Susitna-Watana Hydroelectric Project Document
ARLIS Uniform Cover Page

Title: Appendix to Method 1631 : total mercury in tissue, sludge, sediment, and soil by acid digestion and BrCl oxidation	**SuWa 191**
Author(s) – Personal:	
Author(s) – Corporate: U.S. Environmental Protection Agency, Office of Water	
AEA-identified category, if specified:	
AEA-identified series, if specified:	
Series (ARLIS-assigned report number): Susitna-Watana Hydroelectric Project document number 191	**Existing numbers on document:** EPA-821-R-01-013
Published by: [Anchorage : Susitna-Watana Hydroelectric Project, 2013]	**Date published:** January 2001 (original date)
Published for:	**Date or date range of report:**
Volume and/or Part numbers:	**Final or Draft status, as indicated:**
Document type:	**Pagination:** 13 p.
Related work(s):	**Pages added/changed by ARLIS:**
Notes: Reissued online for the Susitna-Watana Hydroelectric Project in 2013. Originally published: [Washington, D.C.] : U.S. Environmental Protection Agency, Office of Water, 2001.	

All reports in the Susitna-Watana Hydroelectric Project Document series include an ARLIS-produced cover page and an ARLIS-assigned number for uniformity and citability. All reports are posted online at http://www.arlis.org/resources/susitna-watana/

ARLIS
Alaska Resources Library & Information Services

SUSITNA-WATANA HYDRO

EPA-821-R-01-013
January 2001

Appendix to Method 1631
Total Mercury in Tissue, Sludge, Sediment, and Soil by Acid Digestion and BrCl Oxidation

Appendix to Method 1631
Total Mercury in Tissue, Sludge, Sediment, and Soil
by Acid Digestion and BrCl Oxidation[1]

A1.0 Scope and Application

A1.1 This Appendix provides two sample preparation (digestion) procedures for oxidation of total mercury (Hg) in solid and semi-solid sample matrices. These procedures may be used in conjunction with EPA Method 1631B: *Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry* for determination of mercury in tissue, sludge, sediment, soil, industrial samples, and certified reference materials.

A1.2 The digestion procedures in this Appendix, in conjunction with Method 1631B, allow determination of Hg at concentrations ranging from 1.0 to 5000 ng/g in solid and semi-solid matrices. Higher concentrations can be measured by selection of a smaller sample size and/or dilution of the digestate.

A1.3 The detection limit and minimum level of quantitation in this Method usually are dependent on the level of interferences rather than instrumental limitations. The method detection limit (MDL; 40 CFR 136, Appendix B) for Hg has been determined to be in the range of 0.24 to 0.48 ng/g when no interferences are present (see Appendix Tables A3 and A4). The minimum level of quantitation (ML) has been established as 1.0 ng/g. These levels assume a sample size of 0.5 g.

A1.4 Because Hg concentrations in solids are typically 10^3 - 10^7 times higher than those found in aqueous samples, the sensitivity provided by the dual amalgam trap system and fluorescence detector described in Method 1631B may be more sensitive than necessary, and a single trap and/or cold vapor atomic absorption spectroscopy (CVAAS) instrument may be adequate. These modifications are allowed under the equivalency provisions in EPA Method 1631B. See Method 1631B Section 9.1.2. However, the dual amalgam trap system and fluorescence detector provide greater sensitivity and specificity in the presence of interferences, and this system must be used to overcome interferences, if present, and to achieve the sensitivity required, if necessary.

A2.0 Summary

A2.1 Digestion I—This procedure is preferred for matrices containing organic materials, such as sludge and plant and animal tissues, because the organic matter is completely destroyed. In this procedure, a 0.2 - 1.5 g sample is digested with HNO_3/H_2SO_4. The digestate is diluted with BrCl solution to destroy the remaining organic material.

A2.2 Digestion II—This procedure is preferred for geological materials because of rapid and complete dissolution of cinnabar (HgS), which is otherwise more slowly attacked by the BrCl in Digestion I. In this procedure, a 0.5 - 1.5 g sample is digested with aqua regia (HCl/HNO_3) to solubilize inorganic materials.

A2.3 The Hg concentration in the digestate is determined using EPA Method 1631B.

[1] Based on a standard operating procedure provided by Frontier Geosciences, Inc.

A3.0 Definitions

See the Glossary at the end of Method 1631B for definitions of the terms used in this Appendix.

