INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY

SW-846 is not intended to be an analytical training manual. Therefore, method procedures are written based on the assumption that they will be performed by analysts who are formally trained in at least the basic principles of chemical analysis and in the use of the subject technology.

In addition, SW-846 methods, with the exception of required method use for the analysis of method-defined parameters, are intended to be guidance methods which contain general information on how to perform an analytical procedure or technique which a laboratory can use as a basic starting point for generating its own detailed Standard Operating Procedure (SOP), either for its own general use or for a specific project application. The performance data included in this method are for guidance purposes only, and are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

1.0 SCOPE AND APPLICATION

1.1 Inductively coupled plasma-mass spectrometry (ICP-MS) is applicable to the determination of sub-µg/L concentrations of a large number of elements in water samples and in waste extracts or digests (Refs. 1 and 2). When dissolved constituents are required, samples must be filtered and acid-preserved prior to analysis. No digestion is required prior to analysis for dissolved elements in water samples. Acid digestion prior to filtration and analysis is required for groundwater, aqueous samples, industrial wastes, soils, sludges, sediments, and other solid wastes for which total (acid-soluble) elements are required.

1.2 ICP-MS has been applied to the determination of over 60 elements in various matrices. Analytes for which EPA has demonstrated the acceptability of this method in a multi-laboratory study on solid and aqueous wastes are listed below.

Element		CASRN[a]
Aluminum	(Al)	7429-90-5
Antimony	(Sb)	7440-36-0
Arsenic	(As)	7440-38-2
Barium	(Ba)	7440-39-3
Beryllium	(Be)	7440-41-7
Cadmium	(Cd)	7440-43-9
Calcium	(Ca)	7440-70-2
Chromium	(Cr)	7440-47-3
Cobalt	(Co)	7440-48-4
Copper	(Cu)	7440-50-8
Iron	(Fe)	7439-89-6
Lead	(Pb)	7439-92-1
Magnesium	(Mg)	7439-95-4
Manganese	(Mn)	7439-96-5
Mercury	(Hg)	7439-97-6
Nickel	(Ni)	7440-02-0

Element		CASRN[a]
Potassium	(K)	7440-09-7
Selenium	(Se)	7782-49-2
Silver	(Ag)	7440-22-4
Sodium	(Na)	7440-23-5
Thallium	(Tl)	7440-28-0
Vanadium	(V)	7440-62-2
Zinc	(Zn)	7440-66-6

[a]Chemical Abstract Service Registry Number

Acceptability of this method for an element was based upon the multi-laboratory performance compared with that of either furnace atomic absorption spectrophotometry or inductively coupled plasma-atomic emission spectrometry. It should be noted that one multi-laboratory study was conducted in 1988 and advances in ICP-MS instrumentation and software have been made since that time and additional studies have been added with validation and improvements in performance of the method. Performance, in general, exceeds the multi-laboratory performance data for the listed elements. It is expected that current performance will exceed the multi-laboratory performance data for the listed elements (and others) that are provided in Sec. 13.0. The lower limit of quantitation and linear ranges will vary with the matrices, instrumentation, and operating conditions. In relatively simple matrices, quantitation limits will generally be below 0.1 µg/L. Less sensitive elements (like Se and As) and desensitized major elements may be 1.0 µg/L or higher.

1.3 If this method is used to determine any analyte not listed in Sec. 1.2, it is the responsibility of the analyst to demonstrate the accuracy and precision of the method in the waste to be analyzed. The analyst is always required to monitor potential sources of interferences and take appropriate action to ensure data of known quality (see Sec. 9.0). Other elements and matrices may be analyzed by this method if performance is demonstrated for the analyte of interest, in the matrices of interest, at the concentration levels of interest in the same manner as the listed elements and matrices (see Sec. 9.0).

1.4 An appropriate internal standard is required for each analyte determined by ICP-MS. Recommended internal standards are ^{6}Li, ^{45}Sc, ^{89}Y, ^{103}Rh, ^{115}In, ^{159}Tb, ^{165}Ho, ^{74}Ge, and ^{209}Bi. The lithium internal standard should have an enriched abundance of ^{6}Li, so that interference from lithium native to the sample is minimized. Other elements may need to be used as internal standards when samples contain significant native amounts of the recommended internal standards.

1.5 Prior to employing this method, analysts are advised to consult the each preparative method that may be employed in the overall analysis (e.g., a 3000 series method) for additional information on quality control procedures, development of QC acceptance criteria, calculations, and general guidance. Analysts also should consult the disclaimer statement at the front of the manual and the information in Chapter Two for guidance on the intended flexibility in the choice of methods, apparatus, materials, reagents, and supplies, and on the responsibilities of the analyst for demonstrating that the techniques employed are appropriate for the analytes of interest, in the matrix of interest, and at the levels of concern.

In addition, analysts and data users are advised that, except where explicitly specified in a regulation, the use of SW-846 methods is *not* mandatory in response to Federal testing requirements. The information contained in this method is provided by EPA as guidance to be used by the analyst and the regulated community in making judgments necessary to generate results that meet the data quality objectives for the intended application.

1.6 Use of this method is restricted to use by, or under supervision of, properly experienced and trained personnel, including spectroscopists who are knowledgeable in the recognition and in the correction of spectral, chemical, and physical interferences in ICP-MS. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis, samples should be solubilized or digested using the appropriate sample preparation methods (see Chapter Three). When analyzing groundwater or other aqueous samples for dissolved constituents, acid digestion is not necessary if the samples are filtered and acid preserved prior to analysis (refer to Sec. 1.1).

2.2 This method describes the multi-elemental determination of analytes by ICP-MS in environmental samples. The method measures ions produced by a radio-frequency inductively coupled plasma. Analyte species originating in a liquid are nebulized and the resulting aerosol is transported by argon gas into the plasma torch. The ions produced by high temperatures are entrained in the plasma gas and extracted through a differentially pumped vacuum interface and separated on the basis of their mass-to-charge ratio by a mass spectrometer. The ions transmitted through the mass spectrometer are quantified by a channel electron multiplier or Faraday detector and the ion information is processed by the instrument's data handling system. Interferences must be assessed and valid corrections applied or the data qualified to indicate problems. Interference correction must include compensation for background ions contributed by the plasma gas, reagents, and constituents of the sample matrix.

3.0 DEFINITIONS

Refer to Chapter One, Chapter Three, and the manufacturer's instructions for definitions that may be applicable to this procedure.

4.0 INTERFERENCES

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be necessary. Refer to each method to be used for specific guidance on quality control procedures and to Chapter Three for general guidance on the cleaning of glassware. Also refer to the preparative methods to be used for discussions on interferences.

4.2 Isobaric elemental interferences in ICP-MS are caused by isotopes of different elements forming atomic ions with the same nominal mass-to-charge ratio (m/z). A data system must be used to correct for these interferences. This involves determining the signal for another isotope of the interfering element and subtracting the appropriate signal from the analyte isotope signal. Since commercial ICP-MS instruments nominally provide unit resolution at 10% of the peak height, very high ion currents at adjacent masses can also contribute to ion signals at the mass of interest. Although this type of interference is uncommon, it is not easily corrected, and samples exhibiting a significant problem of this type could require resolution improvement, matrix separation, or analysis using another verified and documented isotope, or use of another method.

4.3 Isobaric molecular and doubly-charged ion interferences in ICP-MS are caused by ions consisting of more than one atom or charge, respectively. Most isobaric interferences that could affect ICP-MS determinations have been identified in the literature (Refs. 3 and 4). Examples include $^{75}ArCl^+$ ion on the ^{75}As signal and MoO^+ ions on the cadmium isotopes. While the approach used to correct for molecular isobaric interferences is demonstrated below using the natural isotope abundances from the literature (Ref. 5), the most precise coefficients for an instrument can be determined from the ratio of the net isotope signals observed for a standard solution at a concentration providing suitable (<1%) counting statistics. Because the ^{35}Cl natural abundance of 75.77% is 3.13 times the ^{37}Cl abundance of 24.23%, the chloride correction for arsenic can be calculated (approximately) as follows (where the $^{38}Ar^{37}Cl^+$ contribution at m/z 75 is a negligible 0.06% of the $^{40}Ar^{35}Cl^+$ signal):

Corrected arsenic signal (using natural isotopes abundances for coefficient approximations) =
(m/z 75 signal) - (3.13) (m/z 77 signal) + (2.73) (m/z 82 signal),

where the final term adjusts for any selenium contribution at 77 m/z.

NOTE: Arsenic values can be biased high by this type of equation when the net signal at m/z 82 is caused by ions other than $^{82}Se^+$, (e.g., $^{81}BrH^+$ from bromine wastes [Ref. 6]).

Similarly:

Corrected cadmium signal (using natural isotopes abundances for coefficient approximations) =
(m/z 114 signal) - (0.027)(m/z 118 signal) - (1.63)(m/z 108 signal),

where last 2 terms adjust for any $^{114}Sn^+$ or $^{114}MoO^+$ contributions at m/z 114.

