SW-846 Test Method 3050C
Acid Digestion of Inorganics Found in Sediment, Sludges, and Soils

August 4, 2022

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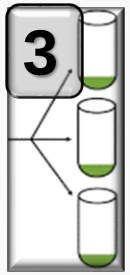
Topics

1. Overview
2. Reference Materials and Elements
3. Comparison of Methods 3050B and 3050C
4. Tiered Statistical Analysis
5. QA/QC
6. Limitations and Uncertainties
7. Current Status

Overview

- Method initially developed in 1986
- Two updates with current version finalized in 1996
- Update to SW-846 Method 3050B for the digestion of solids
  - adjustments to the acid addition for digestion
  - timing of the acid addition
- Mini research study
- Draft method plan
- Multiple laboratory validation study
  - Triplicate analyses
  - 5 reference materials
  - 23-elements
  - Digestion by both Methods 3050B and 3050C
  - Determinative methods (ICP-OES and ICP-MS* – Methods 6010D or 6020B)



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Laboratory ID	Analytical Instruments
C	ICP-OES and ICP-MS
J	ICP-MS
G	ICP-OES and ICP-MS
I	ICP-OES and ICP-MS
K	ICP-OES and ICP-MS
F	ICP-OES and ICP-MS (limited analytes)
B	ICP-OES
D	ICP-OES and ICP-MS
H	ICP-OES and ICP-MS
E	ICP-OES

* ICP-MS currently uses interference reduction technologies (e.g., Dynamic Reaction Cell, Collision Cell, triple quadrupole) to remove chloride-based interferences, and the addition of HCl improves the recoveries and increases the digestate stability for certain elements (e.g., Ag, Sb).

Reference Materials and Elements

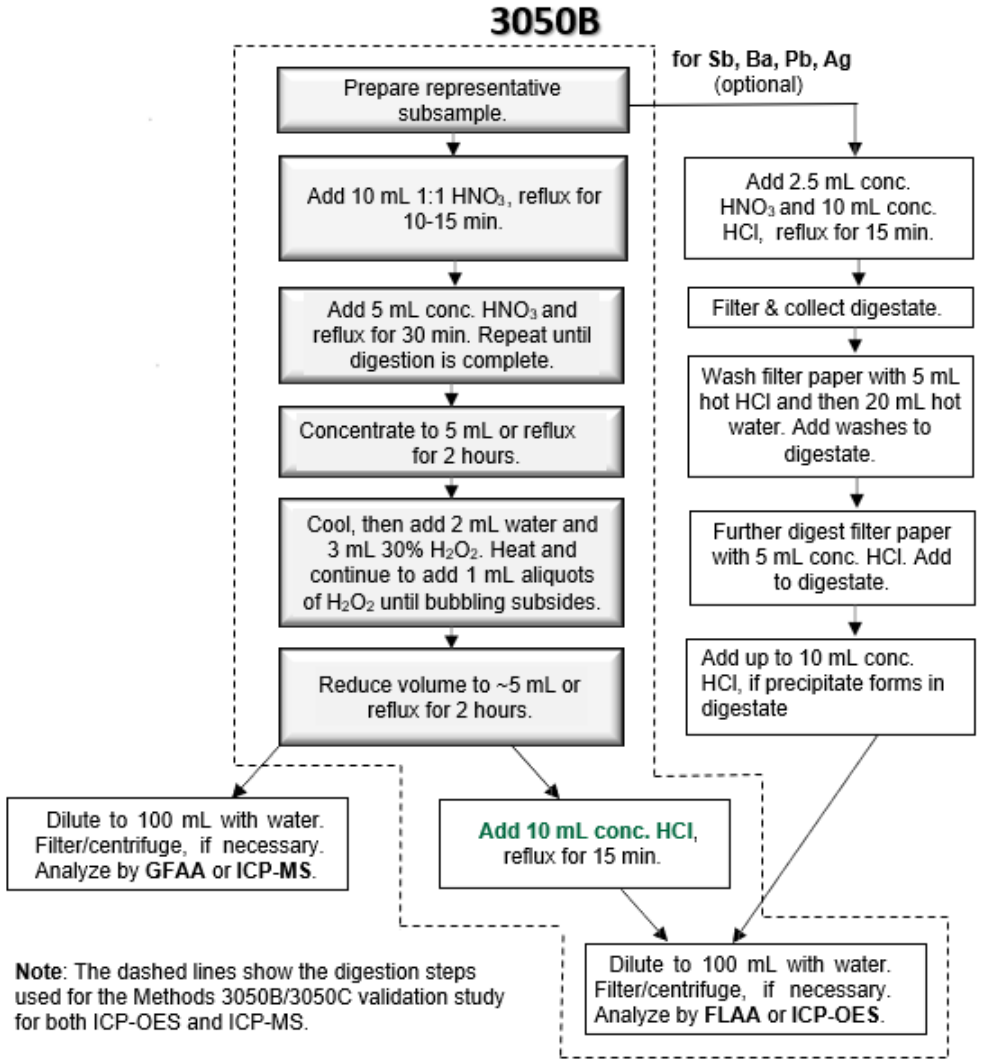
Reference Materials
• NIST§ 2710a – **Montana I Soil** (highly elevated trace element concentrations), • NIST§ 2782 – **Industrial Sludge**, • NIST§ 1646a – **Estuarine Sediment**, • ERA¥ Metals in **Soil** - Catalog #540, and • ERA¥ Metals in **Sewage Sludge** - Catalog #160

