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METHOD 6020B

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 quality control (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-leachable) elements are required. The analyst should insure that a sample digestion method is chosen that is appropriate for each analyte and the intended use of the data. Refer to Chapter Three for the appropriate digestion procedures.

1.2 ICP-MS has been applied to the determination of over 60 elements in various matrices. Analytes for which the acceptability of Method 6020 has been demonstrated through multi-laboratory testing on solid and aqueous wastes are listed below.

Element	Symbol	CASRN[a]	Element	Symbol	CASRN[a]
Aluminum	Al	7429-90-5	Magnesium	Mg	7439-95-4
Antimony	Sb	7440-36-0	Manganese	Mn	7439-96-5
Arsenic	As	7440-38-2	Mercury	Hg	7439-97-6
Barium	Ba	7440-39-3	Nickel	Ni	7440-02-0
Beryllium	Be	7440-41-7	Potassium	K	7440-09-7

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Element	Symbol	CASRN[a]	Element	Symbol	CASRN[a]
Cadmium	Cd	7440-43-9	Selenium	Se	7782-49-2
Calcium	Ca	7440-70-2	Silver	Ag	7440-22-4
Chromium	Cr	7440-47-3	Sodium	Na	7440-23-5
Cobalt	Co	7440-48-4	Thallium	Tl	7440-28-0
Copper	Cu	7440-50-8	Vanadium	V	7440-62-2
Iron	Fe	7439-89-6	Zinc	Zn	7440-66-6
Lead	Pb	7439-92-1			

[a]Chemical Abstract Service Registry Number

The performance acceptability of ICP-MS for the determination of the listed elements was based upon comparison of the multi-laboratory testing results with those obtained from either furnace atomic absorption spectrophotometry or inductively coupled plasma—optical emission spectrometry. It should be noted that one multi-laboratory study was conducted in 1988. As advances in ICP-MS instrumentation and software have been made since that time, other elements have been added through validation and with additional improvements in performance of the method. Performance, in general, presently exceeds the original multi-laboratory performance data for the listed elements (and others) that are provided in Sec. 13.0. Instrument detection limits (IDLs), lower limits of quantitation (LLOQs) and linear ranges will vary with the matrices, instrumentation, and operating conditions. In relatively simple matrices, IDLs will generally be < 0.1 µg/L. For less sensitive elements (e.g., Se and As) and desensitized major elements, IDLs may be ≥ 1.0 µg/L.

1.3 If Method 6020 is used to determine any analyte not listed in Sec. 1.2, it is the responsibility of the analyst to demonstrate the precision and bias of the method for the waste to be analyzed. The analyst must always 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 Use of this method should be restricted to spectroscopists who are knowledgeable in the recognition and correction of spectral, chemical, and physical interferences in ICP-MS analysis.

1.5 An appropriate internal standard is necessary 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, and ^{209}Bi. The lithium internal standard should have an enriched abundance of ^{6}Li, so that

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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 as indicated by high bias of internal standard recoveries.

Note: Other potential causes of a high bias should also be considered before a final decision is made that the internal standard high bias is caused by an excessive concentration of the internal standard isotope in the sample.

1.6 Prior to employing this method, analysts are advised to consult the preparatory method for each type of procedure that may be employed in the overall analysis (e.g., Methods 3005, 3010, 3015, 3031, 3040, 3050, 3051, 3052, 7000, and 6800) for additional information on QC 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 (DQOs) for the intended application.

1.7 This method is restricted to use by, or under supervision of, properly experienced and trained personnel. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis, aqueous and solid samples are solubilized or digested using the appropriate sample preparation methods (see Chapter Three). When analyzing groundwater samples for dissolved constituents, acid digestion is not necessary, if the samples are filtered and acid-preserved prior to analysis (e.g., Methods 3005, 3010, 3015, 3031, 3050, 3051 and 3052). For oils, greases, or waxes, use the solvent dissolution procedure in method 3040 to prepare the samples.

2.2 This method describes multi-element determinations using ICP-MS in environmental samples. The method measures ions produced by a radio-frequency inductively coupled plasma. Analyte species in 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 introduced, by means of an interface, into a mass spectrometer. The ions produced in the plasma are sorted according to their mass-to-charge (*m/z*) ratios and quantified with a channel electron multiplier. Interferences must be assessed and valid corrections applied or the data flagged to indicate problems. Interference correction must include compensation for background ions contributed by the plasma gas, reagents, and constituents of the sample matrix.

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3.0 DEFINITIONS

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

4.0 INTERFERENCES

4.1 Isobaric elemental interferences in ICP-MS are caused by isotopes of different elements forming atomic ions with the same nominal *m/z* ratio. 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.

4.2 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 of the interfering element at a concentration which produces sufficient interference at the isotopes of interest that a reliable measurement can be made. 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 the abundances of natural isotopes for coefficient approximations) =

(*m/z* 75 signal) - (3.13) [(*m/z* 77 signal) - (0.87) (*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]).

NOTE: The coefficients should be verified experimentally using the procedures or coefficients provided by the instrument manufacturer.

Similarly,

Corrected cadmium signal (using the abundances of natural isotopes for coefficient approximations) =

(*m/z* 114 signal) - (0.027)(*m/z* 118 signal) - (1.63)(*m/z* 108 signal)

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where, the 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: With respect to the arsenic equation above, the coefficients could be improved. For example, the coefficient to modify "3.13" (in the equation above) for a particular instrument can be determined from the observed ratio of the m/z 75 to the m/z 77 net isotope signals for a solution of hydrochloric acid. The concentration of HCl used should provide enough signal at the measured isotopes to ensure that a reliable measurement can be made, while not exceeding the linear range of the detector.

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 IDL, bias, and precision specifications for analysis of the samples can be met.

4.3 As technology continues to develop, modifications to existing ICP-MS instrumentation can reduce or completely remove common interferences thus eliminating the need for reliance on correction equations. Instruments must be able to demonstrate successful freedom from interferences. Examples of such modifications are discussed in more detail below:

4.3.1 Recent ICP-MS instruments may include collision or reaction cells for removal of molecular isobaric interferences. This type of interference removal is effective, and highly recommended for complex and/or varying matrices. The systems work either by collision of molecular species with an inert gas (usually helium) or by reaction of molecular species or the target analyte with reactive gases (e.g., ammonia or methane). Manufacturer recommendations should be followed for the configuration of the collision/reaction cell. This technique may eliminate the need for most correction equations, but freedom from interference still needs to be demonstrated using the spectral interference check (SIC) solutions described in sections 7.23 and 9.9.

