METHOD 3050B

ACID DIGESTION OF SEDIMENTS, SLUDGES, AND SOILS

1.0 SCOPE AND APPLICATION

1.1 This method has been written to provide two separate digestion procedures, one for the preparation of sediments, sludges, and soil samples for analysis by flame atomic absorption spectrometry (FLAA) or inductively coupled plasma atomic emission spectrometry (ICP-AES) and one for the preparation of sediments, sludges, and soil samples for analysis of samples by Graphite Furnace AA (GFAA) or inductively coupled plasma mass spectrometry (ICP-MS). The extracts from these two procedures are not interchangeable and should only be used with the analytical determinations outlined in this section. Samples prepared by this method may be analyzed by ICP-AES or GFAA for all the listed metals as long as the detecion limits are adequate for the required end-use of the data. Alternative determinative techniques may be used if they are scientifically valid and the QC criteria of the method, including those dealing with interferences, can be achieved. Other elements and matrices may be analyzed by this method if performance is demonstrated for the analytes of interest, in the matrices of interest, at the concentration levels of interest (See Section 8.0). The recommended determinative techniques for each element are listed below:

FLAA/ICP-AES		GFAA/ICP-MS
Aluminum	Magnesium	Arsenic
Antimony	Manganese	Beryllium
Barium	Molybdenum	Cadmium
Beryllium	Nickel	Chromium
Cadmium	Potassium	Cobalt
Calcium	Silver	Iron
Chromium	Sodium	Lead
Cobalt	Thallium	Molybdenum
Copper	Vanadium	Selenium
Iron	Zinc	Thallium
Lead		
Vanadium		

1.2 This method is not a total digestion technique for most samples. It is a very strong acid digestion that will dissolve almost all elements that could become “environmentally available.” By design, elements bound in silicate structures are not normally dissolved by this procedure as they are not usually mobile in the environment. If absolute total digestion is required use Method 3052.

2.0 SUMMARY OF METHOD

2.1 For the digestion of samples, a representative 1-2 gram (wet weight) or 1 gram (dry weight) sample is digested with repeated additions of nitric acid (HNO_3) and hydrogen peroxide (H_2O_2).

2.2 For GFAA or ICP-MS analysis, the resultant digestate is reduced in volume while heating and then diluted to a final volume of 100 mL.

2.3 For ICP-AES or FLAA analyses, hydrochloric acid (HCl) is added to the initial digestate and the sample is refluxed. In an optional step to increase the solubility of some metals (see Section 7.3.1: NOTE), this digestate is filtered and the filter paper and residues are rinsed, first

with hot HCl and then hot reagent water. Filter paper and residue are returned to the digestion flask, refluxed with additional HCl and then filtered again. The digestate is then diluted to a final volume of 100 mL.

2.4 If required, a separate sample aliquot shall be dried for a total percent solids determination.

3.0 INTERFERENCES

3.1 Sludge samples can contain diverse matrix types, each of which may present its own analytical challenge. Spiked samples and any relevant standard reference material should be processed in accordance with the quality control requirements given in Sec. 8.0 to aid in determining whether Method 3050B is applicable to a given waste.

4.0 APPARATUS AND MATERIALS

4.1 Digestion Vessels - 250-mL.

4.2 Vapor recovery device (e.g., ribbed watch glasses, appropriate refluxing device, appropriate solvent handling system).

4.3 Drying ovens - able to maintain 30°C $\pm$ 4°C.

4.4 Temperature measurement device capable of measuring to at least 125°C with suitable precision and accuracy (e.g., thermometer, IR sensor, thermocouple, thermister, etc.)

4.5 Filter paper - Whatman No. 41 or equivalent.

4.6 Centrifuge and centrifuge tubes.

4.7 Analytical balance - capable of accurate weighings to 0.01 g.

4.8 Heating source - Adjustable and able to maintain a temperature of 90-95°C. (e.g., hot plate, block digestor, microwave, etc.)