NOTE: Cadmium values will be biased low by this type of equation when $^{92}ZrO^+$ ions contribute at m/z 108, but use of m/z 111 for Cd is even subject to direct ($^{94}ZrOH^+$) and indirect ($^{90}ZrO^+$) additive interferences when Zr is present.

NOTE: As for the arsenic equation above, the coefficients could be improved. The most appropriate coefficients for a particular instrument can be determined from the ratio of the net isotope signals observed for a standard solution at a concentration providing suitable (<1%) counting precision.

The accuracy of these types of equations is based upon the constancy of the observed isotopic ratios for the interfering species. Corrections that presume a constant fraction of a molecular ion relative to the "parent" ion have not been found (Ref. 7) to be reliable, e.g., oxide levels can vary with operating conditions. If a correction for an oxide ion is based upon the ratio of parent-to-oxide ion intensities, the correction must be adjusted for the degree of oxide formation by the use of an appropriate oxide internal standard previously demonstrated to form a similar level of oxide as the interferent. For example, this type of correction has been reported (Ref. 7) for oxide-ion corrections using ThO^+/Th^+ for the determination of rare earth elements. The use of aerosol desolvation and/or mixed gas plasmas have been shown to greatly reduce molecular interferences (Ref. 8). These techniques can be used provided that the lower limits of quantitation, accuracy, and precision requirements for analysis of the samples can be met.

4.4 Additionally, solid phase chelation may be used to eliminate isobaric interferences from both element and molecular sources. An on-line method has been demonstrated for environmental waters such as sea water, drinking water and acid decomposed samples. Acid decomposed samples refer to samples decomposed by methods similar to Methods 3052, 3051, 3050 or 3015. Samples with percent levels of iron and aluminum should be avoided. The

method also provides a method for preconcentration to enhance quantitation limits simultaneously with elimination of isobaric interferences. The method relies on chelating resins such as imminodiacetate or other appropriate resins and selectively concentrates the elements of interest while eliminating interfering elements from the sample matrix. By eliminating the elements that are direct isobaric interferences or those that form isobaric interfering molecular masses, the mass region is simplified and these interferences can not occur. The method has been proven effective for the certification of standard reference materials and validated using SRMs (Refs. 13 through 15). The method has the potential to be used on-line or off-line as an effective sample preparation method specifically designed to address interference problems.

4.5 Physical interferences are associated with the sample nebulization and transport processes as well as with ion-transmission efficiencies. Nebulization and transport processes can be affected if a matrix component causes a change in surface tension or viscosity. Changes in matrix composition can cause significant signal suppression or enhancement (Ref. 9). Dissolved solids can deposit on the nebulizer tip of a pneumatic nebulizer and on the interface skimmers (reducing the orifice size and the instrument performance). Total solid levels below 0.2% (2,000 mg/L) are recommended (Ref. 10) to minimize solid deposition. An internal standard can be used to correct for physical interferences, if it is carefully matched to the analyte so that the two elements are similarly affected by matrix changes (Ref. 11). When intolerable physical interferences are present in a sample, a significant suppression of the internal standard signals (to less than 30% of the signals in the calibrations standard) will be observed. Dilution of the sample fivefold (1+4) will usually eliminate the problem (see Sec. 9.5).

4.6 Memory interferences or carry-over can occur when there are large concentration differences between samples or standards which are analyzed sequentially. Sample deposition on the sampler and skimmer cones, spray chamber design, and the type of nebulizer affect the extent of observed memory interferences. The rinse period between samples must be long enough to eliminate significant memory interference.

5.0 SAFETY

5.1 This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses.

5.2 Concentrated nitric and hydrochloric acids are moderately toxic and extremely irritating to skin and mucus membranes. Use these reagents in a hood and if eye or skin contact occurs, flush with large volumes of water. Always wear safety glasses or a shield for eye protection when working with these reagents. Hydrofluoric acid is a very toxic acid and penetrates the skin and tissues deeply if not treated immediately. Injury occurs in two stages; first, by hydration that induces tissue necrosis and then by penetration of fluoride ions deep into the tissue and by reaction with calcium. Boric acid and other complexing reagents and appropriate treatment agents should be administered immediately. Consult appropriate safety literature and have the appropriate treatment materials readily available prior to working with this acid. See Method 3052 for specific suggestions for handling hydrofluoric acid from a safety and an instrument standpoint.

5.3 Many metal salts are extremely toxic if inhaled or swallowed. Extreme care must be taken to ensure that samples and standards are handled properly and that all exhaust gases are properly vented. Wash hands thoroughly after handling.

5.4 The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. For this reason, the acidification and digestion of samples should be performed in an approved fume hood.

6.0 EQUIPMENT AND SUPPLIES

6.1 Inductively coupled plasma-mass spectrometer -- A system capable of providing resolution, better than or equal to 1.0 amu at 10% peak height is required. The system must have a mass range from at least 6 to 240 amu and a data system that allows corrections for isobaric interferences and the application of the internal standard technique. Use of a mass-flow controller for the nebulizer argon and a peristaltic pump for the sample solution is recommended.

6.2 Argon gas supply -- High-purity grade (99.99%).

7.0 REAGENTS AND STANDARDS

7.1 Reagent- or trace metals-grade chemicals must be used in all tests. Unless otherwise indicated, it is intended that all reagents 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.

7.2 Acids used in the preparation of standards and for sample processing must be of high purity. Redistilled acids are recommended because of the high sensitivity of ICP-MS. Nitric acid at less than 2% (v/v) is required for ICP-MS to minimize damage to the interface and to minimize isobaric molecular-ion interferences with the analytes. Many more molecular-ion interferences are observed when hydrochloric and sulfuric acids are used (Refs. 3 and 4). Concentrations of antimony and silver between 50-500 µg/L require 1% (v/v) HCl for stability; for concentrations above 500 µg/L Ag, additional HCl will be needed. Consequently, accuracy of analytes requiring significant chloride molecular ion corrections (such as As and V) will degrade.

7.3 Reagent water -- All references to water in the method refer to reagent water, unless otherwise specified. Reagent water must be free of interferences.

7.4 Standard stock solutions for each analyte may be purchased or prepared from ultra-high purity grade chemicals or metals (99.99 or greater purity). See Method 6010 for instructions on preparing standard solutions from solids.

7.4.1 Bismuth internal standard stock solution (1 mL = 100 µg of Bi) -- Dissolve 0.1115 g of Bi_2O_3 in a minimum amount of dilute HNO_3. Add 10 mL of conc. HNO_3 and dilute to 1,000 mL with reagent water.

7.4.2 Germanium internal standard stock solution (1 mL = 100 µg of Ge) -- Dissolve 0.2954 g of $GeCl_4$ in a minimum amount of dilute HNO_3. Add 10 mL of conc. HNO_3 and dilute to 1,000 mL with reagent water.

7.4.3 Holmium internal standard stock solution (1 mL = 100 µg of Ho) -- Dissolve 0.1757 g of $Ho_2(CO_3)_2 \cdot 5H_2O$ in 10 mL of reagent water and 10 mL of HNO_3. After dissolution is complete, warm the solution to degas. Add 10 mL conc. of HNO_3 and dilute to 1,000 mL with reagent water.

7.4.4 Indium internal standard stock solution (1 mL = 100 µg of In) -- Dissolve 0.1000 g of indium metal in 10 mL of conc. HNO_3. Dilute to 1,000 mL with reagent water.

7.4.5 Lithium internal standard stock solution (1 mL = 100 µg of ^6Li) -- Dissolve 0.6312 g of 95-atom-% ^6Li, Li_2CO_3 in 10 mL of reagent water and 10 mL of HNO_3. After dissolution is complete, warm the solution to degas. Add 10 mL conc. of HNO_3 and dilute to 1,000 mL with reagent water.

7.4.6 Rhodium internal standard stock solution (1 mL = 100 µg of Rh) -- Dissolve 0.3593 g of ammonium hexachlororhodate (III) $(NH_4)_3RhCl_6$ in 10 mL reagent water. Add 100 mL of conc. HCl and dilute to 1,000 mL with reagent water.

7.4.7 Scandium internal standard stock solution (1 mL = 100 µg of Sc) -- Dissolve 0.15343 g of Sc_2O_3 in 10 mL (1+1) of hot HNO_3. Add 5 mL of conc. HNO_3 and dilute to 1,000 mL with reagent water.

7.4.8 Terbium internal standard stock solution (1 mL = 100 µg of Tb) -- Dissolve 0.1828 g of $Tb_2(CO_3)_3 \cdot 5H_2O$ in 10 mL (1+1) of HNO_3. After dissolution is complete, warm the solution to degas. Add 5 mL of conc. HNO_3 and dilute to 1,000 mL with reagent water.