4.3.2 High resolution ICP-MS instruments are available based on several mass analyzer designs with much higher mass resolution within the mass range of traditional ICP-MS instruments. These mass analyzers are not based on quadrupole mass analyzers and have orders of magnitude resolution above quadrupoles, which helps reduce or eliminate interference from polyatomic ions with the same nominal mass. These mass analyzers reduce or eliminate the need for most correction equations, but the instrument needs to be operated at sufficient resolution to remove the expected

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interference. For example, resolving ^{52}Cr from $^{40}Ar^{12}C$ requires a resolution of around 4000, while resolving ^{75}As from $^{40}Ar^{35}Cl$ requires a resolution of around 8000. Freedom from interferences needs to be demonstrated for the particular higher resolution mass analyzers ICP-MS.

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% levels of iron and aluminum should be avoided. The method also provides a method for preconcentration to enhance detection 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 cannot occur. The method has been proven effective for the certification of reference materials and validated using reference materials (Refs. 13-15). 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 Since commercial quadrupole 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 need resolution improvement, matrix separation, or analysis using another verified and documented isotope, or otherwise the use of another method.

4.6 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). Dissolved solid levels below 0.2% (2,000 mg/L) have been currently recommended (Ref. 10) to minimize solid deposition, although currently-available ICP-MS systems may be able to tolerate much higher levels. 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 five-fold (i.e., dilute one part sample with four parts diluent [1:5 = 1+4]) will usually eliminate the problem.

4.7 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 the memory interferences which are observed. The rinse period between samples must be long enough to eliminate significant memory interference.

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4.8 Reagents and sample processing hardware may yield artifacts and/or interferences to sample analysis. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents may be necessary. Refer to each method to be used for specific guidance on QC procedures.

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.

5.3 **Hydrofluoric acid is a very toxic acid and penetrates the skin and tissues deeply if not treated immediately.** Injury occurs in two stages: firstly, by hydration that induces tissue necrosis; and secondly, by penetration of fluoride ions deep into the tissue and thereby reacting with calcium. Boric acid and/or other complexing reagents and appropriate treatment agents should be administered immediately.

WARNING: Consult appropriate safety literature for determining the proper protective eyewear, clothing and gloves to use when handling hydrofluoric acid. **Always have appropriate treatment materials readily available prior to working with this acid.** See Method 3052 for additional recommendations for handling hydrofluoric acid from a safety and an instrument standpoint.

5.4 Many metal salts, are extremely toxic if inhaled or swallowed.

WARNING: Exercise extreme care to ensure that samples and standards are handled safely and properly and that all exhaust gases are properly vented. Wash hands thoroughly after handling.

6.0 EQUIPMENT AND SUPPLIES

6.1 Inductively coupled plasma-mass spectrometer:

6.1.1 The system must be capable of providing resolution, better than or equal to 1.0 u (unified atomic mass unit) at 10% peak height. The system must have a mass range from at least 6 to 240 u 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 are recommended.

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6.1.2 Argon gas, high-purity grade (99.99%).

6.2 Volumetric flasks of suitable material composition, precision and accuracy

6.3 Volumetric pipets of suitable material composition, precision and accuracy

This section does not list all common laboratory ware (e.g., beakers) that might be used.

7.0 REAGENTS AND STANDARDS

7.1 Reagent-grade, and whenever necessary, ultra-high purity-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 Reagent water - Reagent water must be interference free. All references to water in this method refer to reagent water unless otherwise specified.

7.3 Ultra high-purity or equivalent acids must be used in the preparation of standards and for sample processing. Redistilled acids are recommended because of the high sensitivity of ICP-MS. Nitric acid at less than 2% (v/v) is necessary 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). The use of 1% (v/v) HCl is necessary for the stability of antimony and silver concentrations in the range of 50 - 500 µg/L. For concentrations greater than 500 µg/L silver, additional HCl will be needed. As a consequence, the accuracy of analytes that need significant chloride molecular-ion corrections (e.g., As and V) will degrade.

7.3.1 Nitric acid (concentrated), HNO_3

7.3.2 Nitric acid (50% [v/v]), HNO_3 - Prepare by adding 500 mL concentrated HNO_3 to 400 mL water and diluting to 1 L.

7.3.3 Nitric acid (1% [v/v]), HNO_3 - Prepare by adding 10 mL concentrated HNO_3 to 400 mL water and diluting to 1 L.

7.3.4 Hydrochloric acid (concentrated), HCl

7.3.5 Hydrochloric acid (37%), HCl - Prepare by adding 370 mL concentrated HCl to 400 mL water and diluting to 1L.

7.3.6 Hydrofluoric acid (concentrated), HF

7.3.7 Phosphoric acid (concentrated), H_3PO_4

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7.3.8 Phosphoric acid (85% [v/v]), H_3PO_4 - Prepare by adding 850 mL concentrated H_3PO_4 to 100 mL water and diluting to 1 L.

7.3.9 Sulfuric acid (concentrated), H_2SO_4

7.3.10 Sulfuric acid (96% [v/v]) H_2SO_4, - Prepare by adding 40 mL water to a 2 L glass beaker. While gently stirring, carefully add 960 mL concentrated H_2SO_4 to the beaker. Mix until combined. Allow to cool. Carefully, quantitatively transfer solution to a 1-L volumetric flask. Bring to volume with additional water if necessary. Mix thoroughly through inversion to combine.

WARNING: Considerable heat is generated upon combining sulfuric acid and water. The use of appropriate personal protection (e.g. proper gloves, safety glasses and protective clothing) is necessary to avoid personal injury such as thermal burns or acid burns due to solution splatter. Also, always add acid to water (rather than water to acid) to reduce splatter.