4.9 Funnel or equivalent.

4.10 Graduated cylinder or equivalent volume measuring device.

4.11 Volumetric Flasks - 100-mL.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. If the purity of a reagent is questionable, analyze the reagent to determine the level of impurities. The reagent blank must be less than the MDL in order to be used.

5.2 Reagent Water. Reagent water will be interference free. All references to water in the method refer to reagent water unless otherwise specified. Refer to Chapter One for a definition of reagent water.

5.3 Nitric acid (concentrated), HNO_3. Acid should be analyzed to determine level of impurities. If method blank is < MDL, the acid can be used.

5.4 Hydrochloric acid (concentrated), HCl. Acid should be analyzed to determine level of impurities. If method blank is < MDL, the acid can be used.

5.5 Hydrogen peroxide (30%), H_2O_2. Oxidant should be analyzed to determine level of impurities. If method blank is < MDL, the peroxide can be used.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be demonstrated to be free of contamination at or below the reporting limit. Plastic and glass containers are both suitable. See Chapter Three, Section 3.1.3, for further information.

6.3 Nonaqueous samples should be refrigerated upon receipt and analyzed as soon as possible.

6.4 It can be difficult to obtain a representative sample with wet or damp materials. Wet samples may be dried, crushed, and ground to reduce subsample variability as long as drying does not affect the extraction of the analytes of interest in the sample.

7.0 PROCEDURE

7.1 Mix the sample thoroughly to achieve homogeneity and sieve, if appropriate and necessary, using a USS #10 sieve. All equipment used for homogenization should be cleaned according to the guidance in Sec. 6.0 to minimize the potential of cross-contamination. For each digestion procedure, weigh to the nearest 0.01 g and transfer a 1-2 g sample (wet weight) or 1 g sample (dry weight) to a digestion vessel. For samples with high liquid content, a larger sample size may be used as long as digestion is completed.

> NOTE: All steps requiring the use of acids should be conducted under a fume hood by properly trained personnel using appropriate laboratory safety equipment. The use of an acid vapor scrubber system for waste minimization is encouraged.

7.2 For the digestion of samples for analysis by GFAA or ICP-MS, add 10 mL of 1:1 HNO_3, mix the slurry, and cover with a watch glass or vapor recovery device. Heat the sample to 95°C ± 5°C and reflux for 10 to 15 minutes without boiling. Allow the sample to cool, add 5 mL of concentrated HNO_3, replace the cover, and reflux for 30 minutes. If brown fumes are generated, indicating oxidation of the sample by HNO_3, repeat this step (addition of 5 mL of conc. HNO_3) over and over until no brown fumes are given off by the sample indicating the complete reaction with HNO_3. Using a ribbed watch glass or vapor recovery system, either allow the solution to evaporate to approximately 5 mL without boiling or heat at 95°C ± 5°C without boiling for two hours. Maintain a covering of solution over the bottom of the vessel at all times.

NOTE: Alternatively, for direct energy coupling devices, such as a microwave, digest samples for analysis by GFAA or ICP-MS by adding 10 mL of 1:1 HNO_3, mixing the slurry and then covering with a vapor recovery device. Heat the sample to 95°C ± 5°C and reflux for 5 minutes at 95°C ± 5°C without boiling. Allow the sample to cool for 5 minutes, add 5 mL of concentrated HNO_3, heat the sample to 95°C ± 5°C and reflux for 5 minutes at 95°C ± 5°C. If brown fumes are generated, indicating oxidation of the sample by HNO_3, repeat this step (addition of 5 mL concentrated HNO_3) until no brown fumes are given off by the sample indicating the complete reaction with HNO_3. Using a vapor recovery system, heat the sample to 95°C ± 5°C and reflux for 10 minutes at 95°C ± 5°C without boiling.

7.2.1 After the step in Section 7.2 has been completed and the sample has cooled, add 2 mL of water and 3 mL of 30% H_2O_2. Cover the vessel with a watch glass or vapor recovery device and return the covered vessel to the heat source for warming and to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence. Heat until effervescence subsides and cool the vessel.

