A Collaborative Approach to Updating EPA Method 3050

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Outline

- Overview
- 3050B vs. Draft 3050C (original rev)
- Initial Proof of Concept Experiments
- Revision of Draft 3050C
- Multi-Lab Validation Study
- Conclusions

Note: Data presented remains under EPA review and may not be final.

Overview

Updating EPA Method 3050B

- EPA's Office of Resource Conservation and Recovery (ORCR) proposed an update to SW-846 Method 3050B for the digestion of solids for metals analysis.
  - Draft Method 3050C: changes to the acids added and the timing of the acid additions
- Draft method pre-released to a small group of labs
  - → Issues were identified with some elements (in particular, Ag and Sb)
  - → Hypothesis: HCl needed at end of digestion to stabilize some elements
- Mini-research study to determine the optimal timing and volume of the acid additions.
- Draft method was then revised and distributed to 15 laboratories for a full multi-laboratory validation study:
  - Triplicate analyses on 5 reference materials for 23-element lists
  - Digestion by both Method 3050B and Draft Method 3050C

What is Method 3050?

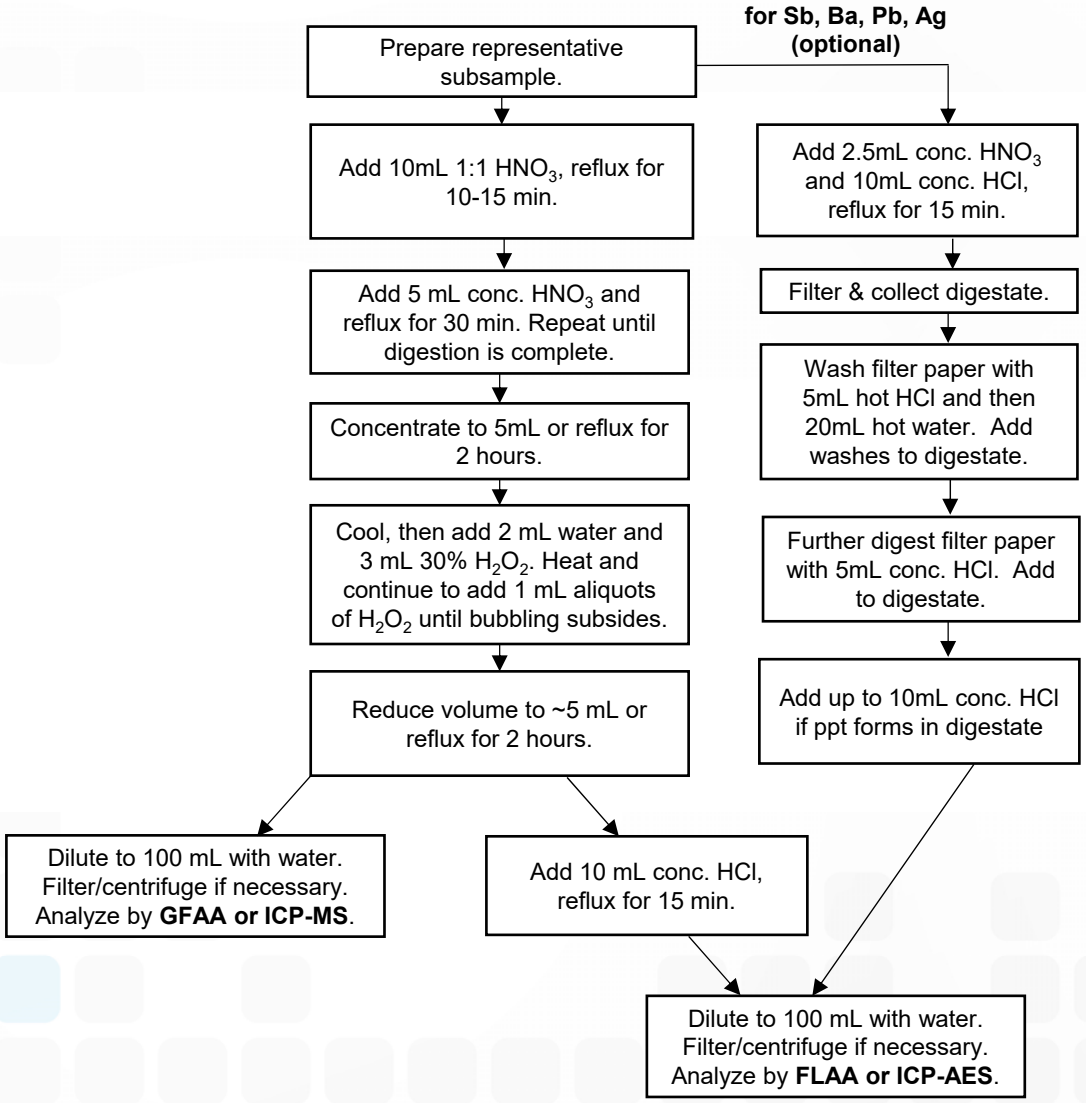
- Very strong acid digestion for total recoverable metals in sediment, sludge, soil
- Biggest difference between “total” and “total recoverable” is for elements such as noble metals, refractory elements (e.g., Pd, Si, W, Zr), or elements bound in silicate structures
- Addition of HCl was optional in 3050B, since HCl was an interference for the determination of some key elements (e.g., As, Cr) by standard ICP-MS
- Modern ICP-MS instruments use interference reduction technology (i.e., DRC, CC, QQQ) to remove many Cl-based interferences, and the addition of HCl improved recoveries and increased digestate stability for elements such as Sb and Ag.