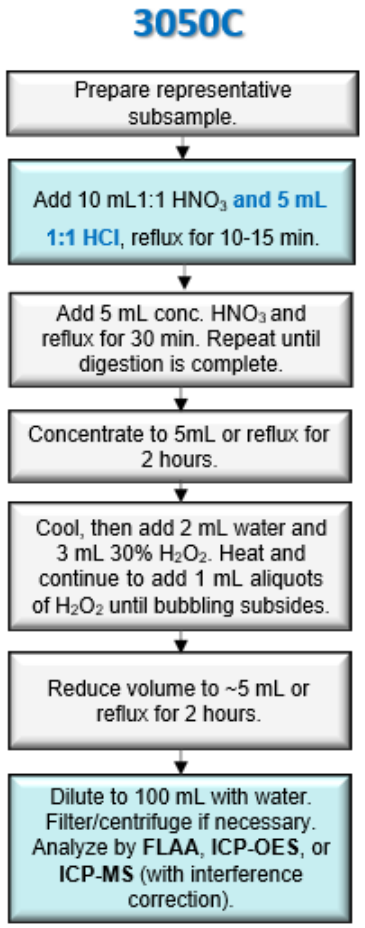
§ National Institute of Standards and Technology's (NIST's) Standard Reference Materials (SRMs)

¥ ERA: provider of Proficiency Testing (PT) and Certified Reference Materials (CRMs)

Element List	
Aluminum	Magnesium
Antimony	Manganese
Arsenic	Molybdenum
Barium	Nickel
Beryllium	Potassium
Calcium	Selenium
Cadmium	Silver
Chromium	Sodium
Cobalt	Thallium
Copper	Vanadium
Iron	Zinc
Lead	

