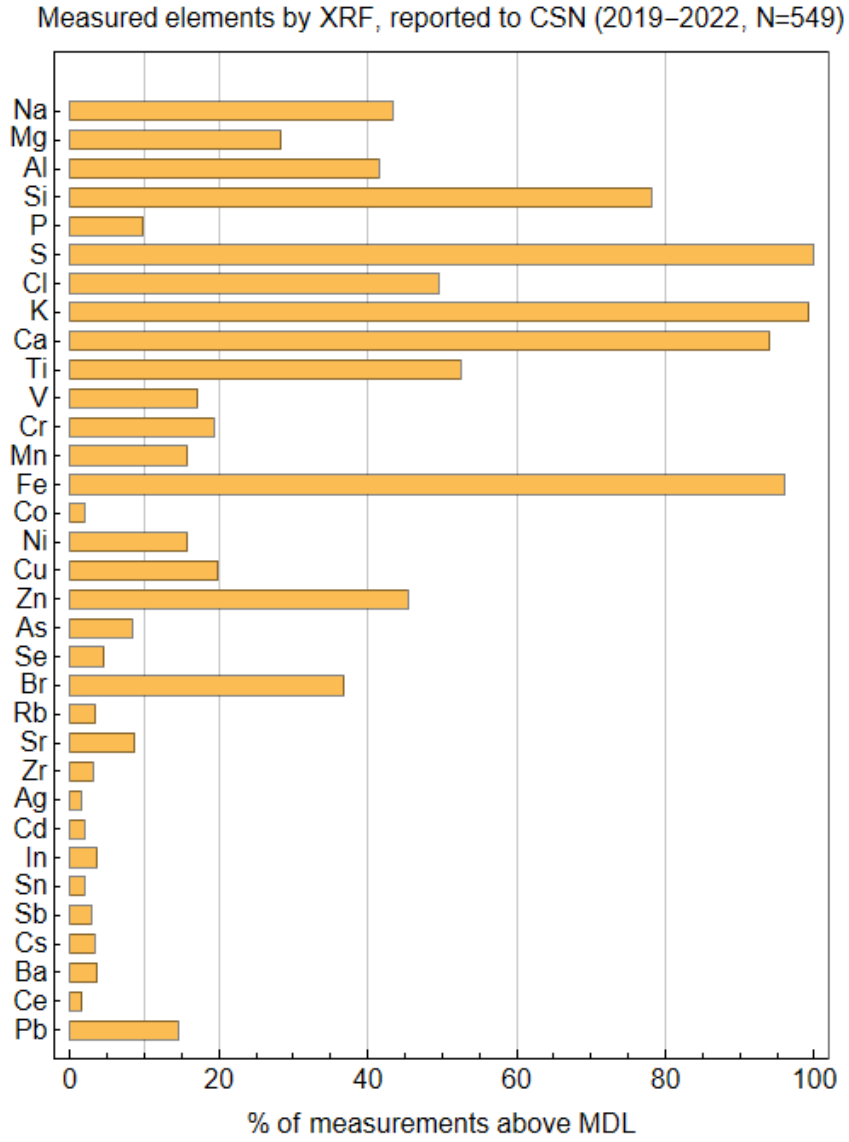
  Intra-method: inter-elemental comparison; collocated samples (precision)