7.3.11 Citric acid, $HO_2CCH_2C(OH)(CO_2H)CH_2CO_2H$

7.4 Bismuth(III) oxide, Bi_2O_3

7.5 Holmium(III) carbonate pentahydrate, $Ho_2(CO_3)_3 \cdot 5H_2O$

7.6 Indium (powder), In

7.7 Lithium[^{6}Li] carbonate (95 atom % ^{6}Li), $^6Li_2CO_3$

7.8 Ammonium hexachlororhodate(III), $(NH_4)_3RhCl_6$

7.9 Scandium(III) oxide, Sc_2O_3

7.10 Terbium(III) carbonate pentahydrate, $Tb_2(CO_3)_3 \cdot 5H_2O$

7.11 Yttrium(III) carbonate, $Y_2(CO_3)_3 \cdot 3H_2O$

7.12 Ammonium hexafluorotitanate(IV), $(NH_4)_2TiF_6$

7.13 Ammonium molybdate(VI) $(NH_4)_2MoO_4$

7.14 Aluminum(III) nitrate nonahydrate, $Al(NO_3)_3 \cdot 9H_2O$

7.15 Calcium carbonate, $CaCO_3$

7.16 Iron powder, Fe

7.17 Magnesium oxide, MgO

7.18 Sodium carbonate, Na_2CO_3

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7.19 Potassium carbonate, K_2CO_3

7.20 Standard stock solutions - Purchase standard stock solutions from an appropriate commercial source. Otherwise, prepare them manually in the laboratory using only ultra, high-purity grade chemicals or metals (≥ 99.99% purity). See Method 6010 for instructions on preparing standard solutions from solids. Replace stock standards when succeeding dilutions for the preparation of calibration standards cannot be verified.

7.20.1 Bismuth internal standard stock solution (100 µg/mL Bi) - Dissolve 0.1115 g Bi_2O_3 in a minimum amount of dilute HNO_3. Add 10 mL concentrated HNO_3 and dilute to 1 L with reagent water.

7.20.2 Holmium internal standard stock solution (100 µg/mL Ho) - Dissolve 0.1757 g $Ho_2(CO_3)_3 \cdot 5H_2O$ in 10 mL reagent water and 10 mL concentrated HNO_3. After dissolution is complete, warm the solution to degas. Add 10 mL concentrated HNO_3 and dilute to 1 L with reagent water.

7.20.3 Indium internal standard stock solution (100 µg/mL In) - Dissolve 0.1000 g indium in 10 mL concentrated HNO_3. Dilute to 1 L with reagent water.

7.20.4 Lithium internal standard stock solution (100 µg/mL ^6Li) - Dissolve 0.6312 g $^6Li_2CO_3$ (95% atomic abundance) in 10 mL of reagent water and 10 mL concentrated HNO_3. After dissolution is complete, warm the solution to degas. Add 10 mL concentrated HNO_3 and dilute to 1 L with reagent water.

7.20.5 Rhodium internal standard stock solution (100 µg/mL Rh) - Dissolve 0.3593 g $(NH_4)_3RhCl_6$ in 10 mL reagent water. Add 100 mL concentrated HCl and dilute to 1 L with reagent water.

7.20.6 Scandium internal standard stock solution (100 µg/mL Sc) - Dissolve 0.15343 g Sc_2O_3 in 10 mL 50% hot HNO_3. Add 5 mL concentrated HNO_3 and dilute to 1 L with reagent water.

7.20.7 Terbium internal standard stock solution (100 µg/mL Tb) - Dissolve 0.1828 g $Tb_2(CO_3)_3 \cdot 5H_2O$ in 10 mL 50% HNO_3. After dissolution is complete, warm the solution to degas. Add 5 mL concentrated HNO_3 and dilute to 1 L with reagent water.

7.20.8 Yttrium internal standard stock solution (100 µg/mL Y) - Dissolve 0.2316 g $Y_2(CO_3)_3 \cdot 3H_2O$ in 10 mL 50% HNO_3. Add 5 mL concentrated HNO_3 and dilute to 1 L with reagent water.

7.20.9 Titanium interference stock solution (100 µg/mL Ti) - Dissolve 0.4133 g $(NH_4)_2TiF_6$ in reagent water. Add 2 drops concentrated HF and dilute to 1 L with reagent water.

7.20.10 Molybdenum interference stock solution (100 µg/mL Mo) - Dissolve 0.2043 g $(NH_4)_2MoO_4$ in reagent water. Dilute to 1 L with reagent water.

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7.20.11 Gold preservative stock solution for mercury (100 µg/mL Au) - Purchase as a commercially prepared, high-purity solution of $AuCl_3$ in dilute HCl matrix.

7.21 Mixed-calibration standard solutions - Prepare by diluting stock standard solutions to levels in the linear range for the instrument, using the same combination and concentrations of acids used in the preparation of the sample digestates (approximately 1% HNO_3). 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 u removed from the analyte. Recommended internal standards include ^{6}Li, ^{45}Sc, ^{89}Y, ^{103}Rh, ^{115}In, ^{159}Tb, ^{169}Ho, and ^{209}Bi. Prior to preparing the mixed standards, each stock standard solution must be analyzed separately to determine possible spectral interferences or the presence of impurities.

NOTE: Care should be taken when preparing the calibration standards to ensure that the elements are compatible and stable when mixed together. Standards which interfere with another analyte, or which are contaminated with another analyte, may not be included in the same calibration standard as that analyte.

Transfer the mixed-standard solutions to an appropriate container for storage. Freshly mixed standards must be prepared as needed with the realization that concentrations can change upon aging. Calibration standards must be initially verified using a QC standard (see Sec. 7.24).

7.22 Blanks - Three types of blanks are necessary for analysis: (1) the calibration blank, which is used in establishing the calibration curve; (2) the method blank, which is used to monitor for possible contamination resulting from the sample preparation procedure; and (3) the rinse blank, which is used to flush the system between all samples and standards.

7.22.1 Calibration blank - Prepare by acidifying reagent water using the same combination and concentrations of acids used in the preparation of the matrix-matched calibration standards (Sec. 7.21) along with the selected concentrations of internal standards, such that there is an appropriate internal standard element for each of the target analytes. The use of HCl for antimony and silver is discussed in Sec. 7.3. The calibration blank will also be used for all initial calibration blank (ICB) and continuing calibration blank (CCB) determinations.

7.22.2 Method blank — Prepare by a processing either a volume of reagent water equal to that used for actual aqueous samples, or, otherwise, a clean, empty container, equivalent to that used for actual solid samples through all of the preparatory and instrument determination steps used for making ICP-MS determinations in samples. These steps may include, but are not limited to, pre-filtering, digestion, dilution, filtering, and analysis (refer to Sec. 9.5).

7.22.3 Rinse blank - Prepare as a 1 - 2% HNO_3 solution. Prepare a sufficient quantity such that it may be used to flush the system in between standards and samples. If mercury is to be analyzed, the rinse blank should also contain 2 µg/mL $AuCl_3$.