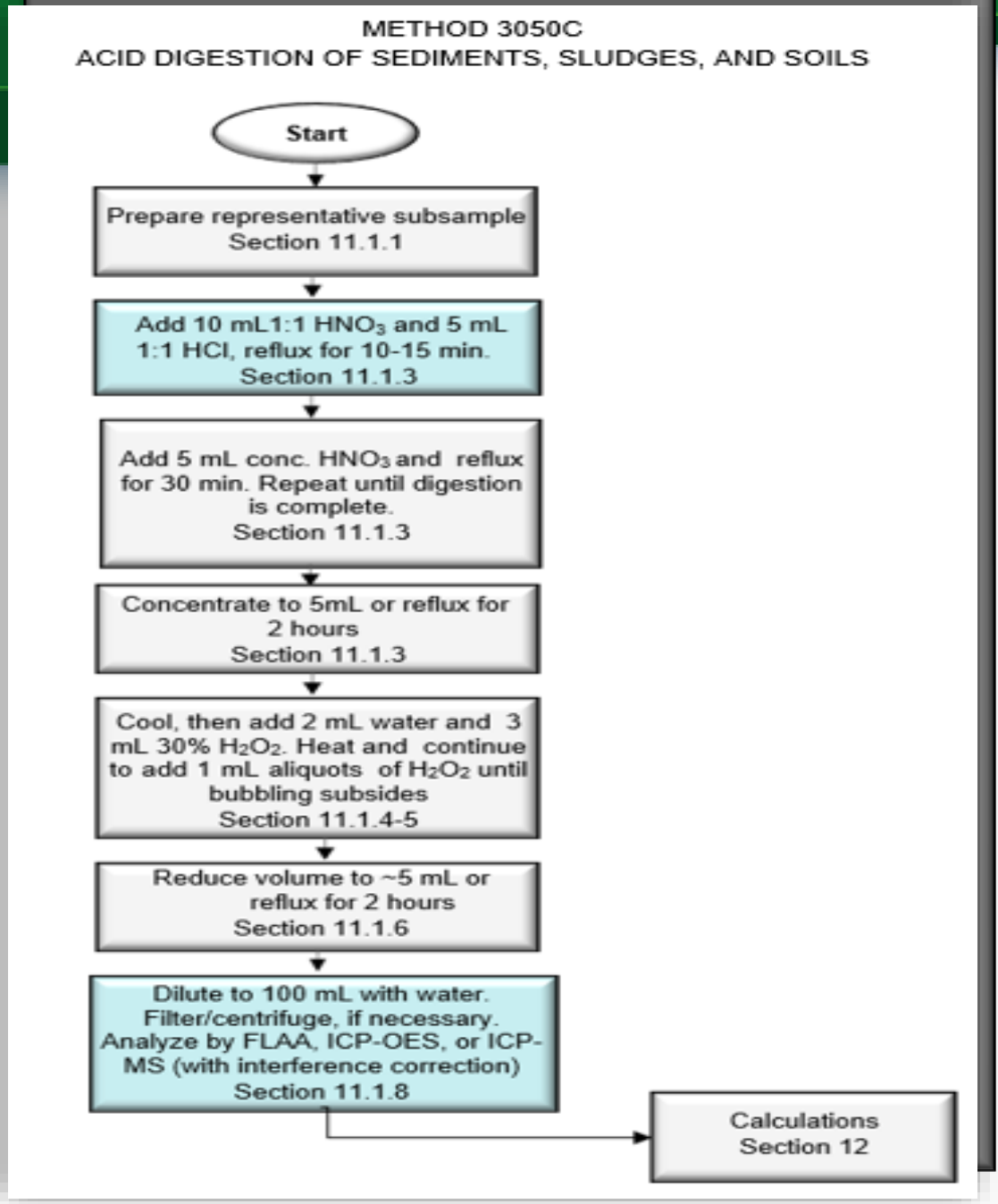
Comparison of Methods 3050B and 3050C





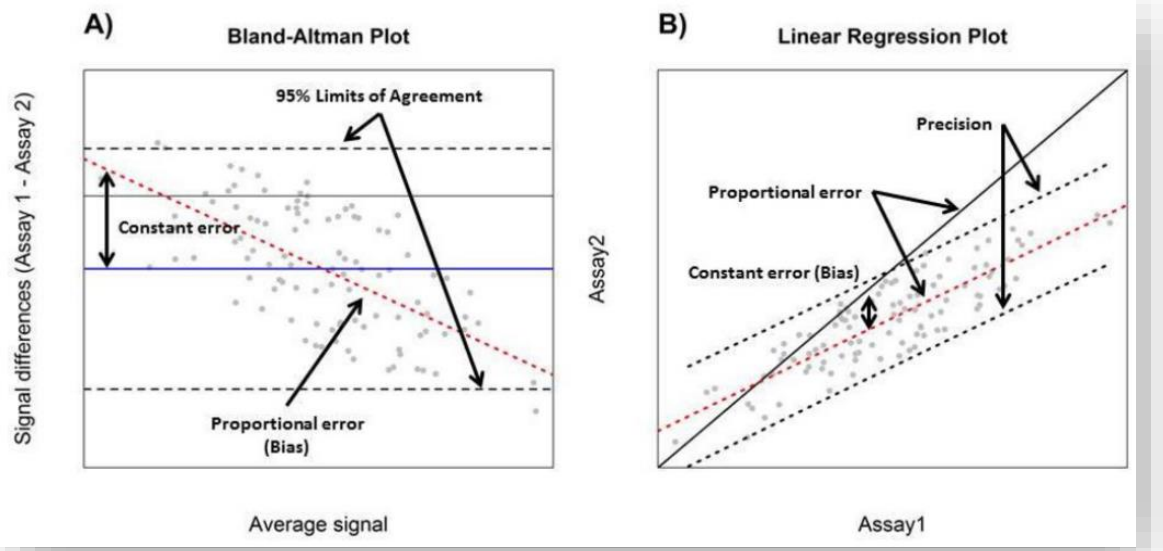
Parameter	3050B	3050C
Digestion Equipment	Hot plate, hot block, or microwave	Hot plate or hot block; **microwave removed** (ref. EPA Method 3051)
Determinitive Methods	FLAA, GFAA, ICP-OES, ICP-MS	FLAA, ICP-OES, ICP-MS
Analytes	FLAA/ICP-OES: **Al**, **Sb**, **Ba**, Be, Cd, **Ca**, Cr, Co, **Cu**, Fe, Pb, **Mg**, **Mn**, Mo, **Ni**, **K**, **Ag**, **Na**, Tl, **V**, **Zn** GFAA/ICP-MS: **As**, Be, Cd, Cr, Co, Fe, Pb, Mo, **Se**, Tl	FLAA/ICP-OES/ICP-MS: Al, Sb, As, Ba, Be, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, K, Se, Ag, Na, Tl, V, Zn **(note that standard ICP-MS and GFAA may not be applicable for all elements)**
ICP-MS Options	Allowed only for digests without HCl.	Allowed for digests including HCl if equipped with interference removal technologies
Initial Digestion	10 mL 1:1 HNO_3	10 mL 1:1 HNO_3 **and 5 mL 1:1 HCl**
Final Digestion	Varies - depending on analytical technique and analytes	**15 min. reflux with conc. HCl** (after 2hr reflux of HNO_3 / H_2O_2 mixture)
Alternate Digestion 1	10 mL conc. HCl added after HNO_3/H_2O_2 digestion complete - for FLAA/ICP-OES only	Not applicable (incorporated into the digestion method)
Alternate Digestion 2	Modified aqua regia primarily for Sb, Ba, Pb, Ag - for FLAA/ICP-OES only	Not applicable