NOTE: Alternatively, for direct energy coupled devices: After the Sec. 7.2 "NOTE" step has been completed and the sample has cooled for 5 minutes, add slowly 10 mL of 30% H_2O_2. Care must be taken to ensure that losses do not occur due to excessive vigorous effervesence. Go to Section 7.2.3.

7.2.2 Continue to add 30% H_2O_2 in 1-mL aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged.

NOTE: Do not add more than a total of 10 mL 30% H_2O_2.

7.2.3 Cover the sample with a ribbed watch glass or vapor recovery device and continue heating the acid-peroxide digestate until the volume has been reduced to approximately 5 mL or heat at 95°C ± 5°C without boiling for two hours. Maintain a covering of solution over the bottom of the vessel at all times.

NOTE: Alternatively, for direct energy coupled devices: Heat the acid-peroxide digestate to 95°C ± 5°C in 6 minutes and remain at 95°C ± 5°C without boiling for 10 minutes.

7.2.4 After cooling, dilute to 100 mL with water. Particulates in the digestate should then be removed by filtration, by centrifugation, or by allowing the sample to settle. The sample is now ready for analysis by GFAA or ICP-MS.

7.2.4.1 Filtration - Filter through Whatman No. 41 filter paper (or equivalent).

7.2.4.2 Centrifugation - Centrifugation at 2,000-3,000 rpm for 10 minutes is usually sufficient to clear the supernatant.

7.2.4.3 The diluted digestate solution contains approximately 5% (v/v) HNO_3. For analysis, withdraw aliquots of appropriate volume and add any required reagent or matrix modifier.

7.3 For the analysis of samples for FLAA or ICP-AES, add 10 mL conc. HCl to the sample digest from 7.2.3 and cover with a watch glass or vapor recovery device. Place the sample on/in the heating source and reflux at 95°C ± 5°C for 15 minutes.

NOTE: Alternatively, for direct energy coupling devices, such as a microwave, digest samples for analysis by FLAA and ICP-AES by adding 5 mL HCl and 10 mL H_2O to the sample digest from 7.2.3 and heat the sample to 95°C ± 5°C, Reflux at 95°C ± 5°C without boiling for 5 minutes.

7.4 Filter the digestate through Whatman No. 41 filter paper (or equivalent) and collect filtrate in a 100-mL volumetric flask. Make to volume and analyze by FLAA or ICP-AES.

NOTE: Section 7.5 may be used to improve the solubilities and recoveries of antimony, barium, lead, and silver when necessary. These steps are optional and are not required on a routine basis.

7.5 Add 2.5 mL conc. HNO_3 and 10 mL conc. HCl to a 1-2 g sample (wet weight) or 1 g sample (dry weight) and cover with a watchglass or vapor recovery device. Place the sample on/in the heating source and reflux for 15 minutes.

7.5.1 Filter the digestate through Whatman No. 41 filter paper (or equivalent) and collect filtrate in a 100-mL volumetric flask. Wash the filter paper, while still in the funnel, with no more than 5 mL of hot (~95°C) HCl, then with 20 mL of hot (~95°C) reagent water. Collect washings in the same 100-mL volumetric flask.

7.5.2 Remove the filter and residue from the funnel, and place them back in the vessel. Add 5 mL of conc. HCl, place the vessel back on the heating source, and heat at 95°C ± 5°C until the filter paper dissolves. Remove the vessel from the heating source and wash the cover and sides with reagent water. Filter the residue and collect the filtrate in the same 100-mL volumetric flask. Allow filtrate to cool, then dilute to volume.

NOTE: High concentrations of metal salts with temperature-sensitive solubilities can result in the formation of precipitates upon cooling of primary and/or secondary filtrates. If precipitation occurs in the flask upon cooling, do not dilute to volume.

7.5.3 If a precipitate forms on the bottom of a flask, add up to 10 mL of concentrated HCl to dissolve the precipitate. After precipitate is dissolved, dilute to volume with reagent water. Analyze by FLAA or ICP-AES.