A4.0 Contamination and Interferences

A4.1 For the complete recovery of mercury by Method 1631B, all Hg in the sample must be converted to Hg(II). This is accomplished by free halogens present in the digestion step.

A4.2 In Digestion I, the addition of BrCl to the sample after it is fully solubilized HNO_3/H_2SO_4 is critical to convert methyl Hg to Hg(II). If the acid digestates are analyzed by Method 1631B without BrCl oxidation of tissues or geological media, a significant low bias may occur.

A4.3 In Digestion II, the reaction between concentrated HCl and HNO_3 in aqua regia generates nitrosyl chloride (NOCl) and free Cl_2, both of which are very strong oxidants for Hg-containing compounds including cinnabar (HgS) and precious metal amalgams that are not attacked by either acid alone. Aqua regia also converts all methyl Hg to Hg(II). The aqua regia procedure in Digestion II leaches but does not dissolve silicate minerals. Crustal elements such as Fe, Al, Cr, Ba, and Si may not be quantitatively recovered in some media using this procedure.

A4.4 Digestates from both Digestion I and II contain free halogens and extreme caution must be taken to avoid purging these free halogens onto the gold sand traps (see Section 4.4.2 in Method 1631B). Introduction of free halogens may be avoided by analyzing an aliquot of the sample digestate smaller than 5 mL (Appendix Section A12.3), and by pipetting aliquots of the digestate into bubbler water already containing $SnCl_2$. The use of hydroxylamine hydrochloride to remove free halogens (as prescribed in Method 1631B for aqueous samples) is not needed for solid sample digestates; there is a sufficient amount of $SnCl_2$ in the bubbler to reduce both Hg(II) and free halogens in digestate aliquots smaller than 5 mL.

A4.5 If iodized coal or other elemental carbon samples are to be analyzed, the final acid concentration in the diluted sample must be greater than 40% (v/v), and all carbon particles must be settled prior to analysis to avoid re-adsorption of Hg on the carbon and an ensuing low bias.

A5.0 Safety

Observe the safety precautions in Method 1631B.

A6.0 Apparatus and Materials

A6.1 Digestion vessel—50-mL borosilicate Erlenmeyer flask, calibrated to 40 ± 0.5 mL; or any other acid-cleaned, flat-bottomed, borosilicate glass container calibrated to 40 ± 0.5 mL.

A6.2 Pressure release digestion cap—Clear glass sphere or inverted fluoropolymer cone, approximately 1.5 - 2.0 cm in diameter, initially cleaned by heating overnight in hot concentrated nitric acid. The sphere or cone acts as a pressure release valve during gas evolution. A common clear glass marble may be used as the sphere, or the cone may be custom manufactured. Colored glass marbles contain high levels of trace metals and must not be used. The cap must completely cover the opening of the digestion vessel without falling in, yet not be so large as to risk falling off when slightly lifted by the gas pressure in the vessel.

A6.3 Electric hot plate—A temperature controlled electric hot-plate capable of maintaining a temperature of 100-110°C. A commonly available fluoropolymer-coated pancake griddle is excellent for this purpose. Do not use the griddle for heating flammable solvents.

A6.4 Dilution vessels—Volumetric flasks, glass, 25, 50.0, and 100.0 mL, cleaned per the procedures in Method 1631B.

A6.5 Digestate storage vessel—VOA vial, glass, 40-mL, with fluoropolymer-lined cap, cleaned per the procedures in Method 1631B, or purchase I-Chem level 300, trace metal clean, with fluoropolymer-lined cap, or equivalent.

A6.6 Balance—Analytical, capable of weighing 1.0 mg.

A7.0 Reagents and Standards

A7.1 Reference matrices

A7.1.1 Biota, including tissue and wet and dry municipal sludge—Chicken breast, skinless, boneless, purchased at a local supermarket, or other tissue demonstrated to be free of mercury at the MDL in Table A1.

A7.1.2 Soil, sediment, and other geological samples—Playground sand or other sand-like material demonstrated to be free from mercury at the MDL in Table A1.

A7.2 Nitric acid (concentrated)—Reagent grade, containing less than 5 pg/mL Hg. The HNO_3 must be pre-analyzed for Hg before use.

A7.3 Sulfuric acid (concentrated)—Reagent grade, containing less than 5 pg/mL Hg. The H_2SO_4 must be pre-analyzed for Hg before use.