- Oct 2017 – Memo from EPA’s ORCR about updating SW-846 Method 3050B. Goals:
  - Streamline (one method to cover all analytes)
  - Encourage use of HCl to facilitate improved digestion and solubility
  - Solicit volunteer labs from ACIL to produce validation data

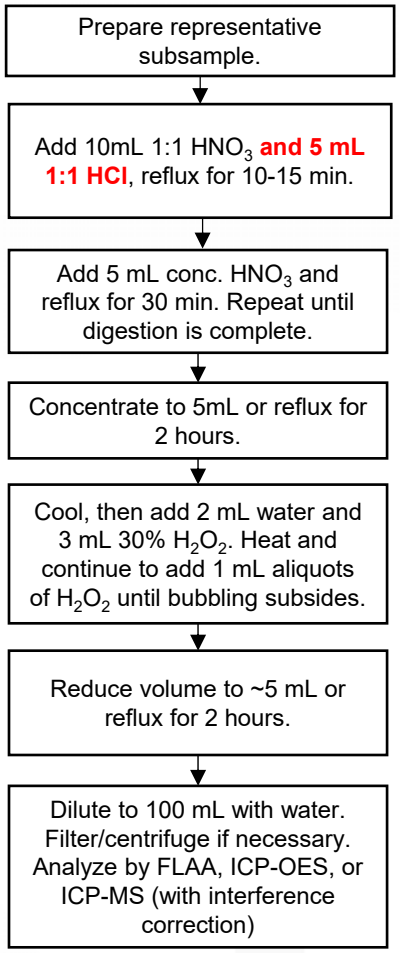
Method 3050B Analyte List

Aluminum (Al)	Antimony (Sb)	Arsenic (As)
Barium (Ba)	Beryllium (Be)	Cadmium (Cd)
Calcium (Ca)	Chromium (Cr)	Cobalt (Co)
Copper (Cu)	Iron (Fe)	Lead (Pb)
Magnesium (Mg)	Manganese (Mn)	Molybdenum (Mo)
Nickel (Ni)	Potassium (K)	Selenium (Se)
Silver (Ag)	Sodium (Na)	Thallium (Tl)
Vanadium (V)	Zinc (Zn)	

3050B



3050C (Initial Draft)



Issue

- Initial version of 3050C only added HCl at the beginning of the prep
- When evaluated at EPA Reg 10 Lab, low recoveries were observed for some elements
- Hypothesis: Rigorous digestion procedure likely causes the loss of too much HCl, resulting in an insufficient amount of HCl to keep all elements solubilized.