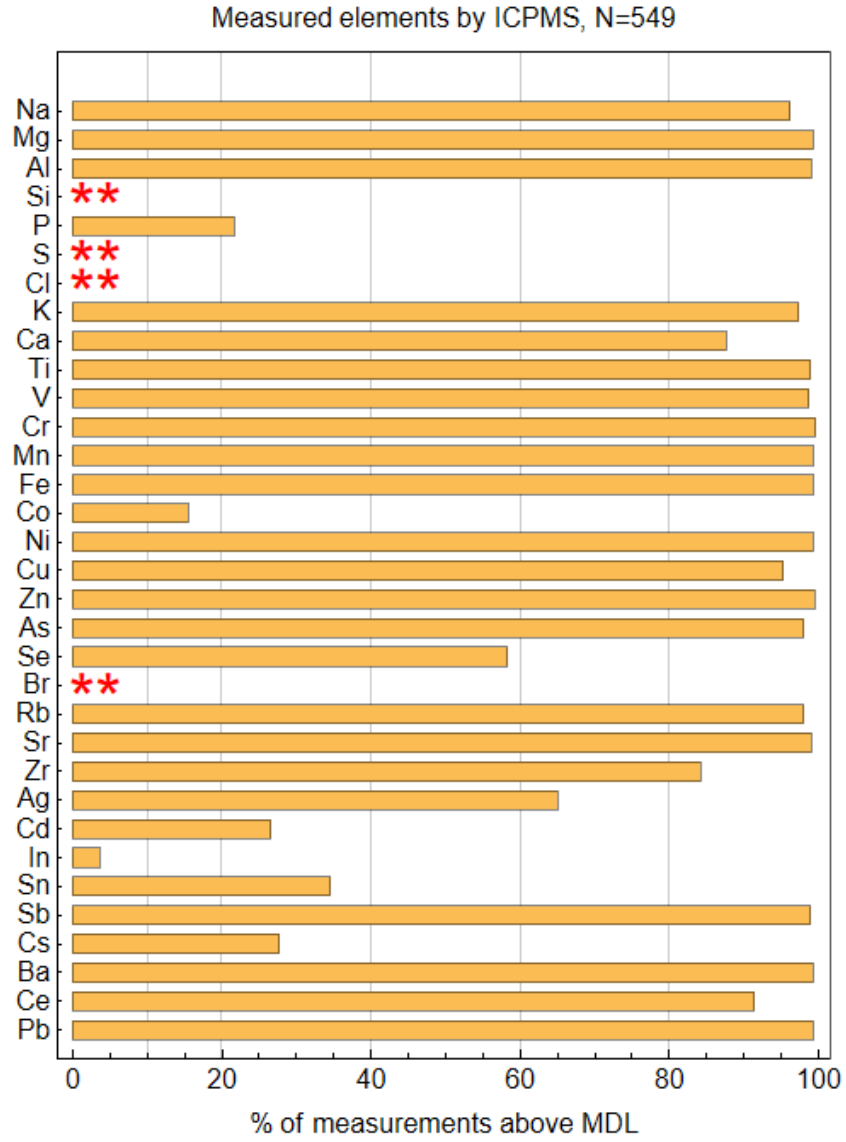
- **Was the ICPMS extraction complete?**

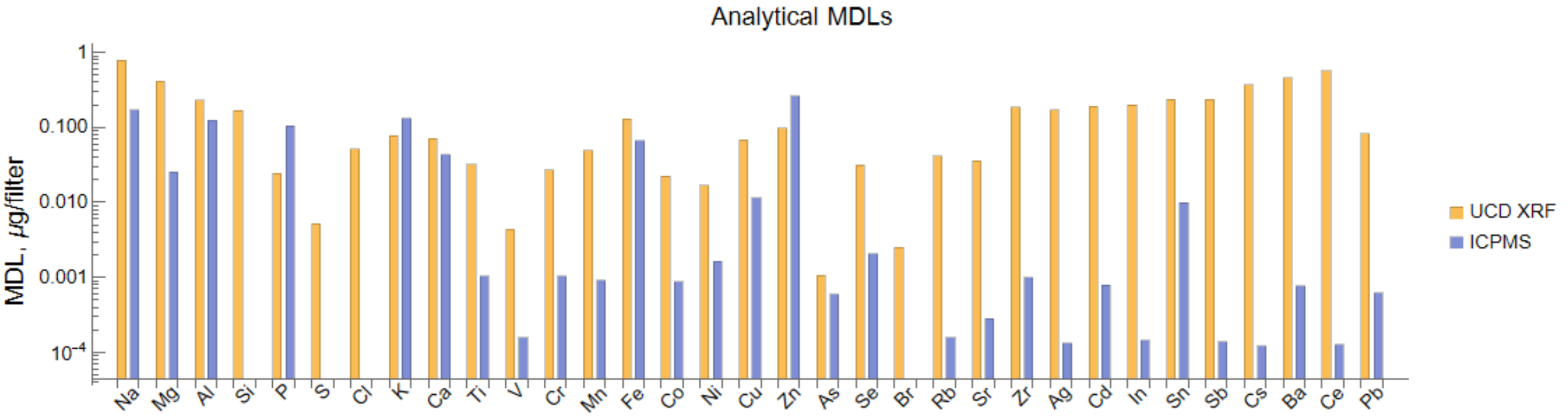
  Evaluated using reference materials (NIST SRM 1648a, 1633)

XRF and ICPMS MDL

- For most elements up to Zn, XRF can detect more than 10% of the time above MDL.
- Because of its lower MDL for most elements, ICPMS can detect elements in samples with lower elemental concentrations.