A7.4 HNO_3/H_2SO_4 solution—In a fume hood, slowly add 300 mL of concentrated H_2SO_4 (Appendix Section A7.3) to 700 mL of concentrated HNO_3 (Appendix Section A7.2) in a fluoropolymer bottle.

Warning: This mixture gets hot and emits caustic fumes.

A7.5 Dilute BrCl solutions—Use the concentrated (0.2N) BrCl solution in Section 7.6 of Method 1631B to produce the following solutions:

A7.5.1 0.07 N bromine monochloride solution—Dilute 300 mL of 0.2N BrCl solution to 1000 mL with reagent water in a fluoropolymer bottle.

A7.5.2 0.02 N bromine monochloride solution—Dilute 100 mL of concentrated BrCl solution to 1000 mL with reagent water in a fluoropolymer bottle.

A8.0 Sample Collection, Preservation, and Storage

A8.1 Samples are collected into acid-cleaned glass, polyethylene, or fluoropolymer jars. For all except very low level and high water content samples, polyethylene bags are also acceptable. Dry solids

such as coal and ores may be collected and stored in heavy gauge paper pouches commonly used by geologists.

A8.2 Samples are collected using clean gloves. Equipment is rinsed between samples to avoid cross-contamination. In general, follow the sampling procedures in Method 1613B. The ultra-low level sampling procedures in EPA Method 1669 may not be necessary because Hg concentrations in solids are typically 10^3 - 10^7 times higher than those found in water samples.

A8.3 Sample shipment, storage, preservation, and holding times

A8.3.1 Dry samples—Samples such as ores, coal, paper, and wood may be shipped unrefrigerated and stored indefinitely in a cool, dry location known to have an atmosphere that is low in mercury.

A8.3.2 Biota samples—Samples containing biota, including wet and dry sludge, are shipped to the laboratory at 0-4 °C and may be processed and stored in one of the following two ways:

A8.3.2.1 Biota samples large enough to sub-sample are homogenized to a fine paste with a stainless steel mill, or finely chopped with stainless steel tools on an acid-cleaned, plastic cutting board. After homogenization, samples are stored frozen at < -15 °C in an acid-cleaned glass or fluoropolymer jar. The jar should be sized to be filled between 50 - 80% with sample. Samples may be stored frozen for a maximum of 1 year.

A8.3.2.2 If not analyzed upon receipt at the laboratory, biota samples may be lyophilized (freeze-dried) prior to homogenization and storage. Once lyophilized, biota samples may be stored unrefrigerated in a low-mercury atmosphere for a maximum of 1 year.

A8.3.3 Wet sediment samples—Wet sediment samples are chilled and shipped to the laboratory at 0-4 °C. Because freezing and thawing may adversely affect homogeneity by causing clumping and separation of the solids from the liquid, wet sediment samples must be aliquoted and weighed at the laboratory and prior to freezing if they are not analyzed upon receipt. Wet sediment samples may be held for 1 year if aliquoted, weighed, and frozen at < -15 °C. Sediment samples may be lyophilized and stored unrefrigerated for 1 year in a low-mercury atmosphere if only total Hg will be determined and no free elemental mercury (Hg^0) is expected to be in the samples.

A9.0 Quality Control

A9.1 The quality control (QC) measures in Section 9 of Method 1631B must be followed when analyzing samples using this Appendix. In addition, this Appendix requires method blanks. Descriptions of the modifications of the quality control measures in Method 1631B that are required for application to solid and semi-solid matrices are provided below.

A9.2 Initial demonstration of laboratory capability

A9.2.1 Method detection limit (see Section 9.2.1 of Method 1631B)—The laboratory must achieve an MDL that is less than or equal to the MDL listed in Table A1.

A9.2.2 Initial precision and recovery (IPR; see Section 9.2.2 of Method 1631B)—Analyze four aliquots of the appropriate reference matrix (see Appendix Section A7.1), each spiked with 4.0 ng of Hg. This amount will be 8 ng/g for a 0.5 g sample. Calculate the average percent recovery (X) and the RSD of percent recovery. Compare X and RSD with the corresponding IPR limits in Table A1. If X and RSD meet the acceptance criteria, system performance is acceptable and analysis of samples may begin. If, however, RSD exceeds the precision limit or X is outside the recovery range, performance of the analytical system is unacceptable. Correct the problem and repeat the test.