3050C Proof of Concept Study Plan

Purpose:

1. Determine whether HCl additions at the end of the digestion increase the robustness of the method with respect to HCl-influenced analytes.
2. Determine the influence of adding different volumes of HCl at the end of the digestion.

Variables:

1. Heating technique: hotplate vs hotblock
2. Volume of HCl added to the digestate at the end of the sample preparation: 0 mL per 100 mL (reflecting the 3050C status quo), 2 mL per 100 mL, 5 mL per 100 mL, and 10 mL per 100 mL (reflecting 3050B status quo with HCl option)

3050C Proof of Concept Study Plan

Participants

3050C Proof of Concept Study Plan

Sample Description	Amount of HCl (mL) to add (following H_2O_2 digestion step)			
Method Blank, rep 1	0	1	2.5	5
Method Blank, rep 2	0	1	2.5	5
Method Blank, rep 3	0	1	2.5	5
Blank Spike (5 mg/kg), rep 1	0	1	2.5	5
Blank Spike (5 mg/kg), rep 2	0	1	2.5	5
Blank Spike (5 mg/kg), rep 3	0	1	2.5	5
NIST 2710A, rep 1	0	1	2.5	5
NIST 2710A, rep 2	0	1	2.5	5
NIST 2710A, rep 3	0	1	2.5	5
NIST 2710A + 100 mg/kg, rep 1	0	1	2.5	5
NIST 2710A + 100 mg/kg, rep 2	0	1	2.5	5
NIST 2710A + 100 mg/kg, rep 3	0	1	2.5	5

Initial 3050C Draft

Current 3050B Alternate Prep

3050C Proof of Concept Study Plan

Results

Antimony (Sb)	Brooks Applied Labs				EPA Region 10				Weck Laboratories, Inc.			
HCl Added (mL)	0	1	2.5	5	0	1	2.5	5	0	1	2.5	5
Blank Spikes (% rec.)	104	103	102	102	97	100	100	105	98	99	98	98
NIST 2710A (mg/kg)	18.4	19.7	20.5	21.8	7.1	15.6	29.3	28.2	15.6	16.3	20.5	20.6
Matrix Spike (% rec.)	50	57	67	72	33	47	66	67	45	50	74	82

Certified Value of NIST 2710A for TOTAL Sb is 52.5 mg/kg; Median Reference Value for Total Recoverable Sb by 3050B is 9.6 mg/kg (range is 5.0 - 12 mg/kg).

All results are means for n=3, hot block prep, and analysis by ICP-MS.

3050C Proof of Concept Study Plan

Results

Silver (Ag)	Brooks Applied Labs				EPA Region 10				WIL Weck Laboratories, Inc.			
HCl Added (mL)	0	1	2.5	5	0	1	2.5	5	0	1	2.5	5
Blank Spikes (% rec.)	91	103	103	103	9	10	76	101	90	97	97	98
NIST 2710A (mg/kg)	5.7	39.8	39.0	38.8	0.6	13.6	38.2	38.0	6.9	32.4	35.3	35.9
Matrix Spike (% rec.)	-2	21	97	104	1	3	91	101	1	34	92	97

Informational Value of NIST 2710A for TOTAL Ag is 40 mg/kg; Median Reference Value for Total Recoverable Ag by 3050B is 36 mg/kg (range is 31 - 39 mg/kg).

All results are means for n=3, hot block prep, and analysis by ICP-MS.