7.6 Calculations

7.6.1 The concentrations determined are to be reported on the basis of the actual weight of the sample. If a dry weight analysis is desired, then the percent solids of the sample must also be provided.

7.6.2 If percent solids is desired, a separate determination of percent solids must be performed on a homogeneous aliquot of the sample.

8.0 QUALITY CONTROL

8.1 All quality control measures described in Chapter One should be followed.

8.2 For each batch of samples processed, a method blank should be carried throughout the entire sample preparation and analytical process according to the frequency described in Chapter One. These blanks will be useful in determining if samples are being contaminated. Refer to Chapter One for the proper protocol when analyzing method blanks.

8.3 Spiked duplicate samples should be processed on a routine basis and whenever a new sample matrix is being analyzed. Spiked duplicate samples will be used to determine precision and bias. The criteria of the determinative method will dictate frequency, but 5% (one per batch) is recommended or whenever a new sample matrix is being analyzed. Refer to Chapter One for the proper protocol when analyzing spiked replicates.

8.4 Limitations for the FLAA and ICP-AES optional digestion procedure. Analysts should be aware that the upper linear range for silver, barium, lead, and antimony may be exceeded with some samples. If there is a reasonable possibility that this range may be exceeded, or if a sample's analytical result exceeds this upper limit, a smaller sample size should be taken through the entire procedure and re-analyzed to determine if the linear range has been exceeded. The approximate linear upper ranges for a 2 gram sample size:

Ag	2,000 mg/kg
As	1,000,000 mg/kg
Ba	2,500 mg/kg
Be	1,000,000 mg/kg
Cd	1,000,000 mg/kg
Co	1,000,000 mg/kg
Cr	1,000,000 mg/kg
Cu	1,000,000 mg/kg
Mo	1,000,000 mg/kg
Ni	1,000,000 mg/kg
Pb	200,000 mg/kg
Sb	200,000 mg/kg
Se	1,000,000 mg/kg
Tl	1,000,000 mg/kg
V	1,000,000 mg/kg
Zn	1,000,000 mg/kg

NOTE: These ranges will vary with sample matrix, molecular form, and size.

9.0 METHOD PERFORMANCE

9.1 In a single laboratory, the recoveries of the three matrices presented in Table 2 were obtained using the digestion procedure outlined for samples prior to analysis by FLAA and ICP-AES. The spiked samples were analyzed in duplicate. Tables 3-5 represents results of analysis of NIST Standard Reference Materials that were obtained using both atmospheric pressure microwave digestion techniques and hot-plate digestion procedures.

10.0 REFERENCES

1. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.

2. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.

3. Edgell, K.; USEPA Method Study 37 - SW-846 Method 3050 Acid Digestion of Sediments, Sludges, and Soils. EPA Contract No. 68-03-3254, November 1988.

4. Kimbrough, David E., and Wakakuwa, Janice R. Acid Digestion for Sediments, Sludges, Soils, and Solid Wastes. A Proposed Alternative to EPA SW 846 Method 3050, Environmental Science and Technology, Vol. 23, Page 898, July 1989.

5. Kimbrough, David E., and Wakakuwa, Janice R. Report of an Interlaboratory Study Comparing EPA SW 846 Method 3050 and an Alternative Method from the California Department of Health Services, Fifth Annual Waste Testing and Quality Assurance Symposium, Volume I, July 1989. Reprinted in Solid Waste Testing and Quality Assurance: Third Volume, ASTM STP 1075, Page 231, C.E. Tatsch, Ed., American Society for Testing and Materials, Philadelphia, 1991.

6. Kimbrough, David E., and Wakakuwa, Janice R. A Study of the Linear Ranges of Several Acid Digestion Procedures, Environmental Science and Technology, Vol. 26, Page 173, January 1992. Presented Sixth Annual Waste Testing and Quality Assurance Symposium, July 1990.