A9.3 Matrix spike/matrix spike duplicate (MS/MSD; see Section 9.3 of Method 1631B)

9.3.1 Spike and analyze 1 out of every 10 samples of the same matrix type, in duplicate, at a concentration 2 - 5 times the background concentration of Hg in the unspiked sample or at the concentration in the IPR (Appendix Section A9.2.2), whichever is greater. Calculate the percent recovery in each aliquot and the RPD between the aliquots. The individual recoveries and the RPD shall meet the MS/MSD recovery acceptance criteria in Table A1. If either recovery or the RPD does not meet the acceptance criteria, correct the problem and repeat the test according to the procedures in Sections 9.3.4 and/or 9.3.5 of Method 1631B.

A9.4 Blanks (see Section 9.4 of Method 1631B)

A9.4.1 Because of the high concentrations of mercury in solid samples, as compared to aqueous samples, field blanks (Section 9.4.3 of Method 1631B) and sampler check blanks (Section 9.4.4.2 of Method 1631B) are not required. However, it may be prudent to collect a sampler check blank the first time that a given set of sampling equipment is used and whenever it is suspected to be contaminated.

A9.4.2 Method blank—For each batch of 20 samples (Section 9.1.7 of Method 1631B), digest and analyze a method blank using the most appropriate reference matrix (Appendix Section A7.1). The laboratory may process a greater number of method blanks, if desired, and average the results. The method blank must include all sample processing steps; e.g., homogenization (Appendix Section A8.3.2.1). The concentration of mercury in the method blank, or the average of multiple method blanks, must meet the QC acceptance criteria in Table A1; otherwise, the source of contamination must be eliminated and the batch reanalyzed.

A9.5 Ongoing precision and recovery (OPR; see Section 9.5 of Method 1631B)—The OPR (laboratory control sample) for solid and semi-solid samples is test of the entire analytical system and includes all sample processing procedures; e.g., homogenization (Appendix Section A8.3.2.1) and digestion (Appendix Section A11.1 or A11.2).

A9.5.1 Analyze an aliquot of the appropriate reference matrix (see Appendix Section A7.1), spiked at the concentration in the IPR (Appendix Section A9.2.2). Calculate the percent recovery.

A9.5.2 Compare percent recovery with the OPR limit in Table A1. If percent recovery meets the acceptance criteria, system performance is acceptable and analysis of samples and blanks may continue. If, however, percent recovery is outside of the acceptance range, analytical system performance is unacceptable. Correct the problem and repeat the test according to Section 9.5.2 of Method 1631B.

A9.6 Quality Control Sample (QCS) - Many certified reference materials (CRMs) are available for total mercury in plants, animals, fish, sediments, soils, and sludge. Recovery and precision for at least one QCS per batch of samples must meet the performance specifications provided by the supplier.

A9.7 Replicate samples—Some samples, particularly sediments, may be heterogeneous. Replicates of these samples should be analyzed to characterize this heterogeneity. Replicate samples may also be required by a specific program to assess the precision of the sample collection, transportation, and storage techniques. The relative percent difference (RPD) between replicates should be less than 30%.

A10.0 Calibration and Standardization

A10.1 Calibrate the CVAFS instrument system using the procedures in Section 10 of Method 1631B. The concentration of the calibration solutions is as given in Section 10.1.1.2 of Method 1613B. The amount of Hg in these solutions will be 0.05, 0.5, 2.5, 5.0, and 10.0 ng.

A10.2 Calibration verification (VER)—Calibration of the CVAFS instrument system must be verified periodically using aqueous standards. In Method 1631B, the OPR is used for this verification because the standards are added to water (see Sections 10.2 and 9.5 of Method 1631B). In contrast, the OPR in this Appendix (Appendix Section A9.5) is used to demonstrate that the end-to-end analytical system remains in control. To avoid confusion, the periodic verification of calibration in this Appendix is referred to as "calibration verification" (VER). The VER is a spiked reagent water sample (an aqueous blank spike) and is used to determine that the CVAFS remains in control.

A10.2.1 Prior to and after the analysis of 10 samples, verify calibration of the CVAFS instrument system using the OPR test in Sections 9.5.1 and 9.5.2 of Method 1631B. Record results as calibration verification (VER).

A10.2.2 The requirements in Section 9.5.2 of Method 1631B must be met for sample results to be valid.

A11.0 Digestion

A11.1 Digestion I: Hot re-fluxing HNO_3/H_2SO_4 digestion followed by BrCl oxidation—This procedure is intended for biota, wood, paper, tissue, municipal sludge, and other primarily organic matrices (excluding coal). It does, however, give quantitative recovery for Hg on finely divided geological matrices such as sediments and soils.