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7.23 Spectral interference check (SIC) solutions - Prepare so as to contain known concentrations of interfering elements that will demonstrate the appropriate magnitude of interferences and provide an adequate test of any corrections. Chloride in the SIC solution 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 SIC is used to verify that the interference levels are corrected by the data system within appropriate QC limits.

NOTE: The final SIC solution concentrations in Table 1 are intended to evaluate corrections for known interferences on only the analytes identified in Sec. 1.0. If the test method is to be used to determine other element(s), it is the responsibility of the analyst to modify the SIC solution accordingly, or prepare an alternative SIC solution, so as to allow adequate verification of interference corrections on the additional element(s) (see Sec. 9.9).

7.23.1 Mixed stock SIC solutions - Prepare the SIC stock solutions using only ultra-pure reagents. They can be obtained commercially or prepared using the following procedures:

7.23.1.1 Mixed SIC stock solution I - Prepare by adding 13.903 g $Al(NO_3)_3 \cdot 9H_2O$, 2.498 g $CaCO_3$ (previously dried at 180 EC for 1 hr), 1.000 g Fe, 1.658 g MgO, 2.305 g Na_2CO_3 and 1.767 g K_2CO_3 to 25 mL of reagent water. Slowly add 40 mL of (50%) HNO_3. After dissolution is complete, warm the solution to degas. Cool and dilute to 1 L with reagent water.

7.23.1.2 Mixed SIC stock solution II - Prepare by slowly adding 7.444 g 85% H_3PO_4, 6.373 g 96% H_2SO_4, 40.024 g 37% HCl, and 10.664 g citric acid ($C_6O_7H_8$) to 100 mL of reagent water. Dilute to 1 L with reagent water.

7.23.2 Mixed working SIC solution - Prepare by combining 10.0 mL of SIC stock solution I, 2.0 mL each of 100-µg/mL titanium stock solution and 100-µg/mL molybdenum stock solution, and 5.0 mL of SIC stock solution II. Dilute to 100 mL with reagent water. Prepare fresh weekly.

7.24 Initial calibration verification (ICV) standard - Prepare by combining compatible metals from standard stock solution sources that differ from those used for the preparation of the calibration standards. The ICV should be prepared so as to contain metal concentrations that are near, but not equal to, the midpoint concentration level of the calibration curve.

7.25 Continuing calibration verification (CCV) standard - Prepare using the same acid matrix and stock standards employed when preparing the calibration standards. The CCV should be prepared so as to contain metal concentrations equal or nearly equivalent to the midpoint concentration of the calibration curve.

7.26 Mass spectrometer tuning solution - Prepare so as to contain elements that represent all of the mass regions of interest (i.e., 10 µg/L Li, Co, In, and Tl) in order to verify that

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the resolution and mass calibration of the instrument are within the designated specifications (see Sec. 10.1).

7.27 If the determination of one or more metals using a non-aqueous solvent is required, then all standards and quality control samples must be prepared on a weight/weight basis in the non-aqueous solvent since the density of non-aqueous solvents is not uniform. Standards and quality control materials containing organometallic materials that are soluble in non-aqueous solvents are available from a variety of vendors.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

Sample collection, preservation and storage requirements may vary by EPA program and may be specified in a regulation or project planning document that requires compliance monitoring for a given contaminant. Where such requirements are specified in the regulation, follow those requirements. In the absence of specific regulatory requirements, use the following information as guidance in determining the sample collection, preservation and storage requirements.

See Chapter Three, Inorganic Analytes, for sample collection and preservation instructions.

9.0 QUALITY CONTROL

9.1 Refer to Chapter One for guidance on quality assurance (QA) and QC protocols. When inconsistencies exist between QC guidelines, method-specific QC criteria take precedence over those criteria given 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 QC data should be maintained for reference or inspection.

9.2 Refer to Methods 3005, 3010, 3015, 3031, 3040, 3050, 3051, 3052, 7000, and 6800 for QC procedures to ensure the proper operation of the various sample preparation techniques. Any more specific QC procedures provided in this method will supersede those noted in Methods 3005, 3010, 3015, 3031, 3040, 3050, 3051, 3052, 7000, and 6800.

9.3 Instrument Detection Limits

Instrument detection limits (IDLs) are useful means 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 limit 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. 9.8. IDLs in µg/L can be estimated as the mean of the blank result plus three times the standard

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deviation of 10 replicate analyses of the reagent blank solution. (Use zero for the mean if the mean is negative). 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 once using new equipment, after major instrument maintenance such as changing the detector, and/or at a frequency designated by the project. An instrument log book should be kept with the dates and information pertaining to each IDL performed.

9.4 Initial demonstration of proficiency

Each laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination by generating data of acceptable precision and bias 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. It is recommended that the laboratory should repeat the demonstration of proficiency whenever new staff members are trained or significant changes in instrumentation are made.

9.5 Initially, before processing any samples, the analyst should demonstrate that all parts of the equipment that come into direct contact with the sample and reagents are interference-free. This is accomplished through the analysis of a method blank. As a continuing check, each time samples are digested and analyzed, and when there is a change in reagents, a method blank should be prepared and analyzed for the compounds of interest as a safeguard against chronic laboratory contamination. If an interference is observed that would prevent the determination of the target analyte, determine the source and eliminate it, if possible, before processing the samples. The method blank should be carried through all stages of sample preparation and instrument determination procedures. When new reagents or chemicals are received, the laboratory should monitor the preparation and/or analysis blanks associated with samples for any signs of contamination. It is not necessary to test every new batch of reagents or chemicals prior to sample preparation if the source shows no prior problems. However, if reagents are changed during a preparation batch, separate blanks need to be prepared for each set of reagents.

9.6 Linear range

The linear range establishes the highest concentration that may be reported without diluting the sample. Following calibration, the laboratory may choose to analyze a standard at a higher concentration than the high standard in the calibration. The standard must recover within 10% of the true value, and if successful, establishes the linear range. The linear range standards must be analyzed in the same instrument run as the calibration they are associated with (i.e., on a daily basis) but may be analyzed anywhere within that run. If a linear range standard is not analyzed for any specific element, the highest standard in the calibration becomes the linear range.

9.7 Sample QC for preparation and analysis

The laboratory must also have procedures for documenting the effect of the matrix on method performance (precision, bias, and sensitivity). At a minimum, this should include the

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analysis of QC samples including a method blank, a matrix spike (MS), a laboratory control sample (LCS), and a duplicate sample in each analytical batch. Any method blanks, LCS, MS samples, and duplicate samples should be subjected to the same preparatory and instrument determination procedures as those used on actual samples (see Sec. 11.0).