Chattopadhyay et al. 2021


METHOD 3050C
ACID DIGESTION OF SEDIMENTS, SLUDGES, AND SOILS
Start
Prepare representative subsample
Section 11.1.1
Add 10 mL1:1 HNO_3 and 5 mL 1:1 HCl, reflux for 10-15 min.
Section 11.1.3
Add 5 mL conc. HNO_3 and reflux for 30 min. Repeat until digestion is complete.
Section 11.1.3
Concentrate to 5mL or reflux for 2 hours
Section 11.1.3
Cool, then add 2 mL water and 3 mL 30% H_2O_2. Heat and continue to add 1 mL aliquots of H_2O_2 until bubbling subsides
Section 11.1.4-5
Reduce volume to ~5 mL or reflux for 2 hours
Section 11.1.6
Dilute to 100 mL with water. Filter/centrifuge, if necessary. Analyze by FLAA, ICP-OES, or ICP-MS (with interference correction)
Section 11.1.8
Calculations
Section 12

Tiered Statistical Analysis

- Correlation Techniques – to show whether, and how strongly, pairs of variables are related.
- Bland and Altman Method - to quantify agreement between two quantitative measurements by constructing limits of agreement.



Misyura et al. 2018

- The Bland-Altman Plot computed by (depending on the study design)
  - **Exactly One Data-Pair per Subject** (no repeatability parameter can be computed)
  - **Multiple Replicates for each Method, No Pairing** (overall response mean stays constant)
  - **Multiple Replicates for each Method Obtained as Pairs** (response mean varies)

Statistical Analysis - Highlights

- Performed on the dataset to evaluate the performance of the individual laboratories and the group overall:
  - Summary statistics (mean and standard deviation) and calculation of percent relative standard deviation;
  - Grubbs' test of potential outliers; and
  - Standard deviation of repeatability and standard deviation of reproducibility, including *h* and *k* statistics.
- Determine whether preparation method 3050C performed equally as well as 3050B, in concert with either Method 6010D or Method 6020B:
  - Statistical analyses indicated that preparation method 3050C performed equally as 3050B, regardless of the analytical method. The repeatability and reproducibility of all the laboratories, barring the appearance of a low number of potential outliers within the datasets, was approximately the same.

Tabulated results of statistical tests on Method 3050C multi-laboratory database (based on laboratory)

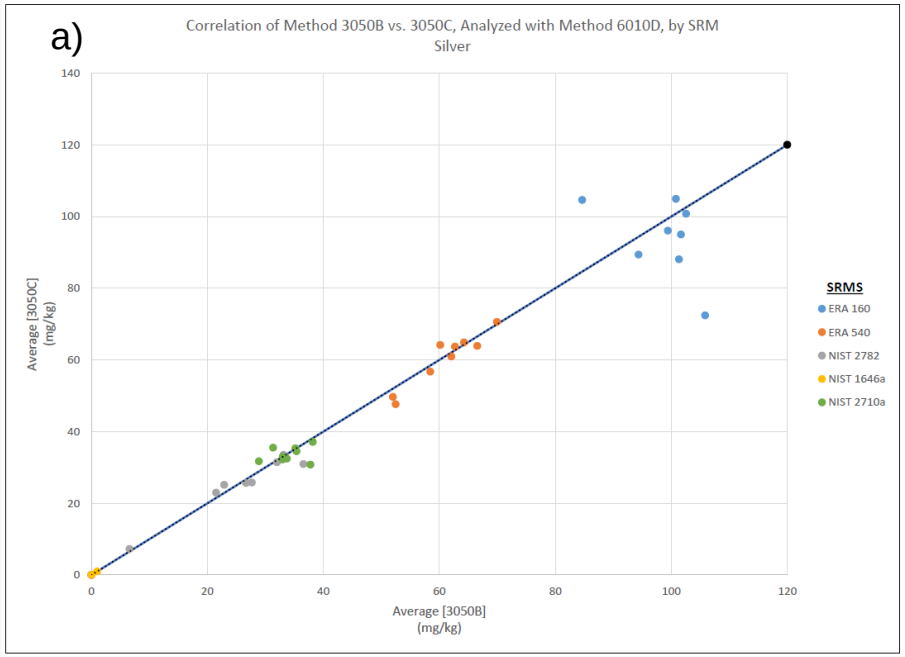
Lab ID	%RSD	Outliers	*h*	*k*
C	Greatest variability in the 0-10% range	No outliers	1 –*h* statistic; 3050C	Both 3050B and 3050C inconsistencies; most are 3050C
J	Greatest variability in the 0-10% range; low number of analyses performed	Both minima and maxima outliers; only 3050B	None	Both 3050B and 3050C inconsistencies; most are 3050B
G	Greatest variability in the 0-10% range	Minima outliers are all 3050C	1 –*h* statistic; 3050C	Both 3050B and 3050C inconsistencies; most are 3050C
I	Greatest variability in the 0-10% range; three sets of analyses >20%	Maxima outliers are only 3050B	Both positive and negative inconsistencies; both 3050B and 3050C	Both 3050B and 3050C; most are 3050B
I-a	Greatest variability in the 0-10% range; low number of analyses performed	Maxima outliers are only 3050C	Both positive and negative inconsistencies; 3050C only	Both 3050B and 3050C; most are 3050B
K	Greatest variability in the 0-10% range; two sets of analyses >20%	Both minima and maxima outliers; both 3050B and 3050C	Both positive and negative inconsistencies; both 3050B and 3050C	Both 3050B and 3050C inconsistencies; most are 3050B
F	Greatest variability in the 0-10% range; three sets of analyses >20%	Both minima and maxima outliers; both 3050B and 3050C	Both positive and negative inconsistencies; both 3050B and 3050C	Both 3050B and 3050C inconsistencies; most are 3050B
B	Greatest variability in the 0-10% range; two sets of analyses >20%	Most outliers of any lab. Both minima and maxima outliers; both 3050B and 3050C	Both positive and negative inconsistencies; both 3050B and 3050C	Most 3050B and 3050C inconsistencies; most are 3050C
D	Greatest variability in the 0-10% range; three sets of analyses >20%	Maxima outliers are 3050C	Both positive and negative inconsistencies; both 3050B and 3050C	Both 3050B and 3050C inconsistencies; 3050B v. 3050C approx. equal
H	Greatest variability in the 0-10% range; two sets of analyses >20%	Maxima outliers are both 3050B and 3050C	Both positive and negative inconsistencies; both 3050B and 3050C	Both 3050B and 3050C inconsistencies; 3050B v. 3050C approx. equal
E	Greatest variability in the 0-10%	Both minima and maxima outliers; both 3050B and	Both positive and negative inconsistencies; both 3050B and	Both 3050B and 3050C inconsistencies; most are