A11.1.1 Accurately weigh (to the nearest mg) an aliquot of sample directly into a tared digestion vessel (Appendix Section A6.1). For organic matter such as biota, weigh 0.2-0.4 gram; for tissue (e.g., fish), plant material, or sludge, weigh 0.5-1.5 grams; for dried material

such as wood, paper, and CRMs, weigh 0.2-0.4 gram. The use of too much organic material will consume all of the acid in the digestion, resulting in a low recovery.

A11.1.2 To each sample, add 10.0 mL of HNO_3/H_2SO_4 solution (Appendix Section A7.4). Place the digestion vessel in an acid fume hood and loosely cap with a clean marble or inverted fluoropolymer cone (Appendix Section A6.2). For wood, paper, or other dry carbohydrates that can react violently with the HNO_3/H_2SO_4 solution, allow the sample to sit in the cold acid for at least 4 hours before heating.

A11.1.3 After digesting at room temperature, place the digestion vessel on a hot plate in the hood and slowly bring to a gentle boil by incrementally increasing the plate temperature over a 1-hour period. If excessive sample foaming occurs, bring to temperature more slowly. Reflux for 2-3 hours to fully oxidize remaining organic matter. The mineral portion of soil and sediment samples will not dissolve but will be effectively leached by this digestion.

A11.1.4 After the digestion is complete, bring to the calibration mark on the digestion vessel (40 ± 0.5 mL; Appendix Section A6.1) with 0.02 N BrCl solution (Appendix Section A7.5.2) and mix thoroughly. Shake the sample/BrCl solution to homogenize, and allow to sit at least 4 hours prior to analysis to oxidize remaining dissolved methyl Hg. Analyze the oxidized digestate per Appendix Section A12.0.

Note: Some highly organic matrices will require higher levels of BrCl (Appendix Section A7.5.1) and longer digestion times or elevated temperatures. The amount of reagent added to a sample must be the same as the amount added to the reagent blank to detect contamination in the reagents, and to the method blank and the OPR to demonstrate that mercury can be recovered quantitatively. BrCl oxidation must be continued until it is complete.

A11.2 Digestion II: Cold aqua regia followed by BrCl oxidation—This procedure is intended for coal, ores, sediments, soils, and other geological media. It does, however, give quantitative recovery for Hg on finely divided biological media such as tissues, paper, and wood, because the organic matrix is leached rather than dissolved. Solid, dry geological media such as rocks, ores, and coal must be pulverized using a contamination-free mill prior to digestion. Otherwise, mercury will not be recovered from the interior of large particles.

A11.2.1 Accurately weigh (to the nearest mg) an aliquot of the sample directly into a tared digestion vessel. For wet sediments and soils, weigh 0.5-1.5 grams; for dried materials such as coal, ores, and CRMs, weigh 0.5-1.0 gram. To better assure homogeneity, sediments and soils should be screened through a 2-mm plastic sieve to remove large rocks and sticks before digestion.

A11.2.2 In a fume hood, add 8.0 mL of concentrated HCl (Method 1631B Section 7.3), swirl, and add 2.0 mL of concentrated HNO_3 to the sample in the digestion vessel. Cap the vessel with a clean glass marble or inverted fluoropolymer cone. Allow to digest at room temperature for at least 4 hours but preferably overnight.

A11.2.3 For coal or other elemental carbon-containing sample, dilute the digestate to the calibration mark (40 ± 0.5 mL) with 0.07 N BrCl solution and shake the flask to mix thoroughly. The addition of BrCl ensures that Hg will not re-adsorb to the carbon

particles, producing low recoveries. After dilution and shaking, allow the sample to settle overnight, or centrifuge prior to analysis. Be sure that all fine-grained particles are completely settled prior to analysis. This settling can be hastened by centrifuging for 20 minutes at 3000 RPM or by filtering the sample through a 0.45-mm filter. Analyze per Appendix Section A12.0.

A11.2.4 For other than coal or elemental carbon-containing samples, dilute the digestate to volume (40 ± 0.5 mL) with reagent water so that the meniscus is at the calibration line in the neck of the digestion vessel. Shake vigorously and allow settling until the supernatant is clear prior to analysis. Analyze per Appendix Section A12.0.

A11.3 The diluted digestates may be stored up to one year in glass or fluoropolymer containers prior to analysis, or for future re-analysis, if needed.