9.7.1 For each batch of samples analyzed, at least one method blank must be carried throughout the entire sample preparation and instrument determination process, as described in Chapter One. The importance of the method blank is to aid in identifying when and/or if sample contamination is occurring. The method blank is considered to be acceptable if it does not contain the target analytes at concentration levels that exceed the acceptance limits defined in Chapter One or in the project-specific DQOs. The laboratory should not subtract the results of the method blank from those of any associated samples. Such "blank subtraction" is not reliable because it is based on a single method blank value rather than a statistically determined blank concentration.

Blanks are generally considered to be acceptable if target analyte concentrations are less than ½ the LLOQ or are less than project-specific requirements. Blanks may contain analyte concentrations greater than acceptance limits if the associated samples in the batch are unaffected (i.e. targets are not present in samples or sample concentrations **are ≥10X** the blank). Other criteria may be used depending on the needs of the project.

If the method blank fails to meet the necessary acceptance criteria, it should be re-analyzed once. If still unacceptable, then all samples associated with the method blank must be re-prepared and re-analyzed, along with all other appropriate analysis batch QC samples. If the method blank results do not meet the acceptance criteria and reanalysis is not practical, then the laboratory should report the sample results along with the method blank results, and provide a discussion of the potential impact of the contamination on the sample results. However, if an analyte of interest is found in a sample in the batch near its concentration confirmed in the blank, the presence and/or concentration of that analyte should be considered suspect and may require qualification. Refer to Chapter One for additional guidance regarding the proper protocol when analyzing method blanks.

9.7.2 Documenting the effect of the matrix should include the analysis of at least one MS and one duplicate unspiked sample or one matrix spike/matrix spike duplicate (MS/MSD) pair for each batch of samples processed, at a minimum frequency of one per every 20 samples, as described in Chapter One. An MS/MSD pair is used to document the bias and precision of a method in a given sample matrix. The decision on whether to prepare and analyze duplicate samples or an MS/MSD pair must be based on knowledge of the samples in the analysis batch. If samples are expected to contain target analytes above the LLOQ, laboratories may choose to use an MS and a duplicate analysis of an unspiked field sample. If samples are not expected to contain target analytes above the LLOQ, the laboratories should use an MS/MSD pair.

MS/MSD samples should be spiked with each target element at the project-specific action levels, or, when lacking project-specific action levels, between the low- and mid-level standards, as appropriate. Acceptance criteria should be set at laboratory-derived limits, developed through the use of historical analyses, for each matrix type being analyzed. However, historically derived acceptance limits must not exceed ± 25%

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recovery of the target element spike values for bias, and ≤ 20 relative percent difference (RPD) for precision. In the absence of historical data, MS/MSD acceptance limits should be set at ± 25% recovery and ≤ 20 RPD. Refer to Sec. 4.0 of Chapter One for further guidance. If the bias and precision indicators in an analytical batch fail to meet the acceptance criteria, then the interference test discussed in Sec. 9.10 should be performed. Refer to the definitions of bias and precision, in Chapter One, for the proper data reduction protocols.

NOTE: If the background sample concentration is very low or non-detect, a spike of greater than 5 times the background concentration is still acceptable. To assess data precision with duplicate analyses, it is preferable to use a high concentration field sample to prepare unspiked laboratory duplicates for metals analyses.

Calculate the RPD between duplicate or MS determinations 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 = MS or first sample analysis value
D_2 = MSD or duplicate sample analysis value

9.7.3 At least one LCS should be prepared and analyzed with each batch of analytical samples processed, at a minimum frequency of one LCS per every 20 samples, as described in Chapter One. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS should be spiked at the same levels and using the same spiking materials as the corresponding MS/MSD (see above Sec. 9.7.2). When the results of the MS analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can acceptably perform the analysis in a clean matrix.

LCS acceptance criteria should be set at laboratory-derived limits, developed through the use of historical analyses. However, historically derived acceptance limits must not exceed ± 20% of the target element spike values. In the absence of historical data, LCS acceptance limits should be set at ± 20%. If the result of an LCS does not meet the established acceptance criteria, it should be re-analyzed once. If still unacceptable, then all samples associated with the LCS must be re-prepared and re-analyzed, along with all other appropriate analysis batch QC samples.

9.7.4 Reference materials containing known amounts of target elements are recommended when an appropriately similar medium of interest are available as one type of QC after appropriate sample preparation. The reference material may be used as the LCS. For soil reference materials, the manufacturers' established acceptance criterion should be used. For solid reference materials, ± 20% (see Sec. 9.7.3) recovery of the reported manufacturers' target element values may not be achievable. Refer to Chapters One and Three for additional information.

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9.8 Lower Limit of Quantitation (LLOQ) check standard

9.8.1 The laboratory should establish the LLOQ as the lowest point of quantitation which, in most cases, is the lowest concentration in the calibration curve. The LLOQ is initially verified by the analysis of at least 7 replicate samples, spiked at the LLOQ and processed through all preparation and analysis steps of the method. The mean recovery and relative standard deviation of these samples provide an initial statement of precision and accuracy at the LLOQ. In most cases the mean recovery should be +/- 35% of the true value and RSD should be ≤ 20%. In-house limits may be calculated when sufficient data points exist. Monitoring recovery of LLOQ over time is useful for assessing precision and bias. Refer to a scientifically valid and published method such as Chapter 9 of Quality Assurance of Chemical Measurements (Taylor 1987) or the Report of the Federal Advisory Committee on Detection and Quantitation Approaches and Uses in Clean Water Act Programs (http://water.epa.gov/scitech/methods/cwa/det/index.cfm) for calculating precision and bias for LLOQ.

9.8.2 Ongoing LLOQ verification, at a minimum, is on a quarterly basis to validate quantitation capability at low analyte concentration levels. This verification may be accomplished either with clean control material (e.g., reagent water, method blanks, Ottawa sand, diatomaceous earth, etc.) or a representative sample matrix (free of target compounds). Optimally, the LLOQ should be less than the desired regulatory action levels based on the stated project-specific requirements.

