METHOD 6010D

INDUCTIVELY COUPLED PLASMA—OPTICAL EMISSION SPECTROMETRY

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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—optical emission spectrometry (ICP-OES) is a spectrometric technique used to determine trace elements in aqueous solutions. In ICP-OES, a sample solution is aspirated (i.e., nebulized) continuously into an inductively coupled, argon-plasma discharge, where analytes of interest are converted to excited-state, gas-phase atoms or ions. As the excited-state atoms or ions return to their ground state, they emit energy in the form of light at wavelengths that are characteristic of each specific element. The intensity of the energy emitted at the chosen wavelength is proportional to the amount (concentration) of that element in the analyzed sample. Thus, by determining which wavelengths are emitted by a sample and their respective intensities, the elemental composition of the given sample relative to a reference standard may be quantified. For accurate results, direct ICP-OES analysis should be conducted on only relatively clean, aqueous matrices (e.g., pre-filtered groundwater samples). Other, more complex aqueous and/or solid samples need acid digestion prior to analysis; the analyst should ensure 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.

The following RCRA analytes have been determined by this method:

Element	Symbol	CASRN[a]	Element	Symbol	CASRN[a]
Aluminum	Al	7429-90-5	Mercury*	Hg	7439-97-6
Antimony	Sb	7440-36-0	Molybdenum	Mo	7439-98-7
Arsenic	As	7440-38-2	Nickel	Ni	7440-02-0
Barium	Ba	7440-39-3	Phosphorus	P	7723-14-0
Beryllium	Be	7440-41-7	Potassium	K	7440-09-7
Boron	B	7440-42-8	Selenium	Se	7782-49-2
Cadmium	Cd	7440-43-9	Silica	SiO_2	7631-86-9
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	Strontium	Sr	7440-24-6
Copper	Cu	7440-50-8	Thallium	TI	7440-28-0
Iron	Fe	7439-89-6	Tin	Sn	7440-31-5
Lead	Pb	7439-92-1	Titanium	Ti	7440-32-6
Lithium	Li	7439-93-2	Vanadium	V	7440-62-2

Element	Symbol	CASRN[a]	Element	Symbol	CASRN[a]
Magnesium	Mg	7439-95-4	Zinc	Zn	7440-66-6
Manganese	Mn	7439-96-5			

[a]Chemical Abstract Service Registry Number

*NOTE: Mercury is not typically analyzed by this method and is not recommended for low-level quantitative analysis; however, this method can be used as a screening tool (e.g., prior to analysis by a low-level method when high concentrations of mercury are expected).

CAUTION: Also note that mercury memory effects may result from the analysis of samples that contain high level Hg concentration. See Method 6020B Sections 7.20.11, 7.22.3, and 11.1 for guidance when analyzing for mercury.

1.2 The table in Section 1.1 lists the elements for which this method has been validated. The sensitivity and the optimum and linear ranges for each element will vary with the wavelength, spectrometer, matrix, and operating conditions. Refer to the manufacturer's instructions for recommended analytical wavelengths and estimated instrument detection limits (IDLs) for the elements in a clean aqueous matrix with insignificant background interferences. Other elements and matrices may be analyzed by this method if acceptable performance at the concentrations of interest is demonstrated (see Sec. 9.0).

1.3 IDLs are necessarily instrument-specific. Therefore, if needed, an IDL must be determined through a separate experimental study for each instrument in a laboratory. IDLs should be established at minimum on an annual basis, for each matrix type analyzed and for each preparatory/determinative method combination used (refer to Chapters One and Three for guidance).

1.4 Analysts should clearly understand the data quality objectives (DQOs) prior to analysis. Before using the method for routine environmental analysis, analysts should document and have on file the necessary initial demonstration of performance (IDP) data, as described in Section 9.0.

1.5 Use of this method is restricted to spectroscopists who are knowledgeable in the correction of the spectral, chemical, and physical interferences described in this method.

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 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). Samples that are not digested necessitate the use of either an internal standard or should be matrix-matched with the standards. If using the former option, the instrument software should be programmed to correct for the intensity differences of the internal standard between samples and standards.

2.2 This method describes multi-element determinations by ICP-OES using sequential or simultaneous optical systems, and axial or radial viewing of the plasma. The ICP-OES instrument measures characteristic emission spectra by optical spectroscopy. Samples are nebulized and the resulting aerosol is transported to the plasma torch. Element-specific emission spectra are produced by a radio-frequency, inductively coupled plasma. The spectra are dispersed by a grating spectrometer, and the intensities of the emission lines are monitored by photosensitive devices.

2.3 Background correction is necessary for trace element determination. Background emission must be measured adjacent to analyte lines on samples during analysis. The position selected for the background-intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used should be as free as possible from spectral interference and should reflect the same change in background intensity as that which occurs at the analyte wavelength being measured.

Background correction is *not* needed in cases of line broadening, where a background correction measurement would actually degrade the analytical result. Analysts should recognize the possibility of additional interferences, as identified in Sec. 4.0, and make appropriate corrections. Tests for the presence of additional interferences are described in Sec. 9.9. Alternatively, analysts may choose multivariate calibration methods, in which case, point selections for background correction are superfluous, since whole spectral regions are processed.