- XRF MDL are high compared to most elements measured by ICP-MS

XRF MDL is lower	ICPMS MDL is lower
P, K, and Zn	Na, Mg, Al, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, As, Se, Rb, Sr, Zr, Ag, Cd, In, Sn, Sb, Cs, Ba, Ce, Pb

Element	UCD MDL	Blank Median	UCD Percent Above MDL	ICPMS MDL	ICP Percent Above MDL
Na	0.791596	0.0001186	43.3515	0.169934	96.1749
Mg	0.410342	0.0451273	28.4153	0.025551	99.2714
Al	0.23384	0.924072	41.5301	0.1238	99.0893
P	0.0244645	0	9.83607	0.104349	21.6758
K	0.0767471	0.0963032	99.2714	0.13369	97.2678
Ca	0.0711451	0.0348684	93.9891	0.0430899	87.6138
Ti	0.0318934	0.021348	52.459	0.0010327	98.9071
V	0.004392	0	17.122	0.000157343	98.725
Cr	0.0271359	0.0467284	19.3078	0.00103083	99.6357
Mn	0.0488971	0.0697368	15.847	0.000905541	99.2714
Fe	0.128732	0.23127	95.9927	0.06664	99.2714
Co	0.0225206	0.0149436	2.00364	0.000880229	15.4827
Ni	0.0169761	0.0105554	15.847	0.00163975	99.2714
Cu	0.0675928	0.0902546	19.8543	0.0115674	95.2641
Zn	0.0981903	0.0279896	45.3552	0.26422	99.4536
As	0.00107128	−0.000593	8.37887	0.000595477	97.9964
Se	0.0316518	0.0240758	4.55373	0.00208469	58.2878
Rb	0.0414033	0.0315476	3.46084	0.000159129	97.9964
Sr	0.03547	0.0447122	8.74317	0.000283082	99.0893
Zr	0.187611	0.196164	3.09654	0.00100512	84.153
Ag	0.170774	0.211701	1.45719	0.000131314	65.0273
Cd	0.189166	0.221308	2.00364	0.000793441	26.5938
In	0.199677	0.263292	3.64299	0.000143529	3.64299
Sn	0.23887	0.339789	2.00364	0.0099216	34.6084
Sb	0.238031	0.327514	2.91439	0.000137836	98.9071
Cs	0.372381	0.514546	3.27869	0.000120559	27.6867
Ba	0.46248	0.755956	3.64299	0.00077041	99.2714
Ce	0.565944	0.876988	1.63934	0.000125839	91.439
Pb	0.0823247	0.145997	14.5719	0.000618232	99.2714

How MDL were calculated

Analytical MDL calculations

UCD XRF

$$MDL = P_{95} - median$$

- P95 = 95th percentile of at least 50 lab blanks
- median= median of at least 50 lab blanks

ICP-MS

- EPA-821-R-16-006: Definition and Procedure for the Determination of the Method Detection Limit, Revision 2
- The greater value when comparing the spiked and the blank was taken as the MDL.

ICP-MS Analytical MDL

EPA-821-R-16-006: Definition and Procedure for the Determination of the Method Detection Limit, Revision 2

$$MDL_S = t_{(n-1,\ 1-\alpha=0.99)} S_S$$

where:

MDL_s = the method detection limit based on spiked samples

$t_{(n-1,\ 1-\alpha = 0.99)}$ = the Student's *t*-value appropriate for a single-tailed 99th percentile *t* statistic and a standard deviation estimate with n-1 degrees of freedom. See Addendum Table 1.

S_s = sample standard deviation of the replicate spiked sample analyses.

$$MDL_b = \overline{X} + t_{(n-1,1-\alpha=0.99)} S_b$$

where:

MDL_b = the MDL based on method blanks

$\overline{X}$ = mean of the method blank results (use zero in place of the mean if the mean is negative)