9.9 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 hours of continuing sample analysis, whichever is more frequent. Do this by analyzing the SIC solution. Results for the unspiked elements in the SIC solution should be less than 2 times the LLOQ. Note that it may not be possible to obtain SIC spiking solutions that are completely free of the unspiked elements. If the presence and concentration of an unspiked element can be confirmed via vendor documentation and/or determination of multiple isotopes of the element in the correct ratios, the concentration actually present may be subtracted from the determined value prior to comparing to the LLOQ limits. Refer to Sec. 4.0 for a discussion on interferences and potential solutions to those interferences if additional guidance is needed.

9.10 The intensities of each internal standard must be monitored for every analysis to ensure that it does not decrease below 30%, with respect to its intensity during the initial calibration. If this occurs, a significant matrix effect must be suspected. Under these conditions, the IDL has degraded, and therefore the correction capability of the internal-standardization technique must then be questioned. If this happens, perform the following procedure:

9.10.1 Make sure the instrument has not drifted by observing the internal standard intensities in the nearest clean matrix, i.e., the calibration blank. If the low internal standard intensities are also observed in the nearby calibration blank, terminate the analysis, correct the problem, recalibrate the instrument, verify the new calibration, and reanalyze the affected samples.

9.10.2 If drift has not been demonstrated to occur as outlined in Sec. 9.10.1, matrix effects need to be removed by diluting the affected sample. Dilute the sample five-

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fold (1:5), taking into consideration the need to add the appropriate amounts of internal standards, and reanalyze. If the first dilution does not eliminate the problem, repeat the dilution procedure in an iterative fashion, using ever-increasing dilutions, until the internal-standard intensities exceed the 30% acceptance limit. Correct the reported results using the appropriate dilution factors.

9.11 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 molecular-ion species 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 LLOQ and the concentration of interferents are insignificant, then the data may go uncorrected.

NOTE: Monitoring the interference sources does not inevitably necessitate monitoring of 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 is needed 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 QA.

NOTE: Only isobaric elemental, molecular, and doubly charged interference corrections, which employ 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 this method.

9.12 It is recommended that the laboratory adopt additional QA practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Whenever possible, the laboratory should analyze reference materials and participate in relevant performance evaluation (PE) studies.

9.13 If less than acceptable bias and precision data are generated for the matrix spike(s), the additional QC protocols in Sections 9.13.1 and/or 9.13.2 should be performed 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. If matrix interference effects are confirmed, then an alternative test method should be considered or the current test method modified, so that the analysis is not affected by the same interference. The use of a standard-addition analysis procedure may also be used to compensate for this effect (refer to Method 7000).

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9.13.1 Dilution test

If the analyte concentration is within the linear range of the instrument and sufficiently high (minimally, a factor of 25 times greater than the LLOQ), an analysis of a 1:5 dilution should agree to within ± 20% of the original determination. If not, then a chemical or physical interference effect must be suspected. The matrix spike is often a good choice of sample for the dilution test, since reasonable concentrations of most analytes are present. Elements that fail the dilution test are reported as estimated values.

9.13.2 Post-digestion MS

If a high concentration sample is not available for performing the dilution test, then a post-digestion MS should be performed. The test only needs to be performed for the specific elements that failed original matrix spike limits, and only if the spike concentration added was greater than the concentration determined in the unspiked sample. Following preparation, which may include, but is not limited to, pre-filtration, digestion, dilution and filtration, an aliquot, or dilution thereof, should be obtained from the final aqueous, unspiked-analytical sample, and spiked with a known quantity of target elements. The spike addition should be based on the indigenous concentration of each element of interest in the sample. The recovery of the post-digestion MS should fall within a ± 25 % acceptance range, relative to the known true value, or otherwise within the laboratory-derived acceptance limits. If the post-digestion MS recovery fails to meet the acceptance criteria, the sample results must be reported as estimated values.

9.14 Ultra-trace analysis necessitates the use of clean chemistry practices. Several suggestions for the reduction of contaminants in the analytical blank are provided in Chapter Three, Inorganic Analytes.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Conduct mass calibration and resolution verification checks in the mass regions of interest using the mass spectrometer tuning solution (Sec. 7.26). The mass calibration and resolution verification acceptance criteria must be met prior to the analysis of samples. If the mass calibration differs by more than 0.1 u 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 u full width at 10% peak height.

10.2 At a minimum, the elements required for the project plus any required for interference correction must be calibrated. Recommended isotopes for the analytes in Sec. 1.2 are provided in Table 2. Flush the system in between each standard and sample using the rinse blank (Sec. 7.22.3). The rinse time needs to be sufficient to ensure that analytes present in the linear range are effectively cleaned out prior to analysis of the subsequent sample. Use the average of at least three readings (of a single injection) for both calibration standard and sample analyses.

10.3 Calibration standards should be prepared on an as-needed basis unless stability warrants preparing fresh daily, (or each time a batch of samples is analyzed). If the ICV standard is prepared daily and the results of the ICV analyses meet the acceptance criteria,

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then the calibration standards do not need to be prepared daily and may be prepared and stored for as long as the calibration standard viability can be verified through the use of the ICV. If the ICV fails to meet the acceptance criteria, trouble shoot the situation, and then prepare a new set of calibration standards if needed and recalibrate the instrument

10.4 A calibration curve must be analyzed daily. The instrument may be calibrated using a single point standard and a calibration blank (ICB) or a multipoint calibration curve. If a multipoint curve is used a minimum of three standards are required and the correlation coefficient (r) should be $\geq$ 0.995 or the coefficient of determination (r^2) should be $\geq$ 0.990. Relative Standard Error may be used as an alternative to r or r^2, and should be $\leq$ 20%. If a multipoint calibration is used the low standard must be at or below the LLOQ.

NOTE: Inversely weighted linear regressions or other methods may be used in order to minimize curve fitting errors at the low end of the calibration curve.

10.5 After the initial calibration is completed it is verified using several checks.

10.5.1 Initial Calibration Verification (ICV) - The ICV is a standard prepared from a different source than the initial calibration standards. It is analyzed at approximately the mid-level of the calibration and serves as a check that the initial calibration standards are at the correct concentrations. The acceptance range is 90-110% of the true value.

10.5.2 Low-level readback or verification - For a multi-point calibration, the low level standard should quantitate to within 80-120% of the true value. For a single point calibration, a standard from the same source as the calibration standard and at or below the LLOQ is analyzed and should recover within 80-120% of the true value.

10.5.3 Mid-level readback or verification - For a multi-point calibration, the mid-level standard should quantitate to within 90-110% of the true value. For a single point calibration, a standard from the same source as the calibration standard and at the mid-point of the linear range is analyzed and should recover within 90-110% of the true value.