7. Kimbrough, David E., and Wakakuwa, Janice R. A Study of the Linear Ranges of Several Acid Digestion Procedures, Sixth Annual Waste Testing and Quality Assurance Symposium, Reprinted in Solid Waste Testing and Quality Assurance: Fourth Volume, ASTM STP 1076, Ed., American Society for Testing and Materials, Philadelphia, 1992.

8. NIST published leachable concentrations. Found in addendum to certificate of analysis for SRMs 2709, 2710, 2711 - August 23, 1993.

9. Kingston, H.M. Haswell, S.J. ed., Microwave Enhanced Chemistry, Professional Reference Book Series, American Chemical Society, Washington, D.C., Chapter 3, 1997.

TABLE 1

STANDARD RECOVERY (%) COMPARISON FOR
METHODS 3050A AND 3050B[a]

Analyte	METHOD 3050A[a]	METHOD 3050B w/option[a]
Ag	9.5	98
As	86	102
Ba	97	103
Be	96	102
Cd	101	99
Co	99	105
Cr	98	94
Cu	87	94
Mo	97	96
Ni	98	92
Pb	97	95
Sb	87	88
Se	94	91
Tl	96	96
V	93	103
Zn	99	95

[a] All values are percent recovery. Samples: 4 mL of 100 mg/mL multistandard; n = 3.

TABLE 2

PERCENT RECOVERY COMPARISON FOR METHODS 3050A AND 3050B

Analyte	Percent Recovery[a,c]							
	Sample 4435		Sample 4766		Sample HJ		Average	
	3050A	3050B	3050A	3050B	3050A	3050B	3050A	3050B
Ag	9.8	103	15	89	56	93	27	95
As	70	102	80	95	83	102	77	100
Ba	85	94	78	95	b	b	81	94
Be	94	102	108	98	99	94	99	97
Cd	92	88	91	95	95	97	93	94
Co	90	94	87	95	89	93	89	94
Cr	90	95	89	94	72	101	83	97
Cu	81	88	85	87	70	106	77	94
Mo	79	92	83	98	87	103	83	98
Ni	88	93	93	100	87	101	92	98
Pb	82	92	80	91	77	91	81	91
Sb	28	84	23	77	46	76	32	79
Se	84	89	81	96	99	96	85	94
Tl	88	87	69	95	66	67	74	83
V	84	97	86	96	90	88	87	93
Zn	96	106	78	75	b	b	87	99

a - Samples: 4 mL of 100 mg/mL multi-standard in 2 g of sample. Each value is percent recovery and is the average of duplicate spikes.

b - Unable to accurately quantitate due to high background values.

c - Method 3050B using optional section.

Table 3
Results of Analysis of Nist Standard Reference Material 2704
"River Sediment" Using Method 3050B (µg/g ± SD)

Element	Atm. Pressure Microwave Assisted Method with Power Control	Atm. Pressure Microwave Assisted Method with Temperature Control (gas-bulb)	Atm. Pressure Microwave Assisted Method with Temperature Control (IR-sensor)	Hot-Plate	NIST Certified Values for Total Digestion (µg/g ±95% CI)
Cu	101 ± 7	89 ± 1	98 ± 1.4	100 ± 2	98.6 ± 5.0
Pb	160 ± 2	145 ± 6	145 ± 7	146 ± 1	161 ± 17
Zn	427 ± 2	411 ± 3	405 ± 14	427 ± 5	438 ± 12
Cd	NA	3.5 ± 0.66	3.7 ± 0.9	NA	3.45 ± 0.22
Cr	82 ± 3	79 ± 2	85 ± 4	89 ± 1	135 ± 5
Ni	42 ± 1	36 ± 1	38 ± 4	44 ± 2	44.1 ± 3.0

NA - Not Available

Table 4
Results of Analysis of NIST Standard Reference Material 2710
"Montana Soil (Highly Elevated Trace Element Concentrations)" Using Method 3050B
(µg/g ± SD)