Tabulated results of statistical tests on Method 3050C multi-laboratory database (based on test protocol)

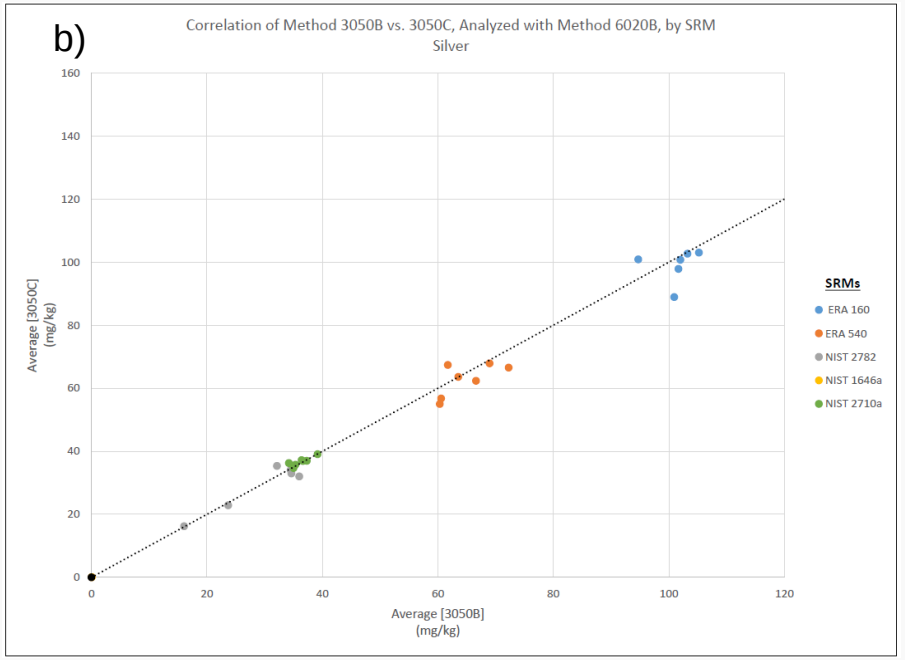
Test Protocol	%RSD	Outliers	*h*	*k*
3050B	Approx. equal variability between 6010 and 6020; mostly 10% RSD	Most outliers are maxima; approx. equal numbers of 6010 and 6020	No. of –*h* and +*h* exceeding a critical value approx. the same as 3050C; mostly 6020	No. of k exceeding a critical value less than 3050C; mostly 6020
3050C	Variability greater in 6010 than 6020; more variable than 3050B	Most outliers are minima; more 6010 than 6020	No. of –*h* and +*h* exceeding a critical value approx. the same as 3050B; mostly 6020	No. of k exceeding a critical value greater than 3050B; mostly 6010.