Parameter	3050B	3050C (Original Draft)	3050C (Modified Draft)
Digestion Equipment	Hot Plate, Hot Block, or Microwave	Hot Plate or Hot Block; **Microwave removed** (discussed separately in EPA Method 3051)	Hot Plate or Hot Block; **Microwave removed** (discussed separately in EPA Method 3051)
Determinitive Methods	FLAA, GFAA, ICP-AES, ICP-MS	FLAA, GFAA, ICP-AES, ICP-MS	FLAA, GFAA, ICP-AES, ICP-MS
Recommended Analyte List	FLAA/ICP-AES: **Al**, **Sb**, **Ba**, Be, Cd, **Ca**, Cr, Co, **Cu**, Fe, Pb, **Mg**, **Mn**, Mo, **Ni**, **K**, **Ag**, **Na**, Tl, **V**, **Zn**	FLAA/ICP-AES/**ICP-MS (with PIC)**: **Al**, **Sb**, As, **Ba**, Be, Cd, **Ca**, Cr, Co, **Cu,** Fe, Pb, **Mg**, **Mn**, Mo, **Ni**, **K**, Se, **Ag**, **Na**, Tl, **V**, **Zn**	FLAA/ICP-AES/ICP-MS/GFAA: Al, Sb, As, Ba, Be, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, K, Se, Ag, Na, Tl, V, Zn **(noted that standard ICP-MS and GFAA may not be applicable for all elements)**
	GFAA/ICP-MS: **As**, Be, Cd, Cr, Co, Fe, Pb, Mo, **Se**, Tl	GFAA/standard ICP-MS: As, Be, Cd, Cr, Co, Fe, Pb, Mo, Se, Tl	
ICP-MS Options	Allowed only for digests without HCl.	Allowed for digests including HCl if equipped with interference removal technologies (e.g., DRC, CRC, or QQQ)	Allowed for digests including HCl if equipped with interference removal technologies (e.g., DRC, CRC, or QQQ)
Incremental Sampling	None incorporated into method	Discussed in Appendix B (Final location of ISM procedure TBD; may be its own method)	Discussed in Appendix B
Initial Digestion Step	10mL 1:1 HNO_3	10mL 1:1 HNO_3 **and 5mL 1:1 HCl**	10mL 1:1 HNO_3 **and 5mL 1:1 HCl**
Final Digestion Step	Varies depending on analytical technique and analyte list	2hr reflux of HNO_3 / H_2O_2 mixture	**15 min. reflux with conc. HCl** (after 2hr reflux of HNO_3 / H_2O_2 mixture)
Alternate Digestion 1	10mL conc HCl added after HNO_3 / H_2O_2 digestion complete; for FLAA/ICP-AES only	N/A (removed)	N/A (incorporated into digestion method)
Alternate Digestion 2	Modified Aqua Regia primarily for Sb, Ba, Pb, Ag; for FLAA/ICP-AES only	N/A (removed)	N/A (removed)

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Multi-Lab Validation Study

Study Plan

- 5 Study Materials
  - NIST 2710A - Montana I Soil
  - NIST 2782 – Industrial Sludge
  - NIST 1646A – Estuarine Sediment
  - ERA Metals in Soils - Catalog #540
  - ERA Metals in Sewage Sludge - Catalog #160
- Samples prepped in triplicate with MS/MSD on each sample
- Prepared by both 3050B and Draft 3050C
- Analyzed by ICP-MS and/or ICP-AES

Multi-Lab Validation Study

Participating Labs that Received Study Materials

1. Analytical Resources, Inc. – Tukwila, WA
2. Brooks Applied Labs – Bothell, WA
3. EPA Region 5 Lab – Chicago, IL
4. EPA Region 10 Lab – Port Orchard, WA
5. EPA ORD/NRMRL Lab – Cincinnati, OH
6. Hampton Roads Sanitation Dist. – Virginia Beach, VA
7. High Purity Standards – Charleston, SC
8. Enthalpy Analytical (Montrose) – Berkeley, CA
9. Enthalpy Analytical (Montrose) – Orange, CA
10. Pace Analytical – Mt. Juliet, TN
11. Pace Analytical – Minneapolis, MN
12. Eurofins TestAmerica – Pittsburgh, PA
13. USACE Env Lab – Vicksburg, MS
14. USACE CRREL – Hanover, NH
15. Weck Laboratories – City of Industry, CA

Only 10 of these labs submitted data back to EPA. The list of participating labs that submitted data has not been released.