A12.0 Digestate Analysis

Diluted digestates are analyzed in a manner analogous to the analysis of standards by Method 1631B (see Section 10.0 of Method 1631B).

A12.1 Pipet a 0.01- to 5.0-mL volume of diluted digestate (Appendix Section A11.1.4, A11.2.3, or A11.2.4) directly into a bubbler containing approximately 100 mL of pre-purged $SnCl_2$-containing water.

Note: The volume of $SnCl_2$-containing water in the bubbler is not critical for the purpose of purging but is assumed to be 0.100 L for the purpose of calculating results (see Appendix Section A13.1.1).

A12.2 Purge the solution onto a gold trap for 20 minutes. These conditions allow measurement of Hg concentrations in the range of 1 – 5,000 ng/g (parts per billion).

A12.3 Change the $SnCl_2$-containing water in the bubbler after a total of 10 mL of digestate has been added. For example, if 2 digestate aliquots of 5 mL each have been added to 100 mL of fresh, pre-purged, $SnCl_2$-containing water, the $SnCl_2$-containing water must be changed and 100 mL of fresh, $SnCl_2$-containing water must be placed in the bubbler and purged for a minimum of 10 minutes prior to addition of another digestate aliquot.

A12.4 For samples known or expected to contain high Hg concentrations, further dilute (usually by a factor of 100) an aliquot of the diluted digestate with 0.02 N BrCl solution, and analyze a sub-aliquot.

A13.0 Data Analysis and Calculations

A13.1 Calculation of solid phase concentrations

A13.1.1 The analytical system in Method 1631B will give analytical results in units of area (or height) for the volume of diluted digestate analyzed. To calculate the solid phase concentration, use the following equation:

$$C_{Hg} = (A_s - A_{BB}) \times V \times d \times 0.1 / (CF_m \times v \times w)$$

where:

C_{Hg}	=	concentration of mercury in the sample (ng/g wet weight)
A_s	=	peak area (or height) for mercury in the sample
A_{BB}	=	peak area (or height) for the average of the bubbler blanks
V	=	volume of diluted digestate (mL) (Appendix Sections A11.1.4, A11.2.3, A11.2.4) = 40 mL
d	=	dilution factor(s); e.g., a factor of 100 in Appendix Section A12.4.
0.1	=	volume in bubbler (L) (Assumed per note in Appendix Section A12.1)
CF_m	=	mean CF from calibration (area (or height))/(ng/L) (Method 1613B Section 10.1.1.4)
v	=	digestate volume analyzed (mL) (Appendix Section A12.1)
w	=	sample weight (g) (Appendix Section A11.1.1 or A11.2.1)

A13.1.2 If desired, determine the moisture content of a sample aliquot and use the dry weight as "w" in the equation above.

A13.2 Reporting

A13.2.1 Report results as required in Method 1631B except use reporting levels and units appropriate to solid samples (ng/g).

A13.2.2 Reagent blank results and method blank results are reported separately and, if requested or required, are subtracted from sample Hg concentrations.

A14.0 Method Performance

A14.1 This Appendix was developed in a single laboratory and validated in a single laboratory. Performance data from these studies are summarized in Tables A2 through A7.

A15.0 References

1. *Development of Digestion Procedures for Determination of Mercury in Solid and Semi-solid Samples*, Frontier Geosciences, available from EPA Sample Control Center DynCorp I&ET, Alexandria, VA 22304 (703-461-2100; SCC@dyncorp.com).

2. *Single Laboratory Validation of Appendix to Method 1631*, June-July 1999, Brooks-Rand Ltd., EPA Sample Control Center Episode Number 6236, DynCorp I&ET, Alexandria, VA 22304 (703-461-2100; SCC@dyncorp.com).

Table A1. Quality control acceptance criteria.

Test	Acceptance Criteria	Spike concentration
Calibration linearity	<15% RSD of CF	0.5, 5, 25, 50, and 100 ng/L = 0.05, 0.5, 2.5, 5.0, and 10.0 ng
Calibration verification (VER)	77-123%	5 ng/L = 0.5 ng
MDL	0.48 ng/g[(1)]	0.8 ng/g
ML	1 ng/g[(2)]	0.05 ng (lowest calibration point)
MS/MSD recovery	70-130%	2x background or level in IPR/OPR, whichever is greater
MS/MSD precision	< 30% RPD	2x background or level in IPR/OPR, whichever is greater
IPR recovery	75-125%	4.0 ng
IPR precision	< 20% RSD	4.0 ng
OPR recovery	70 - 130%	4.0 ng
Method blank	< 0.4 ng or < 0.1x sample, whichever is greater	-

(1) See Appendix Table A4
(2) Assuming a 0.5 g sample

Table A2. Method performance for biological samples and CRMs digested using hot re-fluxing HNO_3 digestion plus BrCl dilution and Method 1631B. Blanks and spikes were on three different instruments, over a period of several weeks. Data provided by Frontier Geosciences.

