

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

Sandip Chattopadhyay^{1,*}, Troy Strock¹, Katie Adams², Kim Kirkland¹

¹ U.S. Environmental Protection Agency, Office of Land and Emergency Management, Materials Recovery and Waste Management Division, Waste Characterization Branch, Washington, D.C.; ² EPA Region 10, Laboratory Services and Applied Sciences Divisions, Port Orchard, WA

*Corresponding author
Chattopadhyay.Sandip@epa.gov
<https://www.epa.gov/hw-sw846>

Introduction

The USEPA's SW-846 Test Method 3050 is an acid digestion for sediment, sludges, and soils that was initially developed in 1986 and has gone through two updates with the current version finalized in 1996. The SW-846 Test Method 3050 is not a total digestion but a method that was designed to prepare and recover sample containing trace elements that typically mobilize in the environment and are not strongly bound to the sorbent (e.g., aluminosilicate, silicate). The aqueous digests can subsequently be analyzed by Flame Atomic Absorption Spectroscopy (FLAA), Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES), or Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The main improvements to Method 3050B that led to the Method 3050C update include using single digestion pathway for the three analytical instruments. The updated Method 3050C includes many changes, among them adjustments to the acids added for digestion and the timing of the acid additions.

What is Method 3050?

- Strong acid digestion for *total recoverable metals* in sediment, sludge, soil
- Addition of HCl was not recommended in 3050B, since hydrochloric acid (HCl) was an interference for the determination of certain key elements (e.g., As, Cr) by standard ICP-MS
- 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).

3050C Update: Acid Digestion of Sediments, Sludges, and Soils

Major changes from 3050B to 3050C:

- Two-pathway digestion option was combined to a single digestion pathway for the three SW-846 determinative methods.
- Nitric acid (HNO₃) (1:1 v/v, 10 mL) and HCl (1:1 v/v, 5 mL) are added together to initiate the digestion.
- Additional 10 mL concentrated hydrochloric acid is added at the end of the procedure.

Reasons:

- Modernization of ICP-MS allows for the removal of chloride related interferences.
- Addition of HCl, especially in the first digestion step, increases the solubility of Ag and Sb.

Validation Study

- Ten (10) laboratories participated using ICP-OES, ICP-MS, or both instruments.
- Digestion performed by both Method 3050B and Draft Method 3050C. ICP-OES was performed using Method 6010D and ICP-MS was performed using Method 6020B.
- Five (5) reference materials were digested in triplicate and analyzed by the given determinative method for the 23 elements.
- Concentrations of elements were evaluated as per ASTM E691-18 (*Standard Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method*).

Materials and Methods

Elements Analyzed

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)	

Reference Materials

- NIST¹ 2710a – **Montana I Soil** (highly elevated trace element concentrations).
 - NIST¹ 2782 – **Industrial Sludge**.
 - NIST¹ 1646a – **Estuarine Sediment**.
 - ERA² Metals in **Soil** - Catalog #540, and
 - ERA² Metals in **Sewage Sludge** - Catalog #160
- ¹ National Institute of Standards and Technology's (NIST) Standard Reference Materials (SRMs)
² ERA: provider of Proficiency Testing (PT) and Certified Reference Materials (CRMs)

Analytical Laboratories and Instruments

Laboratory ID	Analytical Instruments
J	ICP-OES and ICP-MS
C	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

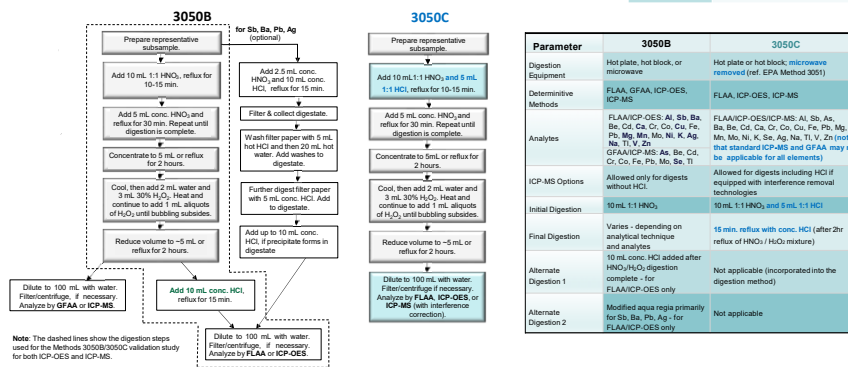


Figure 1. Comparison of Methods 3050B and 3050C.

Key Observations

Data analysis and interpretations were performed considering the total number of samples and overall percentage of data different from the mean by specific laboratory, analytes, and SRM. Average values of the concentrations were also computed to determine whether laboratories were biased low or high.

- All the selected elements, except Sb, followed 1:1 correlation for average concentration in 3050B and 3050C digests across the reference materials, whether analyzed by 6010D or 6020B.
 - Concentrations of Sb were generally higher in 3050C digests.
 - Concentrations of Ag showed similar trend, but no clear difference was observed.

- Differences in average concentrations by 3050B and 3050C in individual labs and reference materials relative to grand average were generally within allowable measurement uncertainty in the methods (e.g., matrix spike recovery 80-120%).
- The digestions of both methods (3050B and 3050C) recovered similar proportions of metals with relatively low solubilization efficiencies in 3050B (e.g., Al).
- Average 3050C results by laboratory had similar or lower frequency of bias relative to grand average when compared to 3050B digests, whether analyzed by 6010D or 6020B.

Statistical Analysis

The statistical analyses were 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.

The results of the four metrics (i.e., %RSD, *h* and *k* statistics, and the Grubbs' test) were weighted to identify the laboratories that had greater precision than others, to determine whether preparation method 3050C performed equally as well as 3050B, in concert with either Method 6010D or Method 6020B. Greater weight was given to the *h* and *k* statistics, which are specifically designed to evaluate both inter- and intra-laboratory performance based on the results produced by the multi-laboratory group. Statistical analyses indicated that preparation method 3050C performed equally as well 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.

Limitations and Uncertainties

Deviations from the study plan (2019) lead to a limitation in the types of statistical treatments that could be conducted on the dataset.

- Not all laboratories performed all the analyses. Thus, 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.

Summary and Next Steps

- The SW 846 Method 3050C validation study results were in general comparable to Method 3050B, except higher recovery of Sb.
- Key next steps involve:
 - Complete Bland-Altman analysis as it this type of analysis is preferred over the correlation coefficient due to the revelation of systematic and random errors, which are missed by the correlation coefficient.
 - Organize a SW-846 Methods Workgroup to review the Method 3050C and relevant supporting information.
 - Publish the Method 3050C for public comment.

No official endorsements should be inferred; the content represents the views of the authors, and not necessarily those of the U.S. EPA. The authors acknowledge the support received from Kristin Gagne (past ORISE-fellow at the USEPA).