Multi-Lab Validation Study

Summary of Lab Info

Lab ID	Method(s)	Int Red Tech Used (ICP-MS)
B	ICP-AES	
C	ICP-AES and ICP-MS	He, H_2, none
D	ICP-AES and ICP-MS	He/H_2 mix
E	ICP-AES	
F	ICP-AES and ICP-MS	not specified
G	ICP-AES and ICP-MS	He, H_2, none
H	ICP-AES and ICP-MS	He, none
I	ICP-AES and ICP-MS	He
J	ICP-MS	NH3, O2, He, H_2, none (QQQ)
K	ICP-AES and ICP-MS	He, none

ICP-AES Datasets: 9
ICP-MS Datasets: 8

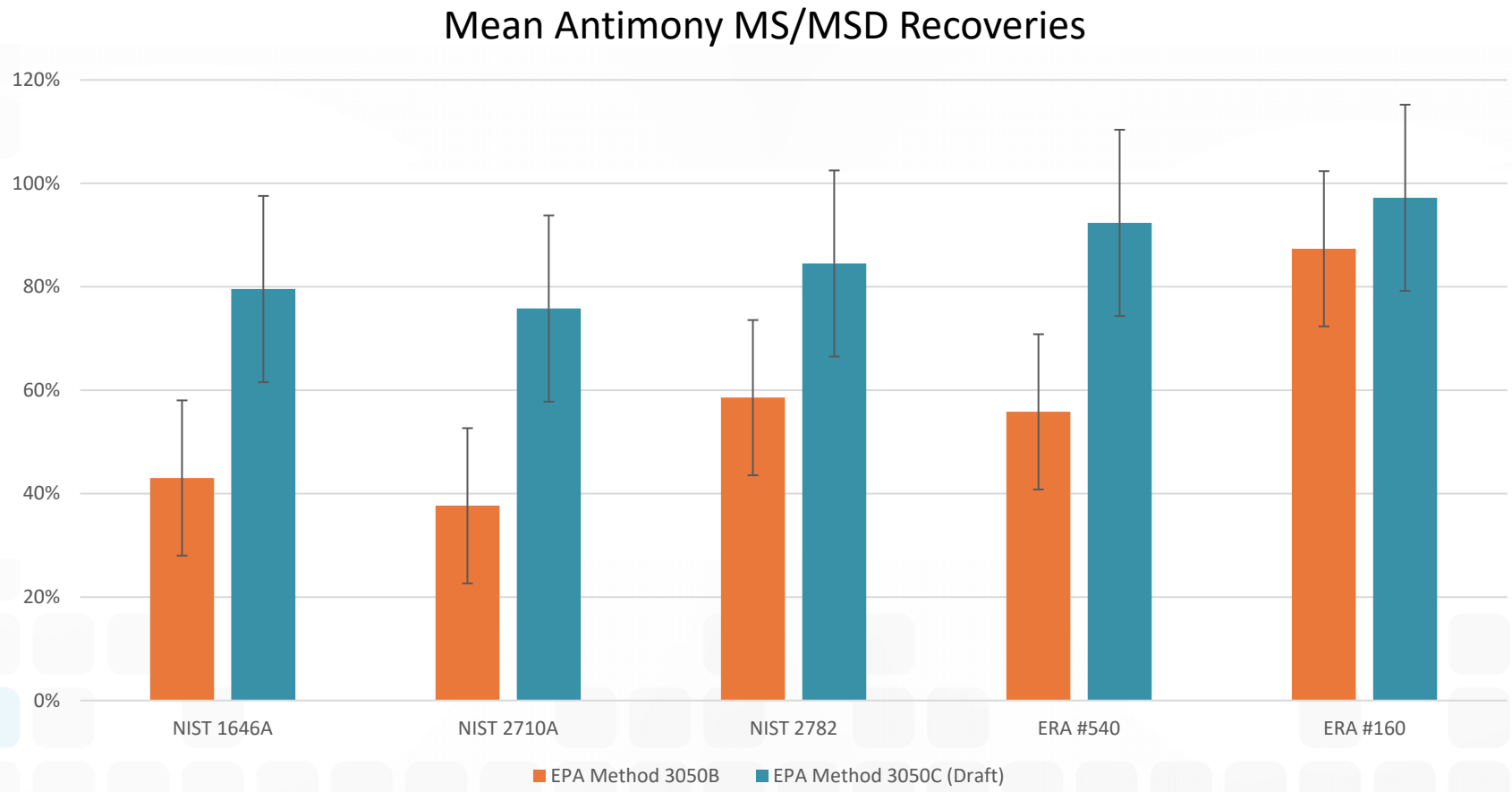
Datapoints: 16,502

Validation Study Results - Antimony

	NIST 2710A		NIST 2782		ERA #540		ERA #160	
True Value (ppm)	52.50		2.00		145.0		247.0	
Prep Method	3050B	3050C	3050B	3050C	3050B	3050C	3050B	3050C
Mean (ppm)	9.97	25.74	1.31	1.98	40.09	80.20	143.3	185.3
Std Dev (ppm)	3.02	7.69	1.54	1.82	10.56	18.58	45.3	33.6
n	42	49	17	17	51	51	47	51
Ave Recovery	19%	49%	66%	99%	28%	55%	58%	75%
RSD	30%	30%	118%	92%	26%	23%	32%	18%

NIST 1646A omitted due to insufficient data points (TV = 0.3 ppm)