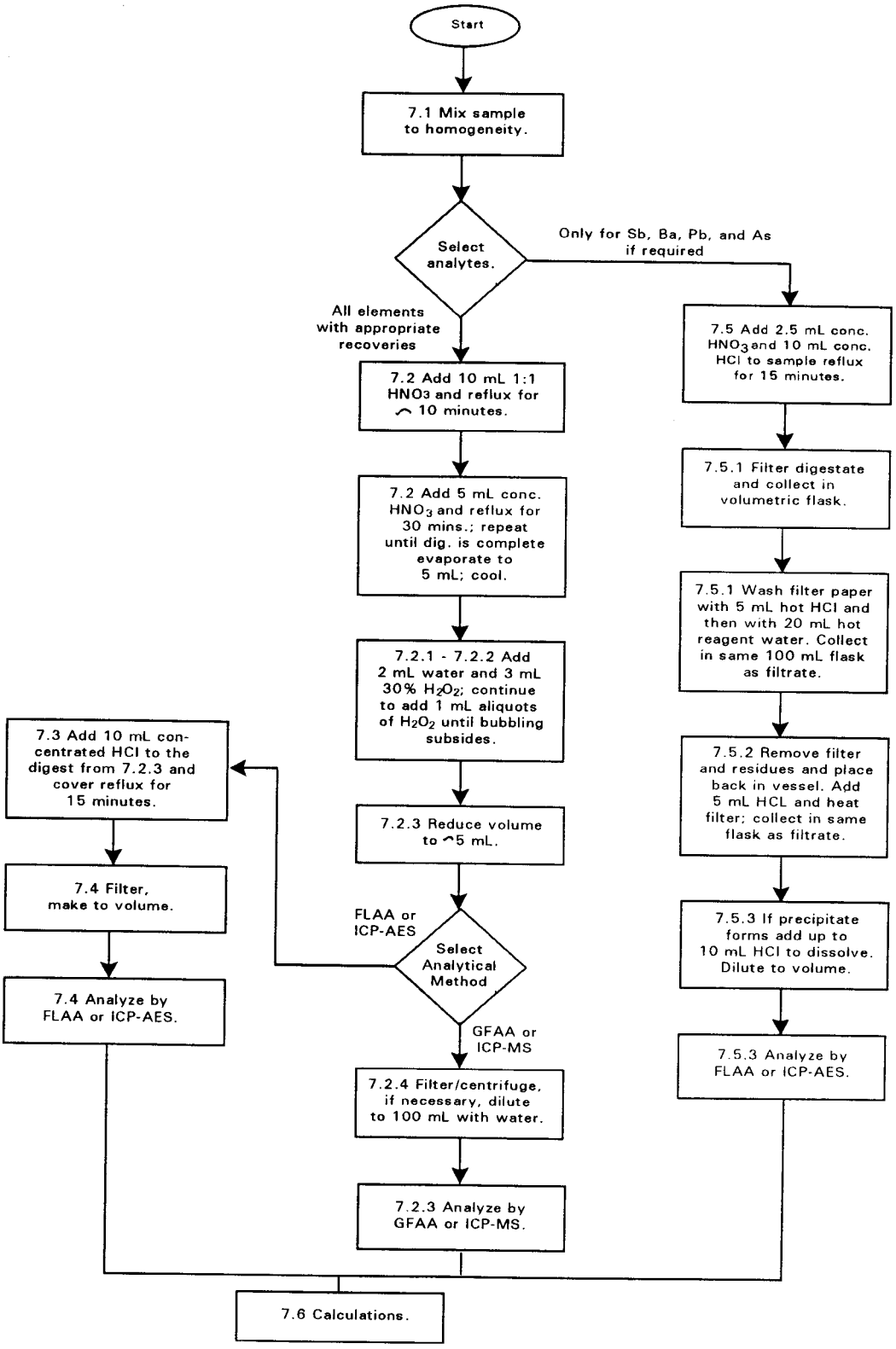
Element	Atm. Pressure Microwave Assisted Method with Power Control	Atm. Pressure Microwave Assisted Method with Temperature Control (gas-bulb)	Atm. Pressure Microwave Assisted Method with Temperature Control (IR-sensor)	Hot-Plate	NIST Leachable Concentrations Using Method 3050	NIST Certified Values for Total Digestion (µg/g ±95% CI)
Cu	2640 ± 60	2790 ± 41	2480 ± 33	2910 ± 59	2700	2950 ± 130
Pb	5640 ± 117	5430 ± 72	5170 ± 34	5720 ± 280	5100	5532 ± 80
Zn	6410 ± 74	5810 ± 34	6130 ± 27	6230 ± 115	5900	6952 ± 91
Cd	NA	20.3 ± 1.4	20.2 ± 0.4	NA	20	21.8 ± 0.2
Cr	20 ± 1.6	19 ± 2	18 ± 2.4	23 ± 0.5	19	39*
Ni	7.8 ± 0.29	10 ± 1	9.1 ± 1.1	7 ± 0.44	10.1	14.3 ± 1.0