Correlation of Method 3050B vs. 3050C, Analyzed with Methods a) 6010D and b) 6020B, by SRM respectively for Silver

a)



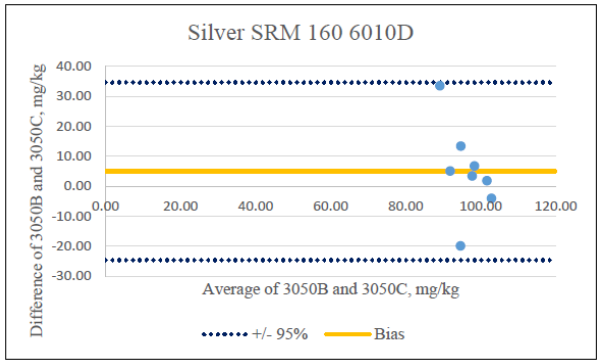
b)

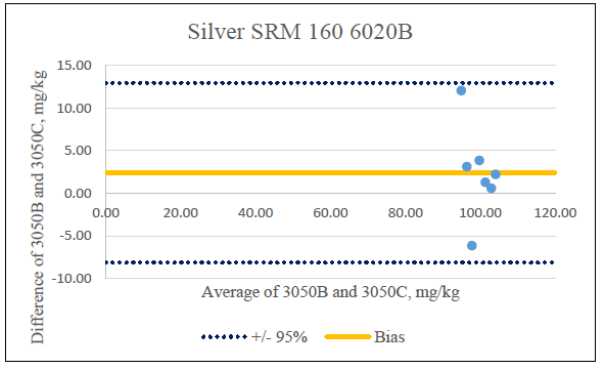


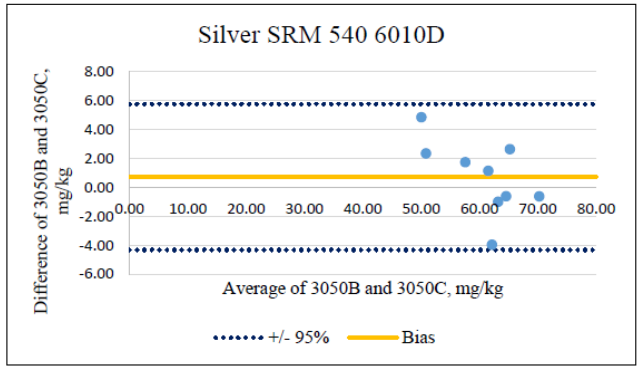
t-test, and graphical analyses were performed on the dataset from the Method 3050C Multi-Laboratory Validation Study; three graphs were prepared for each analyte: one showing Method 3050B vs. 3050C, Method 6010D vs. Method 6020B, all average concentration data and two showing Method 3050B vs. 3050C, by SRM, Method 6010D and Method 6020B graphed separately. A data table was also prepared of the regression statistics y-intercept, slope, R^2, and t-test.

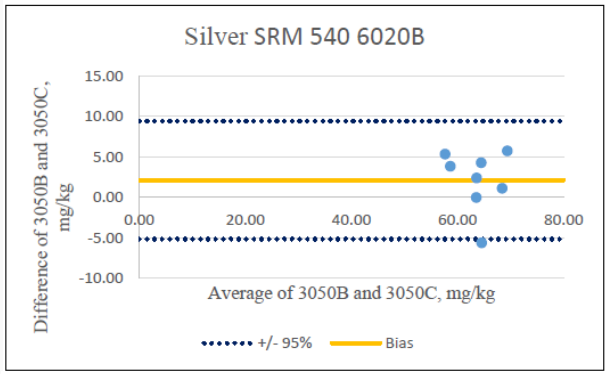
Method 3050B and Method 3050C data are strongly correlated, with a few exceptions related to the presence of potential outliers. In general, wet preparation data analyzed with Method 6010D (ICP-OES) had smaller differences between 3050B and 3050C than the data analyzed with Method 6020B (ICP-MS).