7.4.9 Yttrium internal standard stock solution (1 mL = 100 µg of Y) -- Dissolve 0.2316 g of $Y_2(CO_3)_3 \cdot 3H_2O$ in 10 mL (1+1) of HNO_3. Add 5 mL conc. of HNO_3 and dilute to 1,000 mL with reagent water.

7.4.10 Titanium interference stock solution (1 mL = 100 µg of Ti) -- Dissolve 0.4133 g of $(NH_4)_2TiF_6$ in reagent water. Add 2 drops of conc. HF and dilute to 1,000 mL with reagent water.

7.4.11 Molybdenum interference stock solution (1 mL = 100 µg of Mo) -- Dissolve 0.2043 g of $(NH_4)_2MoO_4$ in reagent water. Dilute to 1,000 mL with reagent water.

7.4.12 Gold preservative stock solution for mercury (1 mL = 100 µg) -- Recommend purchasing as high purity prepared solution of $AuCl_3$ in dilute hydrochloric acid matrix.

7.5 Mixed calibration standard solutions are prepared by diluting the stock-standard solutions to levels in the linear range for the instrument in a solvent consisting of 1% (v/v) HNO_3 in reagent water. The calibration standard solutions must contain a suitable concentration of an appropriate internal standard for each analyte. Internal standards may be added on-line at the time of analysis using a second channel of the peristaltic pump and an appropriate mixing manifold. Generally, an internal standard should be no more than 50 amu removed from the analyte. Recommended internal standards include ^6Li, ^{45}Sc, ^{89}Y, ^{103}Rh, ^{115}In, ^{159}Tb, ^{169}Ho, ^{74}Ge and ^{209}Bi. Prior to preparing the mixed standards, each stock solution must be analyzed separately to determine possible spectral interferences or the presence of impurities. Care must be taken when preparing the mixed standards to ensure that the elements are compatible and stable together. Transfer the mixed standard solutions to freshly acid-cleaned FEP fluorocarbon or previously unused polyethylene or polypropylene bottles for storage. For all intermediate and working standards, especially low level standards (i.e., <1 ppm), stability must be demonstrated prior to use. Fresh mixed standards must be prepared as needed with the realization that concentrations can change on aging. (Refer to Sec. 10.3.1 for guidance on determining the viability of standards.)

7.6 Blanks -- Three types of blanks are required for the analysis. The calibration blank is used in establishing the calibration curve. The method blank is used to monitor for

possible contamination resulting from either the reagents (acids) or the equipment used during sample processing including filtration. The rinse blank is used to flush the system between all samples and standards.

7.6.1 The calibration blank consists of the same concentration(s) of the same acid(s) used to prepare the final dilution of the calibrating solutions of the analytes [often 1% HNO_3 (v/v) in reagent water] along with the selected concentrations of internal standards such that there is an appropriate internal standard element for each of the analytes. Use of HCl for antimony and silver is cited in Sec. 7.2.

7.6.2 The method blank must contain all of the reagents in the same volumes as used in the processing of the samples. The method blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis (refer to Sec. 9.9).

7.6.3 The rinse blank consists of 1 to 2% of HNO_3 (v/v) in reagent water. Prepare a sufficient quantity to flush the system between standards and samples. If mercury is to be analyzed, the rinse blank should also contain 2 µg/mL (ppm) of $AuCl_3$ solution.

7.7 The interference check solution (ICS) is prepared to contain known concentrations of interfering elements that will demonstrate the magnitude of interferences and provide an adequate test of any corrections. Chloride in the ICS provides a means to evaluate software corrections for chloride-related interferences such as $^{35}Cl^{16}O^+$ on $^{51}V^+$ and $^{40}Ar^{35}Cl^+$ on $^{75}As^+$. Iron is used to demonstrate adequate resolution of the spectrometer for the determination of manganese. Molybdenum serves to indicate oxide effects on cadmium isotopes. The other components are present to evaluate the ability of the measurement system to correct for various molecular-ion isobaric interferences. The ICS is used to verify that the interference levels are corrected by the data system within quality control limits.

NOTE: The final ICS solution concentrations in Table 1 are intended to evaluate corrections for known interferences on only the analytes in Sec. 1.2. If this method is used to determine an element not listed in Sec. 1.2, the analyst should modify the ICS solutions, or prepare an alternative ICS solution, to allow adequate verification of correction of interferences on the unlisted element (see Sec. 9.7).

7.7.1 These solutions must be prepared from ultra-pure reagents. They can be obtained commercially or prepared by the following procedure.

7.7.1.1 Mixed ICS solution I may be prepared by adding 13.903 g of $Al(NO_3)_3 \cdot 9H_2O$, 2.498 g of $CaCO_3$ (dried at 180 EC for 1 hr before weighing), 1.000 g of Fe, 1.658 g of MgO, 2.305 g of Na_2CO_3, and 1.767 g of K_2CO_3 to 25 mL of reagent water. Slowly add 40 mL of (1+1) HNO_3. After dissolution is complete, warm the solution to degas. Cool and dilute to 1,000 mL with reagent water.

7.7.1.2 Mixed ICS solution II may be prepared by slowly adding 7.444 g of 85 % H_3PO_4, 6.373 g of 96% H_2SO_4, 40.024 g of 37% HCl, and 10.664 g of citric acid $C_6O_7H_8$ to 100 mL of reagent water. Dilute to 1,000 mL with reagent water.

7.7.1.3 Mixed ICS solution III may be prepared by adding 1.00 mL each of 100-µg/mL arsenic, cadmium, selenium, chromium, cobalt, copper, manganese, nickel, silver, vanadium, and zinc stock solutions to about 50 mL of

reagent water. Add 2.0 mL of concentrated HNO_3, and dilute to 100.0 mL with reagent water.

7.7.1.4 Working ICS solutions

7.7.1.4.1 ICS-A may be prepared by adding 10.0 mL of mixed ICS solution I (Sec. 7.7.1.1), 2.0 mL each of 100-µg/mL titanium stock solution (Sec. 7.4.9) and molybdenum stock solution (Sec. 7.4.10), and 5.0 mL of mixed ICS solution II (Sec. 7.7.1.2). Dilute to 100 mL with reagent water. ICS solution A must be prepared fresh weekly.

7.7.1.4.2 ICS-AB may be prepared by adding 10.0 mL of mixed ICS solution I (Sec. 7.7.1.1), 2.0 mL each of 100-µg/mL titanium stock solution (Sec. 7.4.9) and molybdenum stock solution (Sec. 7.4.10), 5.0 mL of mixed ICS solution II (Sec. 7.7.1.2), and 2.0 mL of mixed ICS solution III (Sec. 7.7.1.3). Dilute to 100 mL with reagent water. Although the ICS solution AB must be prepared fresh weekly, the analyst should be aware that the solution may precipitate silver more quickly.

7.8 The initial calibration verification (ICV) standard is prepared by the analyst (or a purchased second source reference material) by combining compatible elements from a standard source different from that of the calibration standard, and at concentration near the midpoint of the calibration curve (see Sec. 10.4.3 for use). This standard may also be purchased.

7.9 The continuing calibration verification (CCV) standard should be prepared in the same acid matrix using the same standards used for calibration, at a concentration near the mid-point of the calibration curve (see Sec. 10.4.4 for use).

7.10 Mass spectrometer tuning solution. A solution containing elements representing all of the mass regions of interest (for example, 10 µg/L of Li, Co, In, and Tl) must be prepared to verify that the resolution and mass calibration of the instrument are within the required specifications (see Sec. 10.2). This solution is also used to verify that the instrument has reached thermal stability (see Sec. 11.4).

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 See the introductory material in Chapter Three, "Inorganic Analytes."

8.2 Only polyethylene or fluorocarbon (TFE or PFA) containers are recommended for use in this method.

9.0 QUALITY CONTROL

9.1 Refer to Chapter One for additional guidance on quality assurance (QA) and quality control (QC) protocols. When inconsistencies exist between QC guidelines, method-specific QC criteria take precedence over both technique-specific criteria and those criteria given in Chapter One, and technique-specific QC criteria take precedence over the criteria in Chapter One. Any effort involving the collection of analytical data should include development of a structured and systematic planning document, such as a Quality Assurance Project Plan (QAPP) or a Sampling and Analysis Plan (SAP), which translates project objectives and specifications into directions for those that will implement the project and assess the results.

Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated. All data sheets and quality control data should be maintained for reference or inspection.

9.2 Refer to a 3000 series method (Method 3005, 3010, 3015, 3031, 3040, 3050, 3051, or 3052) for appropriate QC procedures to ensure the proper operation of the various sample preparation techniques.

9.3 Instrument detection limits (IDLs) are a useful tool to evaluate the instrument noise level and response changes over time for each analyte from a series of reagent blank analyses to obtain a calculated concentration. They are not to be confused with the lower limits of quantitation, nor should they be used in establishing this limit. It may be helpful to compare the calculated IDLs to the established lower limit of quantitation, however, it should be understood that the lower limit of quantitation needs to be verified according to the guidance in Sec. 10.2.3.