NA - Not Available * Non-certified values, for information only.

Table 5
Results of Analysis of NIST Standard Reference Material 2711
"Montana Soil (Moderately Elevated Trace Element Concentrations)" Using Method 3050B
(µg/g ± SD)

Element	Atm. Pressure Microwave Assisted Method with Power Control	Atm. Pressure Microwave Assisted Method with Temperature Control (gas-bulb)	Atm. Pressure Microwave Assisted Method with Temperature Control (IR-sensor)	Hot-Plate	NIST Leachable Concentrations Using Method 3050	NIST Certified Values for Total Digestion (µg/g ±95% CI)
Cu	107 ± 4.6	98 ± 5	98 ± 3.8	111 ± 6.4	100	114 ± 2
Pb	1240 ± 68	1130 ± 20	1120 ± 29	1240 ± 38	1100	1162 ± 31
Zn	330 ± 17	312 ± 2	307 ± 12	340 ± 13	310	350.4 ± 4.8
Cd	NA	39.6 ± 3.9	40.9 ± 1.9	NA	40	41.7 ± 0.25
Cr	22 ± 0.35	21 ± 1	15 ± 1.1	23 ± 0.9	20	47*
Ni	15 ± 0.2	17 ± 2	15 ± 1.6	16 ± 0.4	16	20.6 ± 1.1

NA - Not Available
* Non-certified values, for information only.


Start
7.1 Mix sample to homogeneity.
Select analytes.
Only for Sb, Ba, Pb, and As if required
All elements with appropriate recoveries
7.2 Add 10 mL 1:1 HNO3 and reflux for ~ 10 minutes.
7.2 Add 5 mL conc. HNO3 and reflux for 30 mins.; repeat until dig. is complete evaporate to 5 mL; cool.
7.2.1 - 7.2.2 Add 2 mL water and 3 mL 30% H2O2; continue to add 1 mL aliquots of H2O2 until bubbling subsides.
7.2.3 Reduce volume to ~5 mL.
FLAA or ICP-AES
Select Analytical Method
GFAA or ICP-MS
7.2.4 Filter/centrifuge, if necessary, dilute to 100 mL with water.
7.2.3 Analyze by GFAA or ICP-MS.
7.3 Add 10 mL concentrated HCl to the digest from 7.2.3 and cover reflux for 15 minutes.
7.4 Filter, make to volume.
7.4 Analyze by FLAA or ICP-AES.
7.5 Add 2.5 mL conc. HNO3 and 10 mL conc. HCl to sample reflux for 15 minutes.
7.5.1 Filter digestate and collect in volumetric flask.
7.5.1 Wash filter paper with 5 mL hot HCl and then with 20 mL hot reagent water. Collect in same 100 mL flask as filtrate.
7.5.2 Remove filter and residues and place back in vessel. Add 5 mL HCL and heat filter; collect in same flask as filtrate.
7.5.3 If precipitate forms add up to 10 mL HCl to dissolve. Dilute to volume.
7.5.3 Analyze by FLAA or ICP-AES.
7.6 Calculations.