10.5.4 Initial Calibration blank (ICB) - If a multi-level calibration is used, an ICB is analyzed immediately after the calibration (or after the ICV) and must not contain target analytes above half the LLOQ. If a single point calibration is used, the calibration is forced through the ICB, but a second ICB is analyzed as a check and must not contain target analytes above half the LLOQ. If the ICB consistently has target analyte concentrations greater than half the LLOQ, the LLOQ should be re-evaluated.

NOTE: After cleaning the sampler and skimmer cones, improved performance in calibration stability has been observed by method users if the instrument is exposed to the SIC solution. Improved performance has also been observed if the instrument is allowed to rinse for 5 - 10 minutes before starting the calibration process.

10.5.5 Verify the ongoing validity of the calibration curve after every 10 samples, and at the end of each analysis batch run, through the analysis of a CCV standard (Sec. 7.25) and a CCB (Sec. 7.22.1). For the curve to be considered valid the analysis result of the CCV standard must be within ± 10% of its true value and the CCB must not contain target analytes above the LLOQ. If the calibration cannot be verified, sample analysis

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must be discontinued, the cause of the problem determined and the instrument recalibrated. All samples following the last acceptable CCV standard must be reanalyzed Flow-injection systems may be used as long as they can meet the performance criteria of the method.

11.0 PROCEDURE

11.1 Preliminary treatment of most samples is necessary because of the complexity and variability of sample matrices. Groundwater samples which have been pre-filtered and acidified will not need acid digestion. Samples which are not digested must either use an internal standard or be matrix-matched with the standards (i.e., acid concentrations should match). Solubilization and digestion procedures are presented in Chapter Three, Inorganic Analytes.

NOTE: 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 gold preservative stock (Sec. 7.20.11) per 100 mL of sample) to preserve the mercury and to prevent it from plating out in the sample introduction system.

11.2 Initiate an appropriate operating configuration of the instrument 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

Tune the instrument by following the instructions provided by the instrument manufacturer. Allow at least 30 minutes for the instrument to equilibrate before analyzing samples.

NOTE: The instrument should have features that protect it from high ion currents. If not, precautions must be taken to protect the detector. A channel electron multiplier or active film multiplier will suffer 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. 7.22.3) until the signal levels return to the data quality objectives or method LLOQs (usually about 30 seconds) before the analysis of each sample. Nebulize each sample until a steady-state signal is achieved (usually about 30 seconds) prior to collecting data.

11.7 Dilute and reanalyze samples that exceed the linear range for an analyte (or species needed for a correction) or measure an alternate, but less-abundant, isotope. The

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linearity at the alternate mass must be confirmed by appropriate calibration (see Sec. 10.4). Alternatively apply solid-phase chelation chromatography to eliminate the matrix as described in Sec. 4.3.

11.8 Determination of percent dry weight

When sample results are to be calculated on a dry-weight basis, a separate portion of sample for this determination should be weighed out at the same time as the portion used for analytical determination.

CAUTION: The drying oven should be contained in a hood or vented. Significant laboratory contamination may result from a heavily contaminated hazardous waste sample.

11.8.1 Immediately after weighing the sample aliquot to be digested, weigh an additional 5- to 10-g aliquot of the sample to the nearest 0.01g into a tared crucible. Dry this aliquot overnight at 105 EC. Allow the sample to cool in a desiccator before weighing.

11.8.2 Calculate the % dry weight as follows:

$$\%\,\text{dry weight} = \frac{\text{g of dry sample}}{\text{g of sample}} \times 100$$

This oven-dried aliquot is not used for the extraction and should be appropriately disposed of once the dry weight is determined.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 If dilutions were performed, apply the appropriate corrections to the sample values.

12.2 If appropriate, or required by the project or regulation for data reporting, calculate results for solids on a dry-weight basis as follows:

$$Concentration_{DW} = \frac{C \times V}{W \times S}$$

where:

$Concentration_{DW}$ = Concentration on a dry weight basis (mg/kg)
C = Digest concentration (mg/L)
V = Final volume after sample preparation (L)
W =Wet sample mass (kg)
S = % Solids/100 = % dry weight/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).

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13.0 METHOD PERFORMANCE

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.

Table 3 summarizes the method performance data for aqueous and sea water samples with interfering elements removed and samples preconcentrated prior to analysis. Table 4 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 operations. 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*, a free publication available from the American Chemical Society (ACS), Committee on Chemical Safety, http://portal.acs.org/portal/fileFetch/C/WPCP_012290/pdf/WPCP_012290.pdf.

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 ACS publication listed in Sec. 14.2.

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17.0 TABLES, DIAGRAMS, FLOW CHARTS, AND VALIDATION DATA

The pages to follow contain the tables, and figures referenced by this method.

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TABLE 1

RECOMMENDED SPECTRAL INTERFERENCE CHECK (SIC) SOLUTION COMPONENTS AND CONCENTRATIONS

Solution Component	SIC Concentration (mg/L)
Al	100.0
Ca	300.0
Fe	250.0
Mg	100.0
Na	250.0
P	100.0
K	100.0
S	100.0
C	200.0
Cl	2000.0
Mo	2.0
Ti	2.0

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TABLE 2

RECOMMENDED ELEMENTAL ISOTOPES FOR SELECTED ELEMENTS

Element of Interest	Mass of Isotope
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**
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, 95, 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

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 necessitate the use of alternative isotopes.

[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.

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TABLE 3

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	CERTIFIED
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

NOTE: 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] 95% confidence limits

TABLE 4

ANALYSIS OF NIST SRM 1643b - TRACE METALS IN WATER [a]

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

NOTE: Data obtained from Ref. 12.

[a] 5.0 mL samples, n=5

[b] 95% confidence limits

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TABLE 5

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

NOTE: Data obtained from Ref. 16.