IDLs in µg/L can be estimated by calculating the average of the standard deviations of three runs on three non-consecutive days from the analysis of a reagent blank solution with seven consecutive measurements per day. Each measurement should be performed as though it were a separate analytical sample (i.e., each measurement must be followed by a rinse and/or any other procedure normally performed between the analysis of separate samples). IDLs should be determined at least every three months or at a project-specific designated frequency and kept with the instrument log book. Refer to Chapter One for additional guidance.

9.4 Initial demonstration of proficiency

Each laboratory must demonstrate initial proficiency with each sample preparation (a 3000 series method) and determinative method combination it utilizes by generating data of acceptable accuracy and precision for target analytes in a clean matrix. If an autosampler is used to perform sample dilutions, before using the autosampler to dilute samples, the laboratory should satisfy itself that those dilutions are of equivalent or better accuracy than is achieved by an experienced analyst performing manual dilutions. The laboratory must also repeat the demonstration of proficiency whenever new staff members are trained or significant changes in instrumentation are made.

9.5 Dilute and reanalyze samples that exceed the linear dynamic range or use an alternate, less sensitive calibration for which quality control data are already established.

9.6 The intensities of all internal standards must be monitored for every analysis. If the intensity of any internal standard in a sample falls below 70% of the intensity of that internal standard in the initial calibration standard, a significant matrix effect must be suspected. As an example, if the initial calibration internal standard response is 100,000 cps, anything below 70,000 cps in the sample would be unacceptable. Under these conditions, the established lower limit of quantitation has degraded and the correction ability of the internal standardization technique becomes questionable. The following procedure is followed -- First, make sure the instrument has not drifted by observing the internal standard intensities in the nearest clean matrix (calibration blank, Sec. 7.6.1). If the low internal standard intensities are also seen in the nearest calibration blank, terminate the analysis, correct the problem, recalibrate, verify the new calibration, and reanalyze the affected samples. If drift has not occurred, matrix effects need to be removed by dilution of the affected sample. The sample must be diluted fivefold (1+4) and reanalyzed with the addition of appropriate amounts of internal standards. If the first dilution does not eliminate the problem, this procedure must be repeated until the internal-standard intensities rise to the minimum 70% limit. Reported results must be corrected for all dilutions.

9.7 To obtain analyte data of known quality, it is necessary to measure more than the analytes of interest in order to apply corrections or to determine whether interference corrections are necessary. For example, tungsten oxide moleculars can be very difficult to distinguish from mercury isotopes. If the concentrations of interference sources (such as C, Cl, Mo, Zr, W) are such that, at the correction factor, the analyte is less than the limit of quantification and the concentration of interferents are insignificant, then the data may go uncorrected. Note that monitoring the interference sources does not necessarily require monitoring the interferant itself, but that a molecular species may be monitored to indicate the presence of the interferent. When correction equations are used, all QC criteria must also be met. Extensive QC for interference corrections are required at all times. The monitored masses must include those elements whose hydrogen, oxygen, hydroxyl, chlorine, nitrogen, carbon and sulfur molecular ions could impact the analytes of interest. Unsuspected interferences may be detected by adding pure major matrix components to a sample to observe any impact on the analyte signals. When an interference source is present, the sample elements impacted must be flagged to indicate (a) the percentage interference correction applied to the data or (b) an uncorrected interference by virtue of the elemental equation used for quantitation. The isotope proportions for an element or molecular-ion cluster provide information useful for quality assurance.

NOTE: Only isobaric elemental, molecular, and doubly charged interference corrections which use the observed isotopic-response ratios or parent-to-oxide ratios (provided an oxide internal standard is used as described in Sec. 4.2) for each instrument system are acceptable corrections for use in Method 6020.

9.8 For each batch of samples processed, at least one method blank must be carried throughout the entire sample preparation and analytical process, as described in Chapter One. A method blank is prepared by using a volume or weight of reagent water at the volume or weight specified in the preparation method, and then carried through the appropriate steps of the analytical process. These steps may include, but are not limited to, prefiltering, digestion, dilution, filtering, and analysis. If the method blank does not contain target analytes at a level that interferes with the project-specific DQOs, then the method blank would be considered acceptable.

In the absence of project-specific DQOs, if the blank is less than 10% of the lower limit of quantitation check sample concentration, less than 10% of the regulatory limit, or less than 10% of the lowest sample concentration for each analyte in a given preparation batch, whichever is greater, then the method blank is considered acceptable. If the method blank cannot be considered acceptable, the method blank should be re-run once, and if still unacceptable, then all samples after the last acceptable method blank should be reprepared and reanalyzed along with the other appropriate batch QC samples. These blanks will be useful in determining if samples are being contaminated. If the method blank exceeds the criteria, but the samples are all either below the reporting level or below the applicable action level or other DQOs, then the sample data may be used despite the contamination of the method blank.

9.9 Laboratory control sample (LCS)

For each batch of samples processed, at least one LCS must be carried throughout the entire sample preparation and analytical process. The laboratory control samples should be spiked with each analyte of interest at the project-specific action level or, when lacking project-specific action levels, at approximately mid-point of the linear dynamic range. Acceptance criteria should either be defined in the project-specifc planning documents or set at a laboratory derived limit developed through the use of historical analyses. In the absence of project-specific or historical data generated criteria, this limit should be set at ± 20% of the spiked value. Acceptance limits derived from historical data should be no wider that ± 20%. If the laboratory control sample is not acceptable, then the laboratory control sample should be re-run once and,

if still unacceptable, all samples after the last acceptable laboratory control sample should be reprepared and reanalyzed.

Concurrent analyses of standard reference materials (SRMs) containing known amounts of analytes in the media of interest are recommended and may be used as an LCS. For solid SRMs, 80 - 120% accuracy may not be achievable and the manufacturer's established acceptance criterion should be used for soil SRMs.

9.10 Matrix spike, unspiked duplicate, or matrix spike duplicate (MS/Dup or MS/MSD)

Documenting the effect of the matrix, for a given preparation batch consisting of similar sample characteristics, should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch or as noted in the project-specific planning documents. If samples are expected to contain target analytes, then laboratories may use one matrix spike and a duplicate analysis of an unspiked field sample. If samples are not expected to contain target analytes, laboratories should use a matrix spike and matrix spike duplicate pair.

For each batch of samples processed, at least one MS/Dup or MS/MSD sample set should be carried throughout the entire sample preparation and analytical process as described in Chapter One. MS/MSDs are intralaboratory split samples spiked with identical concentrations of each analyte of interest. The spiking occurs prior to sample preparation and analysis. An MS/Dup or MS/MSD is used to document the bias and precision of a method in a given sample matrix.

Refer to Chapter One for definitions of bias and precision, and for the proper data reduction protocols. MS/MSD samples should be spiked at the same level, and with the same spiking material, as the corresponding laboratory control sample that is at the project-specific action level or, when lacking project-specific action levels, at approximately mid-point of the linear dynamic range. Acceptance criteria should either be defined in the project-specifc planning documents or set at a laboratory-derived limit developed through the use of historical analyses per matrix type analyzed. In the absence of project-specific or historical data generated criteria, these limits should be set at ± 25% of the spiked value for accuracy and 20 relative percent difference (RPD) for precision. Acceptance limits derived from historical data should be no wider that ± 25% for accuracy and 20% for precision. Refer to Chapter One for additional guidance. If the bias and precision indicators are outside the laboratory control limits, if the percent recovery is less than 75% or greater than 125%, or if the relative percent difference is greater than 20%, then the interference test discussed in Sec. 9.11 should be conducted.

9.10.1 The relative percent difference between spiked matrix duplicate or unspiked duplicate determinations is to be calculated as follows:

$$RPD = \frac{|D_1 - D_2|}{\left(\frac{|D_1 + D_2|}{2}\right)} \times 100$$

where:

RPD = relative percent difference.

D_1 = first sample value.
D_2 = second sample value (spiked or unspiked duplicate).

9.10.2 The spiked sample or spiked duplicate sample recovery should be within ± 25% of the actual value, or within the documented historical acceptance limits for each matrix.

9.11 If less than acceptable accuracy and precision data are generated, additional quality control tests (Secs. 9.11.1 and 9.11.2) are recommended prior to reporting concentration data for the elements in this method. At a minimum these tests should be performed with each batch of samples prepared/analyzed with corresponding unacceptable data quality results. These test will then serve to ensure that neither positive nor negative interferences are affecting the measurement of any of the elements or distorting the accuracy of the reported values. If matrix effects are confirmed, the laboratory should consult with the data user when feasible for possible corrective actions which may include the use of alternative or modified test procedures so that the analysis is not impacted by the same interference.