Test/material	n	Hg concentration (ng/g; ppb)			Performance
		mean	SD	certified[(1)]	
Method blanks	24	0.25	0.13	--	DL = 0.33 ng/g[(2)]
2.0 ng/g matrix spike	28	1.90[(3)]	0.22	2.00	95% rec.; 11% RSD
IRM-007 (sludge)	3	3,680	150	3,150	117% rec.; 4% RSD
DOLT-2 (fish liver)	7	2,164	161	2,140	101% rec.; 7%RSD
DORM-2 (fish muscle)	11	4,682	386	4,640	101% rec.; 8% RSD
NIST-2796 (mussel)	12	60.4	6.7	61.0	99% rec.; 11% RSD

(1) value provided by supplier of reference material
(2) detection limit = 2.5 x SD for 24 method blanks (2.5 = student's t @ 23 degrees of freedom)
(3) net recovered; background concentration (chicken breast) was 0.41 ng/g

Table A3. Method performance for geological samples and CRMs using cold aqua regia digestion and Method 1631B. Data provided by Frontier Geosciences.

Test/material	n	Hg concentration (ng/g; ppb)			Performance
		mean	SD	certified[1]	
Method blanks	23	0.045	0.037	--	DL = 0.09 ng/g[2]
0.5 ng/g blank spike	8	0.465	0.079	0.50	MDL = 0.24 ng/g
NIST-2709 (soil)	9	1393	111	1,400	100% rec.; 8% RSD
NIST-1633 (fly ash)	2	163	3.0	160	102% rec.; 2% RSD
NIST-2710 (soil)	3	30888	2,692	32,610	95% rec.; 9% RSD
IAEA-356 (sediment)	1	7152	--	7.62	94% rec.
PACS-1 (sediment)	1	4402	--	4,540	97% rec.
NIST-1630 (coal)	3	108	5.0	127*	85% rec.; 5% RSD
NIST-1632 (coal)	5	79.3	7.0	78	102% rec.; 9% RSD

(1) value provided by supplier of reference material

(2) detection limit = 2.5 x SD for 24 method blanks (2.5 = student's t @ 23 degrees of freedom)

Table A4. Results of MDL Set 2 analyses (spiked with 0.24 ng; ~0.8 ng/g). Data provided by Brooks-Rand.

Rep	Sample Mass (g)	Measured Hg (ng)	Blank-corrected Hg (ng)	Sample Concentration (ng/g)*
1	1.03	0.39	0.13	0.41
2	1.29	0.50	0.23	0.71
3	1.25	0.48	0.22	0.73
4	1.36	0.53	0.26	0.78
5	1.28	0.49	0.23	0.68
6	1.01	0.39	0.12	0.40
7	1.17	0.45	0.19	0.61
				Average: 0.62 ng/g **Std. Dev.: 0.15 ng/g**
***blank corrected**				**MDL = 0.48**

Table A5. Analyses of spiked catfish samples (spiked with 17 ng of Hg). Data provided by Brooks-Rand

Replicate	Sample Mass (g)	Measured Hg (ng)	Recovered Hg (ng)*	%Recovery*
1	1.02	30.1	17.1	99.3
2	1.21	31.6	16.2	93.7
3	0.97	31.4	19.0	110.2
4	1.17	23.4	8.41	48.7
*background corrected				**Average: 88% Std. Dev.: 27%**

Table A6. Analyses of spiked powdered egg yolk (spiked with 2.9 ng of Hg). Data provided by Brooks-Rand.

Replicate	Sample Mass (g)	Measured Hg (ng)	Recovered Hg* (ng)	%Recovery
1	1.00	3.49	2.34	80.6
2	1.06	3.16	1.94	67
3	1.04	2.56	1.37	47.1
4	1.08	3.75	2.50	86.2
*background corrected				**Average: 70% Std. Dev.: 17%**