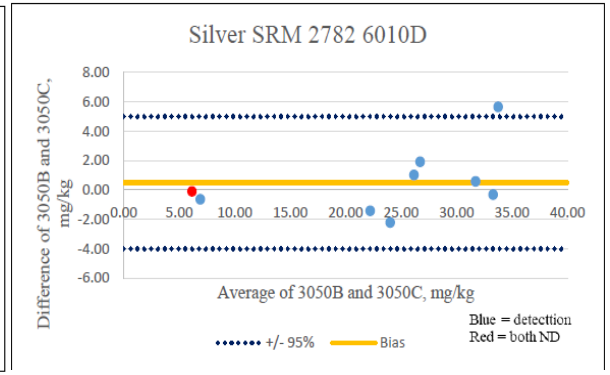
Representative Data

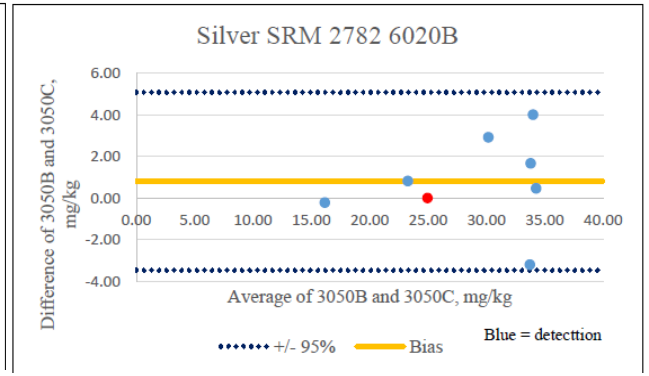


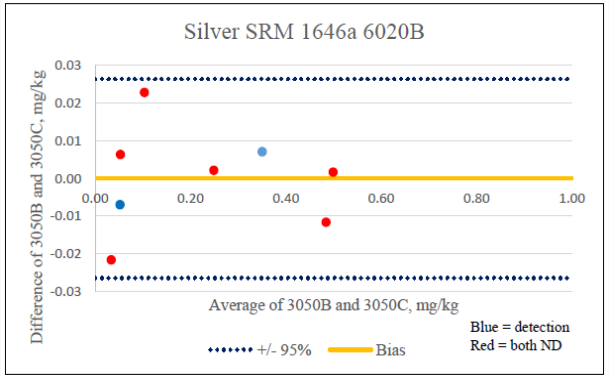


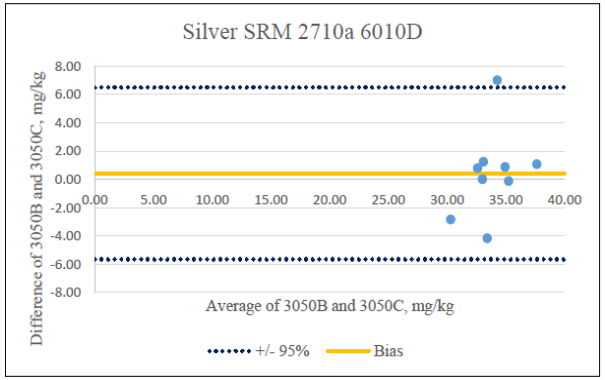


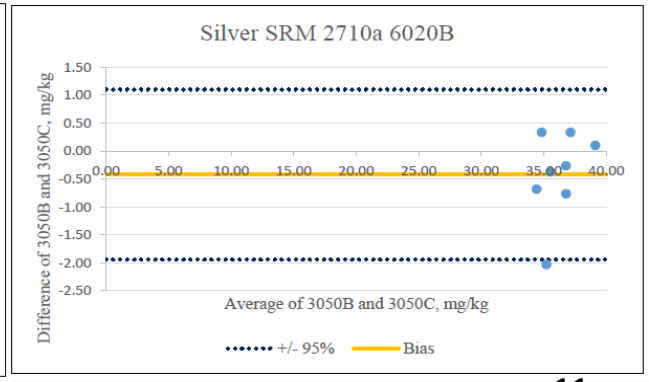












QA/QC

- **Parameters**: method blanks; laboratory control samples (LCS); and matrix spike/matrix spike duplicate (MS/MSD)
- Average LCS percent recoveries were within method QC limits of 80%-120%, with a small number of exceptions. MS/MSD were mostly within the QC limits of 75-125%.
- Antimony had low recovery in almost all SRMs prepared with Method 3050B and showed a marked improvement in recovery upon preparation with Method 3050C.
- Little difference between MS/MSD recoveries for silver, barium, and lead.

LABORATORY CONTROL SAMPLE RECOVERY (%)[a] FOR METHODS 3050B AND 3050C

Element	6010D 3050B	6010D 3050C	6020B 3050B	6020B 3050C
Ag	98	97	104	102
Al	100	99	102	98
As	98	97	101	100
Ba	96	99	103	100
Be	97	96	105	105
Ca	98	99	102	102
Cd	98	100	101	102
Co	95	96	105	102
Cr	97	96	103	101
Cu	97	96	102	101
Fe	100	98	100	101
K	99	99	105	103
Mg	97	99	104	99
Mn	97	96	102	101
Mo	96	96	103	101
Na	97	96	101	100
Ni	100	100	101	98

RESULTS OF ANALYSIS OF STANDARD REFERENCE MATERIAL (SRM) NIST 1646a, ESTUARINE SEDIMENT (mg/kg ± Standard Deviation [SD])