9.11.1 Post digestion spike addition

If the MS/MSD recoveries are unacceptable, the same sample from which the MS/MSD aliquots were prepared should also be spiked with a post digestion spike. Otherwise another sample from the same preparation should be used as an alternative. An analyte spike is added to a portion of a prepared sample, or its dilution, and should be recovered to within 80% to 120% of the known value. The spike addition should produce a minimum level of 10 times and a maximum of 100 times the lower limit of quantitation. If this spike fails, then the dilution test (Sec. 9.11.2) should be run on this sample. If both the MS/MSD and the post digestion spike fail, then matrix effects are confirmed.

9.11.2 Dilution test

If the analyte concentration is sufficiently high (minimally, a factor of 10 above the lower limit of quantitation after dilution), an analysis of a 1:5 dilution should agree within ± 10% of the original determination. If not, then a chemical or physical interference effect should be suspected.

9.12 Ultra-trace analysis requires the use of clean chemistry preparation and analysis techniques. Several suggestions for minimizing analytical blank contamination are provided in Chapter Three.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Set up the instrument with proper operating parameters established as detailed below. The instrument should be allowed to become thermally stable before beginning (usually requiring at least 30 min of operation prior to calibration). For operating conditions, the analyst should follow the instructions provided by the instrument manufacturer.

10.2 Conduct mass calibration and resolution checks in the mass regions of interest. The mass calibration and resolution parameters are required criteria which must be met prior to any samples being analyzed. If the mass calibration differs more than 0.1 amu from the true value, then the mass calibration must be adjusted to the correct value. The resolution must also be verified to be less than 0.9 amu full width at 10% peak height.

10.2.1 Before using this procedure to analyze samples, data should be available documenting the initial demonstration of performance. The required data should document the determination of the linear dynamic ranges; a demonstration of the desired method sensitivity and instrument detection limits; and the determination and verification of the appropriate correction equations or other routines for correcting spectral interferences. These data should be generated using the same instrument, operating conditions, and calibration routine to be used for sample analysis. These data should be kept on file and be available for review by the data user or auditor.

10.2.2 Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference corrections need to be established for each individual target analyte on each particular instrument. All measurements (both target analytes and constituents which interfere with the target analytes) need to be within the instrument linear range where the correction equations are valid.

10.2.3 The lower limits of quantitation should be established for all isotope masses utilized for each type of matrix analyzed and for each preparation method used and for each instrument. These limits are considered the lowest reliable laboratory reporting concentrations and should be established from the lower limit of quantitation check sample and then confirmed using either the lowest calibration point or from a low-level calibration check standard.

10.2.3.1 Lower limit of quantitation check sample

The lower limit of quantitation check (LLQC) sample should be analyzed after establishing the lower laboratory reporting limits and on an as needed basis to demonstrate the desired detection capability. Ideally, this check sample and the low-level calibration verification standard will be prepared at the same concentrations with the only difference being the LLQC sample is carried through the entire preparation and analytical procedure. Lower limits of quantitation are verified when all analytes in the LLQC sample are detected within ± 30% of their true value. This check should be used to both establish and confirm the lowest quantitation limit.

10.2.3.2 The lower limits of quantitation determination using reagent water represents a best case situation and does not represent possible matrix effects of real-world samples. For the application of lower limits of quantitation on a project-specific basis with established data quality objectives, low-level matrix-specific spike studies may provide data users with a more reliable indication of the actual method sensitivity and minimum detection capabilities.

10.2.4 Specific recommended isotopes for the analytes noted in Sec. 1.2 are provided in Table 2. Other isotopes may be substituted if they can provide the needed sensitivity and are corrected for spectral interference. Because of differences among various makes and models of mass spectrometers, specific instrument operating conditions cannot be provided. The instrument and operating conditions utilized for determination must be capable of providing data of acceptable quality for the specific project and data user. The analyst should follow the instructions provided by the instrument manufacturer unless other conditions provide similar or better performance for a given task.

10.3 All masses which could affect data quality should be monitored to determine potential effects from matrix components on the analyte peaks. The recommended isotopes to be monitored are listed in Table 2.

10.4 All analyses require that a calibration curve be prepared to cover the appropriate concentration range based on the intended application and prior to establishing the linear dynamic range. Usually, this means the preparation of a calibration blank and mixed calibration standard solutions (Sec. 7.5), the highest of which would not exceed the anticipated linear dynamic range of the instrument. Check the instrument standardization by analyzing appropriate QC samples as follows.

10.4.1 Individual or mixed calibration standards should be prepared from known primary stock standards every six months to one year as needed based on the concentration stability as confirmed from the ICV analyses. The analysis of the ICV, which is prepared from a source independent of the calibration standards, is necessary to verify the instrument performance once the system has been calibrated for the desired target analytes. It is recommended that the ICV solution be obtained commercially as a certified traceable reference material such that an expiration date can be assigned. Alternately, the ICV solution can be prepared from an independent source on an as needed basis depending on the ability to meet the calibration verification criteria. If the ICV analysis is outside of the acceptance criteria, at a minimum the calibration standards must be prepared fresh and the instrument recalibrated prior to beginning sample analyses. Consideration should also be given to preparing fresh ICV standards if the new calibration cannot be verified using the existing ICV standard.

NOTE: This method describes the use of both a low-level and mid-level ICV standard analysis. For purposes of verifying the initial calibration, only the mid-level ICV needs to be prepared from a source other than the calibration standards.

10.4.1.1 The calibration standards should be prepared using the same type of acid or combination of acids and at similar concentrations as will result in the samples following processing.

10.4.1.2 The response of the calibration blank should be less than the response of the typical laboratory lower limit of quantitation for each desired target analyte. Additionally, if the calibration blank response or continuing calibration blank verification is used to calculate a theoretical concentration, this value should be less than the level of acceptable blank contamination as specified in the approved quality assurance project planning documents. If this is not the case, the reason for the out-of-control condition must be found and corrected, and the sample analyses may not proceed or the previous ten samples need to be reanalyzed.

10.4.2 For the initial and daily instrument operation, calibrate the system according to the instrument manufacturer's guidelines using the mixed calibration standards as noted in Sec. 7.5. The calibration curve should be prepared daily with a minimum of a calibration blank and a single standard at the appropriate concentration to effectively outline the desired quantitation range. Flush the system with the rinse blank (Sec. 7.6.3) between each standard solution. Use the average of at least three integrations for both calibration and sample analyses. The resulting curve should then be verified with mid-level and low-level initial calibration verification standards as outlined in Sec. 10.4.3.

Alternatively, the calibration curve can be prepared daily with a minimum of a calibration blank and three non-zero standards that effectively bracket the desired sample concentration range. If low-level as compared to mid- or high-level sample concentrations are expected, the calibration standards should be prepared at the appropriate concentrations in order to demonstrate the instrument linearity within the anticipated

sample concentration range. For all multi-point calibration scenarios, the lowest non-zero standard concentration should be considered the lower limit of quantitation.

NOTE: Regardless of whether the instrument is calibrated using only a minimum number of standards or with a multi-point curve, the upper limit of the quantitation range may exceed the highest concentration calibration point and can be defined as the "linear dynamic" range, while the lower limit can be identified as the "lower limit of quantitation limit" (LLQL) and will be either the concentration of the lowest calibration standard (for multi-point curves) or the concentration of the low level ICV/CCV check standard. Results reported outside these limits would not be recommended unless they are qualified as estimated. See Sec. 10.4.4 for recommendations on how to determine the linear dynamic range, while the guidance in this section and Sec. 10.4.3 provide options for defining the lower limit of quantitation.

10.4.2.1 To be considered acceptable, the calibration curve should have a correlation coefficient greater than or equal to 0.998. When using a multi-point calibration curve approach, every effort should be made to attain an acceptable correlation coefficient based on a linear response for each desired target analyte. If the recommended linear response cannot be attained using a minimum of three non-zero calibration standards, consideration should be given to adding more standards, particularly at the lower concentrations, in order to better define the linear range and the lower limit of quantitation. Conversely, the extreme upper and lower calibration points may be removed from the multi-point curve as long as three non-zero points remain such that the linear range is narrowed and the non-linear upper and/or lower portions are removed. As with the single point calibration option, the multi-point calibration should be verified with both a mid- and low-level ICV standard analysis using the same 90 - 110% and 70 - 130% acceptance criteria, respectively.

10.4.2.2 Many instrument software packages allow multi-point calibration curves to be "forced" through zero. It is acceptable to use this feature, provided that the resulting calibration meets the acceptance criteria, and can be verified by acceptable QC results. Forcing a regression through zero should NOT be used as a rationale for reporting results below the calibration range defined by the lowest standard in the calibration curve.