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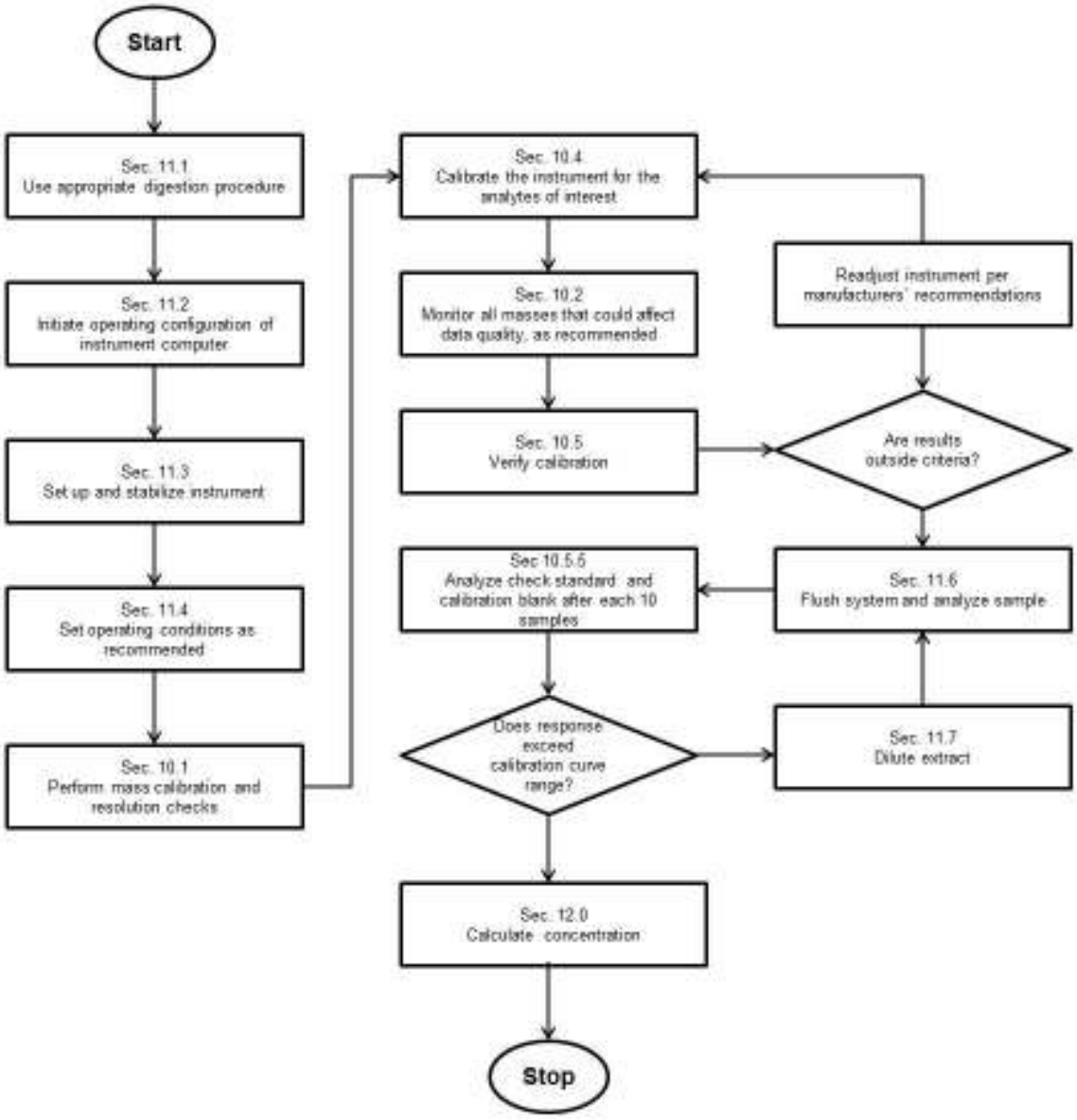
INDUCTIVELY COUPLED PLASMA - MASS SPECTROMETRY



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Appendix A

Summary of Revisions to Method 6020 (From Revision 1, February 2007):

1. Improved overall method formatting for consistency with new SW-846 methods style guidance.
2. Section 1.2 – Changed “Inductively coupled plasma—atomic emission spectrometry” to “Inductively coupled plasma—optical emission spectrometry”.
3. Section 1.6 - inserted references to additional 3000 series preparatory methods to ICP analysis. Also added method 6800 to sections 1.6 and 9.2 as a preparatory method.
4. Inserted additional safety guidance regarding the use of HF.
5. Inserted new section (7.27) regarding analysis of non-aqueous solvents.
6. Reformatted certain paragraphs with the heading "NOTE" or "WARNING" to better denote the importance of the recommendations provided therein.
7. Extensively reformatted “REAGENTS AND STANDARDS” section and to meet current SW-846 method guidelines.
8. Significantly updated and expanded “QUALITY CONTROL” section for better adherence to current SW-846 method guidelines and for improved alignment with current universal practices for published analytical methods.
9. Inserted new sections (Sections 7.23 and 9.9) to describe the preparation and use of the spectral interference check (SIC) solution; also added instructions to match the matrix of this solution to that of the calibration standards.
10. Renamed "QC standard" as "ICV standard" in Sec. 7.24.
11. Added new Sec. 7.25 describing the preparation of a "CCV" standard, consistent with the equivalent section in 6010.
12. Replaced the term “unity” with “uniform” in Section 7.27.
13. Removed all references to method 7000 except for guidance regarding the method of standard addition.
14. The term “accuracy” was replaced by “bias” where appropriate.
15. In Section 9.4, the requirement to repeat the demonstration of proficiency for new staff and instrumentation changes was changed to a recommendation.
16. Section 9.7.2 – Added a note regarding MS/MSD spike concentrations and unspiked laboratory duplicates.
17. The section regarding analysis of reference materials (Sec. 9.7.4) was revised for clarity and the term “Standard Reference Material” was replaced with “reference material” throughout the method.
18. Inserted new section (Sec. 9.8) describing the preparation and use of an LLOQ standard. This section includes two new references for guidance on assessing precision and bias.
19. The section describing matrix interference check samples (Sec. 9.13) has been revised for clarity. The post-digestion MS is only recommended if a high concentration sample is not available for performing the dilution test.
20. Substituted certain terms with new terms (i.e. “must” in place of “shall”) to conform with the Performance-based Methods Approach goal of flexibility.
21. Removed reference to “linear dynamic range” as noted by the Inorganic Methods Work Group. Section 9.6 regarding the linear range was added.
22. Mid-level read back or verification standard added to Section 10.5.3.
23. Moved the sentence “If the ICB consistently has target analyte concentrations greater than half the LLOQ, the LLOQ should be re-evaluated.” From Section 10.5.5 to Section 10.5.4.
24. Added 95 as mass of isotope for molybdenum.

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25. Tables 3 and 4 from 6020A presenting example precision and accuracy data for aqueous and solid matrices were removed.
26. Language was updated in Section 9.7.1 regarding method blanks.

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