Element	6010D 3050B[2]		6010D 3050C		6020B 3050B[2]		6020B 3050C		SRM Values (± 95% CI) [Total Element]
	Result	SD	Result	SD	Result	SD	Result	SD	
Ag	ND	NA	ND	NA	0.05	0.01	0.12	0.19	<0.3
Al	7,200	1,100	7,600	1,300	6,800	830	7,400	1,300	22,970 ± 180
As	5.6	1.0	5.7	1.2	5.4	0.84	5.3	0.86	6.23 ± 0.21
Ba	20	1.8	24	4.4	21	2.1	22	2.9	210
Be	0.29	0.09	0.29	0.14	0.40	0.04	0.45	0.10	<1
Ca	3,600	390	3,600	410	3,300	460	3,400	540	5,190 ± 200
Cd	0.12	0.02	0.14	0.01	0.16	0.03	0.15	0.02	0.148 ± 0.007
Co	3.7	0.28	3.6	0.34	3.7	0.33	3.7	0.42	5
Cr	21	1.3	21	2.0	24	2.4	24	3.1	40.9 ± 1.9
Cu	9.0	0.57	9.3	0.93	9.7	0.74	10	1.8	10.01 ± 0.34
Fe	16,000	2,400	16,000	2,600	15,000	930	17,000	1,400	20,080 ± 390
K	2,100	240	2,200	350	2,100	140	2,200	240	8,640 ± 160
Mg	3,000	360	3,100	410	3,000	170	3,000	170	3,880 ± 90
Mn	110	7.6	120	13	120	26	130	17	234.5 ± 2.8
Mo	1.3	0.10	1.3	0.19	1.3	0.18	1.5	0.19	1.8
Na	4,300	440	4,200	460	4,200	220	4,200	370	7,410 ± 170
Ni	19	1.2	19	1.4	20	1.9	20	1.9	23
Pb	7.3	0.46	7.3	0.47	7.9	0.60	8.3	1.3	11.7 ± 1.2
Sb[1]	1.4	0.06	1.5	0.40	ND	NA	0.16	0.03	0.3
Se	ND	NA	ND	NA	0.82	0.67	0.62	0.52	0.193 ± 0.028
Tl	ND	NA	ND	NA	0.09	0.005	0.09	0.01	<0.5
V	20	1.9	21	2.5	22	3.5	24	4.9	44.84 ± 0.76
Zn	36	3.4	34	3.3	35	4.8	35	5.8	48.9 ± 1.6

CI – Confidence Interval; ND = Not Detected; NA = Not Applicable.

NOTE: Generally, when certifying NIST SRMs, rigorous methods (e.g., neutron activation and digestion with hydrofluoric acid) are used to achieve a true "total element" result, including metals that are bound up in minerals (e.g., silicates) that do not readily dissolve under environmental conditions. Method 3050C is not intended to yield true "total" results but rather more environmentally relevant "total recoverable" results. NIST certified values are provided for comparison purposes only. A recovery of 100% is not expected by this method. The SRM values were determined utilizing the following methods: CVAAS, ED-ICPMS, ETAAS, FAAS, FES, HYDR, ICPMS, ICPOES, ID-ICPMS, ID-TIMS, INAA, RNAA, WDXRF, and EDXRF.

1: Several result discrepancies between 6010D and 6020B may have arisen from spectral interferences due to the high iron content in this sample. 6010D results for Sb may be particularly affected. 2: The 6010D/3050B samples were prepared using the ICP-OES procedure (3050B, Sec. 7.2 and 7.3); the 6020D/3050B samples were prepared using the ICP-MS procedure (3050B, Sec. 7.2).

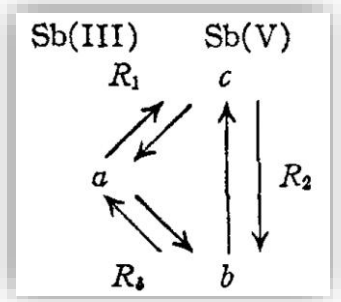
Limitations and Uncertainties

- Deviations from the study plan led to limitations in the types of statistical treatments that could be performed.
- Not all laboratories performed all the analyses. Direct laboratory-to-laboratory comparability was not always possible.
- The analysis of five SRMs, each with varied concentrations of the constituents of interest, reduced the power of the dataset, in that segregation of data by SRM and by preparation/analytical method resulted in small sample sizes.

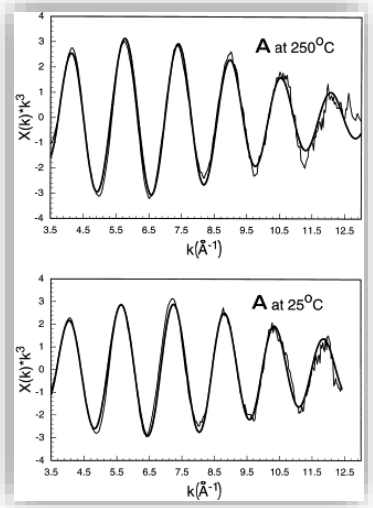
"*Decisions are based on data, analysis and empirical evidence. This includes both an understanding of the uncertainties present as well as potential limitations of the available data*."

Mechanism Perspectives - Antimony

- Interactions with low molecular weight ligands
  - Both Sb(III) and Sb(V) ions hydrolyze easily in aqueous solution, thus making it difficult to keep antimony ions stable in solution except in highly acidic media (Fiella et al. 2002).
- Hydroxyl
- Chloride - Antimony(III) chloride dissolves in strong HCl solutions. Chlorocomplexes, $SbCl_x^{[(x-)+3]+}$, are formed in solution depending on the chloride concentration present.
- Sulfides
- Organic low molecular weight ligands
- Interactions with solid phase



Bonner and Goishi, 1961



Oelkers et al., 1998

Current Status

Questions

Acknowledgements