10.4.3 After initial calibration, the calibration curve should be verified by use of an initial calibration verification (ICV) standard analysis. At a minimum, the ICV standard should be prepared from an independent (second source) material at or near the mid-range of the calibration curve. The acceptance criteria for this mid-range ICV standard should be ±10% of its true value. Additionally, a low-level initial calibration verification (LLICV) standard should be prepared, using the same source as the calibration standards, at a concentration expected to be the lower limit of quantitation. The suggested acceptance criteria for the LLICV is ±30% of its true value. Quantitative sample analyses should not proceed for those analytes that fail the second source standard initial calibration verification, with the exception that analyses may continue for those analytes that fail the criteria with an understanding these results should be qualified and would be considered estimated values. Once the calibration acceptance criteria is met, either the lowest calibration standard or the LLICV concentration can be used to demonstrate the lower limit of quantitation and sample results should not be quantitated below this lowest standard. In some cases depending on the stated project data quality objectives, it may be appropriate to report these results as estimated, however, they should be qualified by noting the results are below the lower limit of quantitation. Therefore, the laboratory's

quantitation limit cannot be reported lower than either the LLICV standard used for the single point calibration option or the low calibration and/or verification standard used during initial multi-point calibration. If the calibration curve cannot be verified within these specified limits for the mid-range ICV and LLICV analyses, the cause needs to be determined and the instrument recalibrated before samples are analyzed. The analysis data for the initial calibration verification analyses should be kept on file with the sample analysis data.

10.4.4 Both the single and multi-point calibration curves should be verified at the end of each analysis batch and after every 10 samples by use of a continuing calibration verification (CCV) standard and a continuing calibration blank (CCB). The CCV should be made from the same material as the initial calibration standards at or near the mid-range concentration. For the curve to be considered valid, the acceptance criteria for the CCV standard should be ±10% of its true value and the CCB should contain target analytes less than the established lower limit of quantitation for any desired target analyte. If the calibration cannot be verified within the specified limits, the sample analysis must be discontinued, the cause determined and the instrument recalibrated. All samples following the last acceptable CCV/CCB must be reanalyzed. The analysis data for the CCV/CCB should be kept on file with the sample analysis data.

The low level continuing calibration verification (LLCCV) standard should also be analyzed at the end of each analysis batch. A more frequent LLCCV analysis, i.e., every 10 samples may be necessary if low-level sample concentrations are anticipated and the system stability at low end of the calibration is questionable. In addition, the analysis of a LLCCV on a more frequent basis will minimize the number of samples for re-analysis should the LLCCV fail if only run at the end of the analysis batch. The LLCCV standard should be made from the same source as the initial calibration standards at the established lower limit of quantitation as reported by the laboratory. The acceptance criteria for the LLCCV standard should be ± 30% of its true value. If the calibration cannot be verified within these specified limits, the analysis of samples containing the affected analytes at similar concentrations cannot continue until the cause is determined and the LLCCV standard successfully analyzed. The instrument may need to be recalibrated or the lower limit of quantitation adjusted to a concentration that will ensure a compliant LLCCV analysis. The analysis data for the LLCCV standard should be kept on file with the sample analysis data.

10.5 Verify the magnitude of elemental and molecular-ion isobaric interferences and the adequacy of any corrections at the beginning of an analytical run or once every 12 hr, whichever is more frequent. Do this by analyzing the interference check solutions A and AB. The analyst should be aware that precipitation from solution AB may occur with some elements, specifically silver. Refer to Sec. 4.0 for a discussion on interferences and potential solutions to those interferences if additional guidance is needed.

NOTE: Analysts have noted improved performance in calibration stability if the instrument is exposed to the interference check solution after cleaning sampler and skimmer cones. Improved performance is also realized if the instrument is allowed to rinse for 5 or 10 min before the calibration blank is run.

10.6 The linear dynamic range is established when the system is first setup, or whenever significant instrument components have been replaced or repaired, and on an as needed basis only after the system has been successfully calibrated using either the single or multi-point standard calibration approach.

The upper limit of the linear dynamic range needs to be established for each wavelength utilized by determining the signal responses from a minimum of three, preferably five, different concentration standards across the range. The ranges which may be used for the analysis of samples should be judged by the analyst from the resulting data. The data, calculations and rationale for the choice of range made should be documented and kept on file. A standard at the upper limit should be prepared, analyzed and quantitated against the normal calibration curve. The calculated value should be within 10% (±10%) of the true value. New upper range limits should be determined whenever there is a significant change in instrument response. At a minimum, the range should be checked every six months. The analyst should be aware that if an analyte that is present above its upper range limit is used to apply a spectral correction, the correction may not be valid and those analytes where the spectral correction has been applied may be inaccurately reported.

NOTE: Some metals may exhibit non-linear response curves due to ionization and self-absorption effects. These curves may be used if the instrument allows it; however the effective range must be checked and the second order curve fit should have a correlation coefficient of 0.998 or better. Third order fits are not acceptable. These non-linear response curves should be revalidated and/or recalculated on a daily basis using the same calibration verification QC checks as a linear calibration curve. Since these curves are much more sensitive to changes in operating conditions than the linear lines, they should be checked whenever there have been moderate equipment changes. Under these calibration conditions, quantitation is not acceptable above or below the calibration standards. Additionally, a non-linear curve should be further verified by calculating the actual recovery of each calibration standard used in the curve. The acceptance criteria for the calibration standard recovery should be ±10% of its true value for all standards except the lowest concentration. A recovery of ±30% of its true value should be achieved for the lowest concentration standard.

10.7 The analyst should (1) verify that the instrument configuration and operating conditions satisfy the project-specific analytical requirements and (2) maintain quality control data that demonstrate and confirm the instrument performance for the reported analytical results.

11.0 PROCEDURE

11.1 Preliminary treatment of most matrices is necessary because of the complexity and variability of sample matrices. Groundwater and other aqueous samples designated for a dissolved metals determination which have been prefiltered and acidified will not need acid digestion. However, all associated QC samples (i.e., method blank, LCS and MS/MSD) must undergo the same filtration and acidification procedures. Samples which are not digested must be matrix-matched with the standards. Solubilization and digestion procedures are presented in Chapter Three, "Inorganic Analytes."

CAUTION: If mercury is to be analyzed, the digestion procedure must use mixed nitric and hydrochloric acids through all steps of the digestion. Mercury will be lost if the sample is digested when hydrochloric acid is not present. If it has not already been added to the sample as a preservative, Au should be added to give a final concentration of 2 mg/L (use 2.0 mL of 7.4.12 per 100 mL of sample) to preserve the mercury and to prevent it from plating out in the sample introduction system.

11.2 Initiate appropriate operating configuration of the instrument’s computer according to the instrument manufacturer's instructions.

11.3 Set up the instrument with the proper operating parameters according to the instrument manufacturer's instructions.

11.4 Operating conditions -- The analyst should follow the instructions provided by the instrument manufacturer. Allow at least 30 min for the instrument to equilibrate before analyzing any samples. This must be verified by an analysis of the tuning solution (Sec. 7.10) at least four integrations with relative standard deviations of #5% for the analytes contained in the tuning solution.

CAUTION: The instrument should have features that protect itself from high ion currents. If not, precautions must be taken to protect the detector from high ion currents. A channel electron multiplier or active film multiplier suffers from fatigue after being exposed to high ion currents. This fatigue can last from several seconds to hours depending on the extent of exposure. During this time period, response factors are constantly changing, which invalidates the calibration curve, causes instability, and invalidates sample analyses.

11.5 Calibrate the instrument following the procedure outlined in Sec. 10.0.

11.6 Flush the system with the rinse blank solution (Sec. 7.6.3) until the signal levels return to the DQO or method's levels of quantitation (usually about 30 sec) before the analysis of each sample (see Sec. 10.0). Nebulize each sample until a steady-state signal is achieved (usually about 30 sec) prior to collecting data. Flow-injection systems may be used as long as they can meet the performance criteria of this method.

11.7 Regardless of whether the initial calibration is performed using a single high standard and the calibration blank or the multi-point option, the laboratory should analyze an LLCCV (Sec. 10.4.4). For all analytes and determinations, the laboratory must analyze an ICV and LLICV (Sec. 10.4.3) immediately following daily calibration. It is recommended that a CCV LLCCV, and CCB (Sec. 10.4.4) be analyzed after every ten samples and at the end of the analysis batch.

11.8 Dilute and reanalyze samples that are more concentrated than the linear range for an analyte (or species needed for a correction) or measure an alternate but less-abundant isotope. The linearity at the alternate mass must be confirmed by appropriate calibration (see Sec. 10.2 and 10.4). Alternatively apply solid phase chelation chromatography to eliminate the matrix as described in Sec. 4.4.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 The quantitative values must be reported in appropriate units, such as micrograms per liter (µg/L) for aqueous samples and milligrams per kilogram (mg/kg) for solid samples. If dilutions were performed, the appropriate corrections must be applied to the sample values. All results should be reported with up to three significant figures.

12.2 If appropriate, or required, calculate results for solids on a dry-weight basis as follows:

(1) A separate determination of percent solids must be performed.