Validation Study Results – Antimony



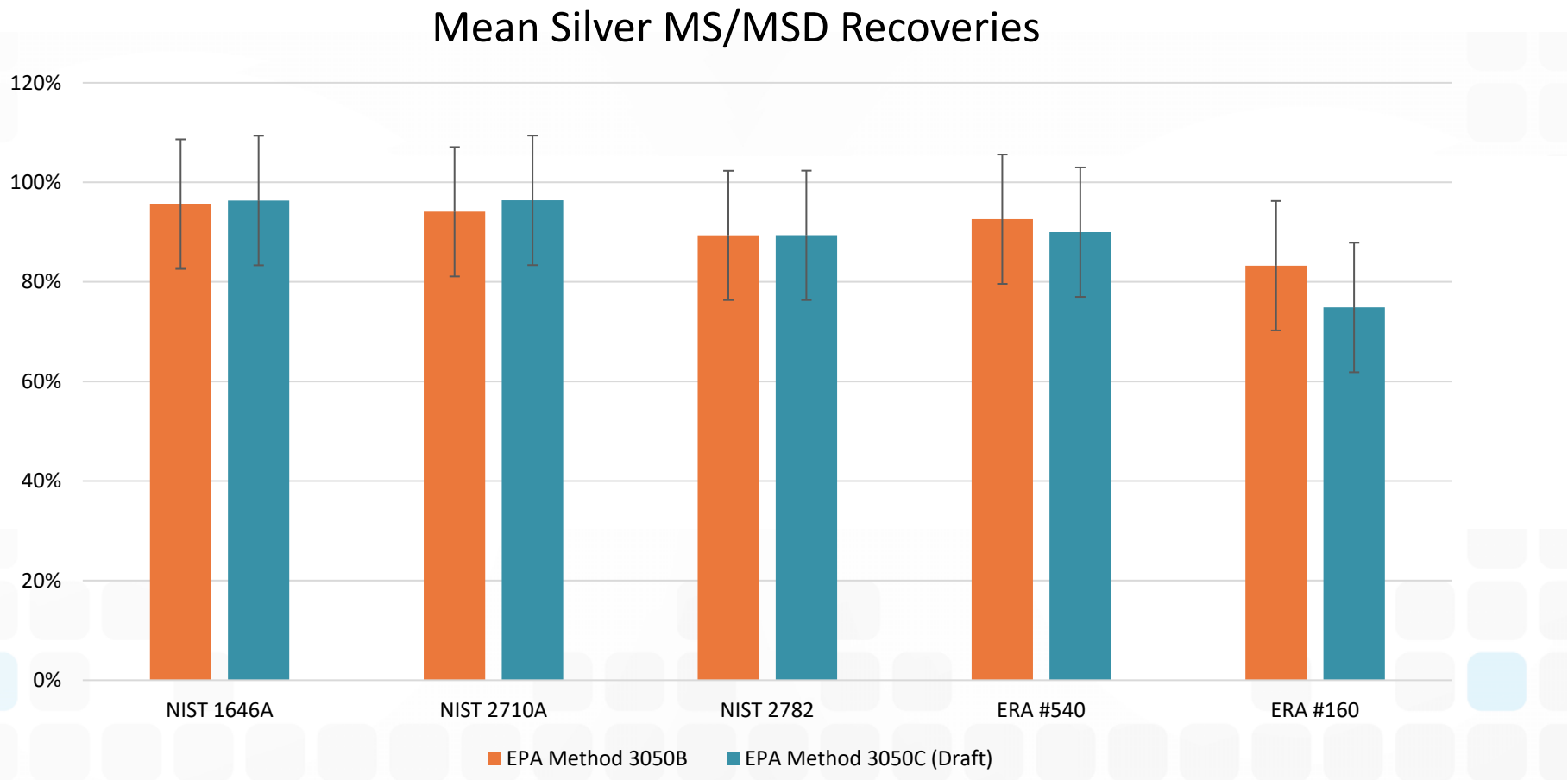
Validation Study Results - Silver

Silver (Ag)	NIST 1646A	NIST 2710A	NIST 2782	ERA #540	ERA #160
True Value (ppm)	< 0.3	40.00	30.60	45.50	110.0
Mean (ppm)	0.1	34.98	27.54	62.10	91.8
Std Dev (ppm)	0.2	2.57	7.80	5.96	19.2
RSD	N/C	7%	28%	10%	21%
n	13	102	88	103	99
Mean Recovery	N/C	87%	90%	136%	83%

Includes data prepped by both 3050B and 3050C; no statistical differences between the results.

ERA #540 Mean Recovery	EPA 3050B	EPA 3050C
ICP-MS (EPA 6020)	136%	134%
ICP-AES (EPA 6010)	136%	136%

Validation Study Results - Silver



NIST SRM 2710A Results

Average results for 3 reps for participating lab (n ≈ 30)