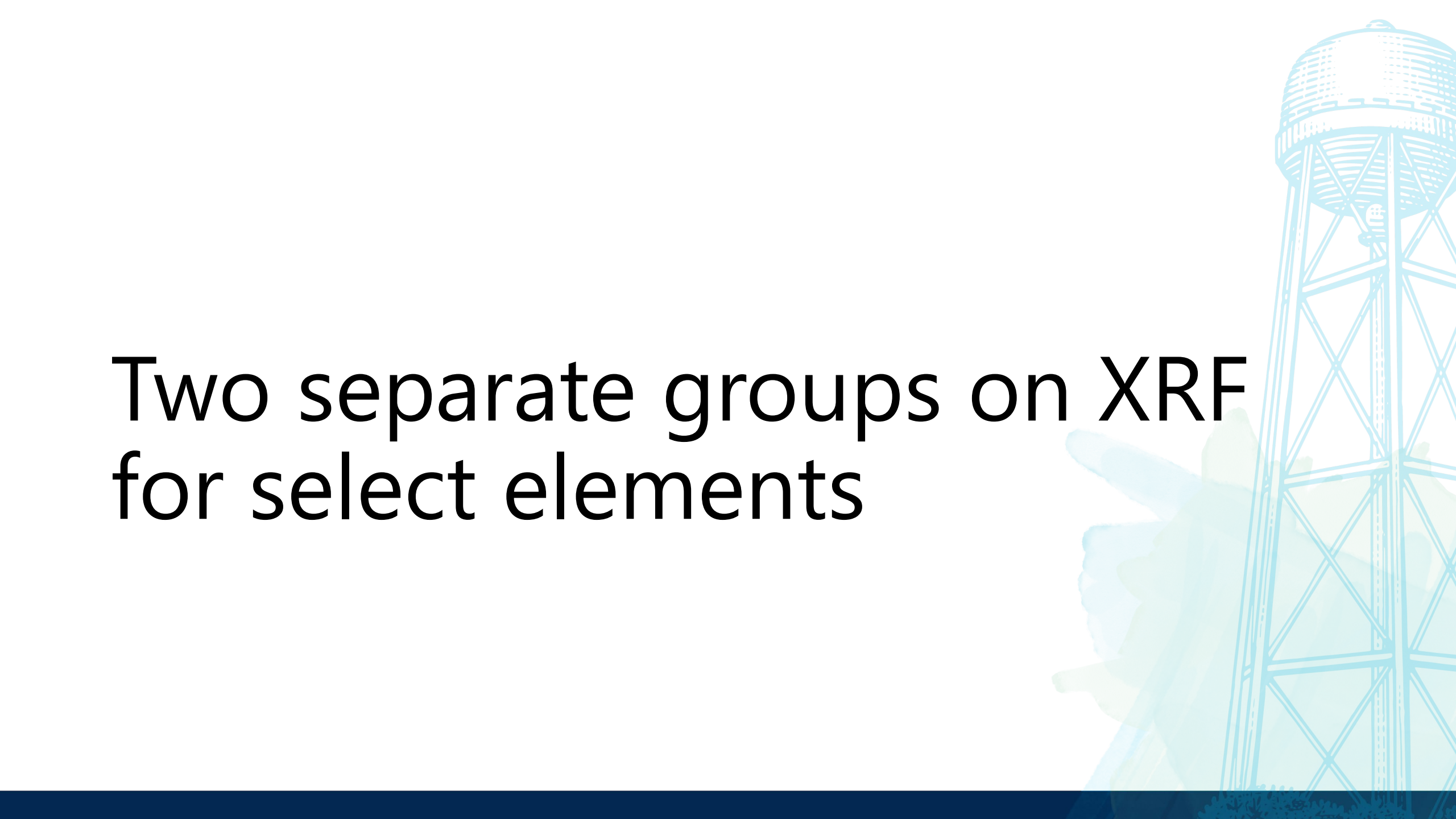
$t_{(n-1,\ 1-\alpha = 0.99)}$ = the Student's *t*-value appropriate for the single-tailed 99th percentile *t* statistic and a standard deviation estimate with n-1 degrees of freedom. See Addendum Table 1.

S_b = sample standard deviation of the replicate method blank sample analyses.

RTI XRF

- The uncertainty is calculated for each sample and element when analyzed. (See Gutknecht, et al 2010)
- MDL = 3x average uncertainty from from 10 blank filters.

Two separate groups on XRF for select elements



Batch 1 N=209 (10, 50, 90th percentile)	**Batch 2** N=146 (collocated pairs)	**Batch 3** N=194 (collocated pairs; high concentration)	**Batch 4*** N=100 (high concentrations of Pb, V, Ni, Cr, and As)

*Batch 4 had no routine/collocated pairs