(2) The concentrations determined in the digest are to be reported on the basis of the dry weight of the sample.

$$\text{Concentration (dry weight)(mg/kg)} = \frac{C \times V}{W \times S}$$

Where,

C = Digest Concentration (mg/L)
V = Final volume in liters after sample preparation
W = Weight in kg of wet sample

$$S = \frac{\%\ \text{Solids}}{100}$$

Calculations must include appropriate interference corrections (see Sec. 4.2 for examples), internal-standard normalization, and the summation of signals at 206, 207, and 208 m/z for lead (to compensate for any differences in the abundances of these isotopes between samples and standards).

12.3 Results must be reported in units commensurate with their intended use and all dilutions must be taken into account when computing final results.

13.0 METHOD PERFORMANCE

13.1 Performance data and related information are provided in SW-846 methods only as examples and guidance. The data do not represent required performance criteria for users of the methods. Instead, performance criteria should be developed on a project-specific basis, and the laboratory should establish in-house QC performance criteria for the application of this method. These performance data are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

13.2 In an EPA multi-laboratory study (Ref. 12), twelve laboratories applied the ICP-MS technique to both aqueous and solid samples. Table 3 summarizes the method performance data for aqueous samples. Performance data for solid samples are provided in Table 4. These data are provided for guidance purposes only.

13.3 Table 5 summarizes the method performance data for aqueous and sea water samples with interfering elements removed and samples preconcentrated prior to analysis. Table 6 summarizes the performance data for a simulated drinking water standard. These data are provided for guidance purposes only.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions consult *Less is Better: Laboratory Chemical management for Waste Reduction* available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St., N.W. Washington, D.C. 20036, http://www.acs.org.

15.0 WASTE MANAGEMENT

The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* available from the American Chemical Society at the address listed in Sec. 14.2.

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16. D. E. Dobb, J. T. Rowan, and D. Cardenas, Lockheed Environmental Systems and Technologies Co., Las Vegas, NV; and L. C. Butler, and E. M. Heithmar, E.M., U.S.EPA, Las Vegas, NV; "Determination of Mercury by ICP-MS."

17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

The following pages contain the tables referenced by this method. A flow diagram of the procedure follows the tables.

TABLE 1

RECOMMENDED INTERFERENCE CHECK SAMPLE COMPONENTS AND CONCENTRATIONS

Solution Component	Solution A Concentration (mg/L)	Solution AB Concentration (mg/L)
Al	100.0	100.0
Ca	300.0	300.0
Fe	250.0	250.0
Mg	100.0	100.0
Na	250.0	250.0
P	100.0	100.0
K	100.0	100.0
S	100.0	100.0
C	200.0	200.0
Cl	2000.0	2000.0
Mo	2.0	2.0
Ti	2.0	2.0
As	0.0	0.100
Cd	0.0	0.100
Cr	0.0	0.200
Co	0.0	0.200
Cu	0.0	0.200
Mn	0.0	0.200
Hg	0.0	0.020
Ni	0.0	0.200
Se	0.0	0.100
Ag	0.0	0.050
V	0.0	0.200
Zn	0.0	0.100

These data are provided for guidance purposes only.

TABLE 2
RECOMMENDED ISOTOPES FOR SELECTED ELEMENTS

Element of Interest	Mass(es)
Aluminum	**27**
Antimony	121, **123**
Arsenic	**75**
Barium	138, 137, 136, **135**, 134
Beryllium	**9**
Bismuth (IS)	209
Cadmium	**114**, 112, **111**, 110, 113, 116, 106
Calcium (I)	42, 43, **44**, 46, 48
Chlorine (I)	35, 37, (77, 82)[a]
Chromium	**52**, **53**, **50**, 54
Cobalt	**59**
Copper	**63**, **65**
Germanium (IS)	74
Holmium (IS)	165
Indium (IS)	**115**, 113
Iron (I)	**56**, **54**, **57**, 58
Lanthanum (I)	139
Lead	**208**, **207**, **206**, 204
Lithium (IS)	6[b], 7
Magnesium (I)	24, **25**, **26**
Manganese	**55**
Mercury	202, **200**, 199, 201
Molybdenum (I)	98, 96, 92, **97**, 94, (108)[a]
Nickel	58, **60**, 62, **61**, 64
Potassium (I)	**39**
Rhodium (IS)	103
Scandium (IS)	45
Selenium	80, **78**, **82**, **76**, **77**, 74
Silver	**107**, **109**
Sodium (I)	**23**
Terbium (IS)	159
Thallium	**205**, 203
Vanadium	**51**, **50**
Tin (I)	120, **118**
Yttrium (IS)	89
Zinc	64, **66**, **68**, **67**, 70

[a] These masses are also useful for interference correction (Sec. 4.2).
[b] Internal standard must be enriched in the ^{6}Li isotope. This minimizes interference from indigenous lithium.

NOTE: Method 6020 is recommended for only those analytes listed in Sec.1.2. Other elements are included in this table because they are potential interferents (labeled I) in the determination of recommended analytes, or because they are commonly used internal standards (labeled IS). Isotopes are listed in descending order of natural abundance. The most generally useful isotopes are underlined and in boldface, although certain matrices may require the use of alternative isotopes.

TABLE 3

EXAMPLE ICP-MS MULTI-LABORATORY PRECISION AND ACCURACY DATA FOR AQUEOUS SOLUTIONS

Element	Comparability[a] Range	%RSD Range	N[b]	S[c]
Aluminum	95 - 100	11 - 14	14 - 14	4
Antimony	d	5.0 - 7.6	16 - 16	3
Arsenic	97 - 114	7.1 - 48	16 - 16	4
Barium	91 - 99	4.3 - 9.0	16 - 16	5
Beryllium	103 - 107	8.6 - 14	13 - 14	3
Cadmium	98 - 102	4.6 - 7.2	18 - 20	3
Calcium	99 - 107	5.7 - 23	17 - 18	5
Chromium	95 - 105	13 - 27	16 - 18	4
Cobalt	101 - 104	8.2 - 8.5	18 - 18	3
Copper	85 - 101	6.1 - 27	17 - 18	5
Iron	91 - 900	11 - 150	10 - 12	5
Lead	71 - 137	11 - 23	17 - 18	6
Magnesium	98 - 102	10 - 15	16 - 16	5
Manganese	95 - 101	8.8 - 15	18 - 18	4
Nickel	98 - 101	6.1 - 6.7	18 - 18	2
Potassium	101 - 114	9.9 - 19	11 - 12	5
Selenium	102 - 107	15 - 25	12 - 12	3
Silver	104 - 105	5.2 - 7.7	13 - 16	2
Sodium	82 - 104	24 - 43	9 - 10	5
Thallium	88 - 97	9.7 - 12	18 - 18	3
Vanadium	107 - 142	23 - 68	8 - 13	3
Zinc	93 - 102	6.8 - 17	16 - 18	5

Data obtained from Ref. 12.

[a] Comparability refers to the percent agreement of mean ICP-MS values to those of the reference technique (ICP-AES or GFAA).

[b] N is the range of the number of ICP-MS measurements where the analyte values exceed the limit of quantitation (3.3 times the average IDL value). A larger number gives a more reliable comparison.

[c] S is the number of samples with results greater than the limit of quantitation.

[d] No comparability values are provided for antimony because of evidence that the reference data is affected by an interference.

These data are provided for guidance purposes only.

TABLE 4

EXAMPLE ICP-MS MULTI-LABORATORY PRECISION AND ACCURACY DATA FOR SOLID MATRICES

Element	Comparability[a] Range	%RSD Range	N[b]	S[c]
Aluminum	83 - 101	11 - 39	13 - 14	7
Antimony	d	12 - 21	15 - 16	2
Arsenic	79 - 102	12 - 23	16 - 16	7
Barium	100 - 102	19 - 34	15 - 16	7
Beryllium	50 - 87	8.6 - 14	12 - 14	5
Cadmium	93 - 100	6.2 - 25	19 - 20	5
Calcium	95 - 109	4.1 - 27	15 - 17	7
Chromium	77 - 98	11 - 32	17 - 18	7
Cobalt	43 - 102	15 - 30	17 - 18	6
Copper	90 - 109	9.0 - 25	18 - 18	7
Iron	87 - 99	6.7 - 21	12 - 12	7
Lead	90 - 104	5.9 - 28	15 - 18	7
Magnesium	89 - 111	7.6 - 37	15 - 16	7
Manganese	80 - 108	11 - 40	16 - 18	7
Nickel	87 - 117	9.2 - 29	16 - 18	7
Potassium	97 - 137	11 - 62	10 - 12	5
Selenium	81	39	12	1
Silver	43 - 112	12 - 33	15 - 15	3
Sodium	100 - 146	14 - 77	8 - 10	5
Thallium	91	33	18	1
Vanadium	83 - 147	20 - 70	6 - 14	7
Zinc	84 - 124	14 - 42	18 - 18	7

Data obtained from Ref. 12.