NIST 2710A Soil	Total TV	Total Rec Value	ICP-MS (6020)		ICP-AES (6010)		Comments
			3050B	3050C	3050B	3050C	
Aluminum	59,500	10,000	13,220	14,200	14,066	14,528	Low total recoverable result compared to “total”
Antimony	52.5	9.6	10.1	26.6	9.8	24.9	Low TR result compared to “total”; 3050C higher than 3050B
Arsenic	1,540	1,400	1,568	1,551	1,488	1,466	
Barium	792	510	504	513	467	492	Low total recoverable result compared to “total”
Beryllium	-	0.48	0.56	0.58	0.41	0.41	ICP-MS higher than ICP-AES
Cadmium	12.3	11	11.2	10.9	10.8	10.4	
Calcium	9,640	1,800	1,876	1,987	2,035	2,041	Low total recoverable result compared to “total”
Chromium	23.00	10	13.50	14.28	17.17	17.39	Low TR result compared to “total”; ICP-MS lower than ICP-AES
Cobalt	5.99	3.8	4.23	4.33	4.27	4.00	Low total recoverable result compared to “total”
Copper	3,420	3,300	3,252	3,286	3,201	3,099	
Iron	43,200	34,000	35,687	37,367	38,228	37,840	
Lead	5,520	5,100	5,092	5,134	5,093	5,048	
Magnesium	7,340	3,500	3,811	3,837	3,813	3,816	Low total recoverable result compared to “total”
Manganese	2,140	1,700	1,652	1,638	1,612	1,581	
Molybdenum	-		7.38	7.58	6.59	6.68	
Nickel	8	5.5	6	7	6	6	Reference Value (not certified)
Potassium	21,700	4,100	4,829	4,938	4,832	5,038	Low total recoverable result compared to “total”
Selenium	1	2.0	1	1	N/C	N/C	Informational Value (not certified); Insufficient ICP-AES data
Silver	40	36	36	36	34	34	Informational Value (not certified)
Sodium	8,940	590	621	645	730	704	Low total recoverable result compared to “total”
Thallium	1.52	3.2	0.72	0.88	N/C	N/C	Reference Value (not certified); Insufficient ICP-AES data
Vanadium	82	38	46	49	43	44	Reference Value (not certified); Low TR result compared to “total”
Zinc	4,180	3,800	3,852	4,003	3,876	3,758	

ERA CRM #540 Results

Average results for 3 reps for participating lab (n ≈ 30)

ERA #540 Soil	Certified Value	ICP-MS (6020)		ICP-AES (6010)		Comments
		3050B	3050C	3050B	3050C	
Aluminum	10,100	9,342	9,814	9,787	10,367	
Antimony	145	43	86	38	75	3050C higher recoveries than 3050B
Arsenic	171	74	72	68	66	Low (QC Limits 113 - 209)
Barium	272	369	366	378	362	High (QC Limits 195 - 325)
Beryllium	102	248	243	222	217	High (QC Limits 73.2 - 122)
Cadmium	225	174	174	160	161	Low (QC Limits 158 - 265)
Calcium	5,190	4,542	4,307	4,910	4,811	
Chromium	144	271	255	253	248	High (QC Limits 95.2 - 177)
Cobalt	48.8	92.8	90.2	89.5	85.9	High (QC Limits 36.1 – 60.2)
Copper	174	287	283	282	272	High (QC Limits 124 - 207)
Iron	15,000	15,640	16,033	16,115	17,675	
Lead	111	235	226	221	212	High (QC Limits 78.8 – 143)
Magnesium	2,570	2,465	2,387	2,460	2,528	
Manganese	232	350	345	330	327	High (QC Limits 165 - 291)
Molybdenum	123	171	165	156	153	High (QC Limits 77.5 - 142)
Nickel	98.3	120.2	116.4	112.9	107.8	
Potassium	2,420	2,260	2,312	2,311	2,493	
Selenium	206	201	194	198	190	
Silver	45.5	64.9	62.7	61.0	60.0	High (QC Limits 30.1 – 56.5)
Sodium	252	194	196	273	273	Low for ICP-MS (but within QC Limits 105 - 332)
Thallium	167	137	137	132	130	
Vanadium	61.8	99.1	99.4	93.1	95.3	High (QC Limits 32.2 - 81.3)
Zinc	207	127	119	122	117	Low (QC Limits 139 - 259)

Conclusions

- The revised draft of EPA Method 3050C will provide a solid digestion that will be appropriate for the listed total recoverable metals
- Beware of using SRMs to assess quality of 3050B and 3050C results
- MS/MSD recoveries for Sb may still be an issue in most matrices (and Ag may be an issue in some matrices)
- Partnership between government labs and volunteer commercial labs worked well
- Much more data processing remains to be completed by the EPA

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- All participating labs!

Thank you for your attention!

Any Questions?

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