[a] Comparability refers to the percent agreement of mean ICP-MS values to those of the reference technique.

[b] N is the range of the number of ICP-MS measurements where the analyte values exceed the limit of quantitation (3.3 times the average IDL value).

[c] S is the number of samples with results greater than the limit of quantitation.

[d] No comparability values are provided for antimony because of evidence that the reference data is affected by an interference.

These data are provided for guidance purposes only.

TABLE 5

EXAMPLE METHOD PERFORMANCE DATA FOR AQUEOUS AND SEA WATER SAMPLES[A]
WITH INTERFERING ELEMENTS REMOVED
AND SAMPLES PRECONCENTRATED PRIOR TO ANALYSIS

ELEMENT	ISOTOPE	CONCENTRATION (ng/mL)[B]		
		9.0 mL	27.0 mL	CERTFIED
Manganese	55	1.8±0.05	1.9±0.2	1.99±0.15
Nickel	58	0.32±0.018	0.32±0.04	0.30±0.04
Cobalt	59	0.033±0.002	0.028±0.003	0.025±0.006
Copper	63	0.68±0.03	0.63±0.03	0.68±0.04
Zinc	64	1.6±0.05	1.8±0.15	1.97±0.12
Copper	65	0.67±0.03	0.6±0.05	0.68±0.04
Zinc	66	1.6±0.06	1.8±0.2	1.97±0.12
Cadmium	112	0.020±0.0015	0.019±0.0018	0.019±0.004
Cadmium	114	0.020±0.0009	0.019±0.002	0.019±0.004
Lead	206	0.013±0.0009	0.019±0.0011	0.019±0.006
Lead	207	0.014±0.0005	0.019±0.004	0.019±0.006
Lead	208	0.014±0.0006	0.019±0.002	0.019±0.006

Data obtained from Ref. 12.
[A] The dilution of the sea-water during the adjustment of pH produced 10 mL samples containing 9 mL of sea-water and 30 mL samples containing 27 mL of sea-water. Samples containing 9.0 mL of CASS-2, n=5; samples containing 27.0 mL of CASS-2, n=3.
[B] Concentration (ng/mL) ± 95% confidence limits.

These data are provided for guidance purposes only.

TABLE 6

ANALYSIS OF NIST SRM 1643b, TRACE METALS IN WATER[A]
AND SAMPLES PRECONCENTRATED PRIOR TO ANALYSIS

ELEMENT	ISOTOPE	CONCENTRATION (ng/mL)[B]	
		DETERMINED	CERTFIED
Manganese	55	30±1.3	28±2
Nickel	58	50±2	49±3
Cobalt	59	27±1.3	26±1
Nickel	60	51±2	49±3
Copper	63	23±1.0	21.9±0.4
Zinc	64	67±1.4	66±2
Copper	65	22±0.9	21.9±0.4
Zinc	66	67±1.8	66±2
Cadmium	111	20±0.5	20±1
Cadmium	112	19.9±0.3	20±1
Cadmium	114	19.8±0.4	20±1
Lead	206	23±0.5	23.7±0.7
Lead	207	23.9±0.4	23.7±0.7
Lead	208	24.2±0.4	23.7±0.7

Data obtained from Ref. 12.

[A] 5.0 mL samples, n=5.
[B] Concentration (ng/mL) ± 95% confidence limits.

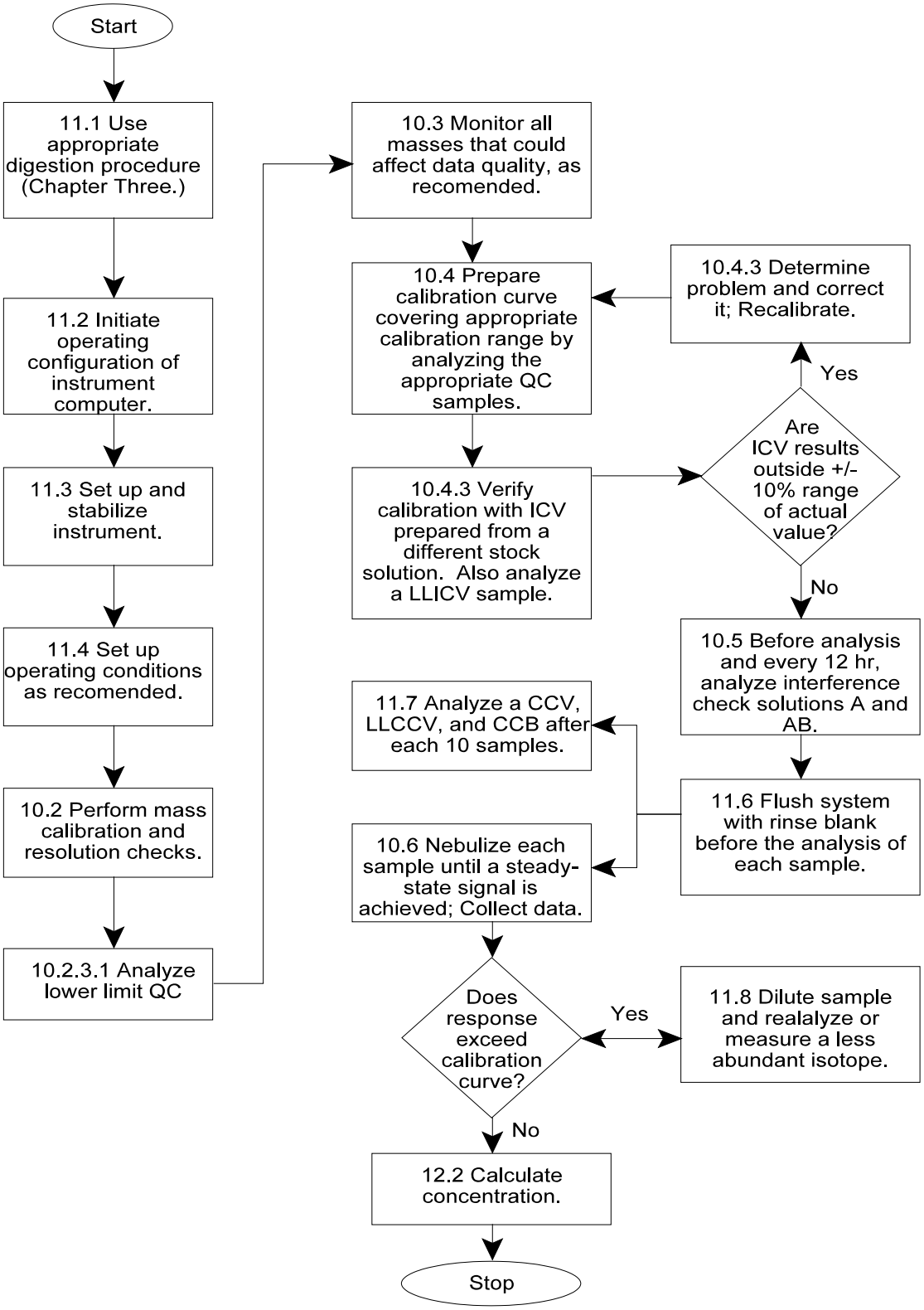
These data are provided for guidance purposes only.

TABLE 7

COMPARISON OF TOTAL MERCURY RESULTS IN HEAVILY CONTAMINATED SOILS

Soil Sample	Mercury in µg/g	
	ICP-MS	CVAA
1	27.8	29.2
2	442	376
3	64.7	58.2
4	339	589
5	281	454
6	23.8	21.4
7	217	183
8	157	129
9	1670	1360
10	73.5	64.8
11	2090	1830
12	96.4	85.8
13	1080	1190
14	294	258
15	3300	2850
16	301	281
17	2130	2020
18	247	226
19	2630	2080

Source: Ref. 16.
These data are provided for guidance purposes only.


Start
11.1 Use appropriate digestion procedure (Chapter Three.)
11.2 Initiate operating configuration of instrument computer.
11.3 Set up and stabilize instrument.
11.4 Set up operating conditions as recomended.
10.2 Perform mass calibration and resolution checks.
10.2.3.1 Analyze lower limit QC
10.3 Monitor all masses that could affect data quality, as recomended.
10.4 Prepare calibration curve covering appropriate calibration range by analyzing the appropriate QC samples.
10.4.3 Verify calibration with ICV prepared from a different stock solution. Also analyze a LLICV sample.
Are ICV results outside +/- 10% range of actual value?
Yes
10.4.3 Determine problem and correct it; Recalibrate.
No
10.5 Before analysis and every 12 hr, analyze interference check solutions A and AB.
11.6 Flush system with rinse blank before the analysis of each sample.
11.7 Analyze a CCV, LLCCV, and CCB after each 10 samples.
10.6 Nebulize each sample until a steady-state signal is achieved; Collect data.
Does response exceed calibration curve?
Yes
11.8 Dilute sample and realalyze or measure a less abundant isotope.
No
12.2 Calculate concentration.
Stop