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

Interferences can arise from a variety of sources and serve to diminish the bias and precision of analytical data, particularly when determining elements at trace levels. Interferences to ICP-OES have been studied in detail and are well understood. A summary of interferences to ICP-OES analysis as well as techniques to mitigate their effects on data are provided in the sections to follow.

4.1 Spectral interferences can arise from several sources. Techniques to identify and compensate for spectral interferences are discussed below.

4.1.1 Background emission from continuous or recombination phenomena and/or stray light from the line emission of high concentration elements

4.1.1.1 Compensation for background emission and stray light can usually be conducted by subtracting the background emission determined through measurements obtained adjacent to the analyte wavelength peak. Spectral scans of samples or single-element solutions in the analyte regions may indicate when the use of alternate wavelengths is desirable because of severe spectral interference. These scans will also show whether the most appropriate estimate of the background emission is provided by an interpolation from measurements obtained on both sides of the wavelength peak, or by measured emission obtained only on one side.

The locations selected for the measurement of background intensity will be determined by the complexity of the spectrum adjacent to the wavelength peak. The locations used for routine measurement must be free of off-line spectral interference (interelement or molecular), or otherwise adequately corrected to reflect the same change in background intensity as that which occurs at the wavelength peak. For multivariate methods using whole spectral regions, background scans should be included in the correction algorithm. Off-line spectral interferences are handled by including spectra on interfering species in the algorithm.

4.1.1.2 To determine the appropriate location for off-line background correction, the area adjacent to the wavelength on either side must be scanned, so that the apparent emission intensity from all other method analytes may be recorded. This spectral information must be documented and kept on file. The location selected for background correction must be either free of off-line inter-element spectral interference or a computer routine must be used for automatic correction on all determinations. If a wavelength other than the recommended wavelength is used, the analyst must determine and document both the overlapping and nearby spectral interference effects from all method analytes and common elements and provide for their automatic correction on all analyses. Tests to determine spectral interference must be performed using analyte concentrations that will adequately describe the interference. Normally, 100-mg/L, single-element solutions are sufficient. However, for analytes such as iron, that may be found in the sample at high concentration, a more appropriate test would be to use a concentration near the upper limit of the analytical range (refer to Chapter Three for additional guidance).

4.1.2 Overlaps from the molecular spectra of the same target element may be avoided through the use of an alternate wavelength for quantitation.

4.1.3 Optical spectral-line overlaps between target elements

4.1.3.1 Interelement spectral overlaps are typically compensated through the use of equations that correct for interelement contributions. Instruments that use equations for interelement correction necessitate that interfering element(s) are analyzed at the same time as the target element(s) of interest. When operative and uncorrected, interelement interferences will produce false positive or positively biased determinations. However, if the interference affects the point selected for background correction, the resulting overcorrection will cause a negative bias. More extensive information on interferent effects at various wavelengths and resolutions is available in reference wavelength tables and books. Analysts may apply interelement-correction equations determined on their instruments with tested concentration ranges to compensate (off-line or on-line) for the effects of interfering elements. Selected potential spectral interferences observed for the recommended wavelengths are given in Table 1.

4.1.3.2 For multivariate calibration methods that employ whole spectral regions, spectral interferences are handled by including spectra of the interfering elements in the calibration algorithm. The interferences listed in Table 1 are those that occur between method analytes. Only interferences of a direct overlap nature are shown. These overlaps were observed with a single instrument having a working resolution of 0.035 nm.

4.1.3.3 When using interelement-correction equations, the interference may be expressed as analyte concentration equivalents (i.e., false positive analyte concentrations) arising from 100 mg/L of the interference element. For example, if As is to be determined at 193.696 nm in a sample containing approximately 10 mg/L of Al, according to Table 1, 100 mg/L of Al will yield a false positive signal equivalent to an As concentration of approximately 1.3 mg/L. Correspondingly, the presence of 10 mg/L of Al will result in a false positive signal for As equivalent to approximately 0.13 mg/L. The analyst is cautioned that alternate instruments may exhibit somewhat different levels of interference than those shown in Table 1. The interference effects must, therefore, be evaluated for each individual instrument, since the intensities will vary (see Sec. 4.1.3.5). It should also be noted that instruments using an Echelle grating are potentially subject to interferences from different diffraction orders. These potential interferences will not be listed in standard tables of emission lines and therefore careful evaluation of interelement corrections as described in Sec. 9.9.1 becomes even more vital.

4.1.3.4 Interelement corrections will vary for the same emission line among instruments because of differences in resolution. Such differences are determined by the grating, entrance and exit slit widths, and by the order of dispersion. Interelement corrections will also vary depending upon the choice of background correction points. Selecting a background correction point where an interfering emission line may appear should be avoided when practical. Interelement corrections that constitute a major portion of an emission signal may

not yield accurate data. Analysts should continuously note that some samples may contain uncommon elements that could contribute spectral interferences.

4.1.3.5 As already noted (Sec. 4.1.3.3), the interelement effects must be evaluated for each individual instrument, whether configured as a sequential or simultaneous instrument. For each instrument, intensities will vary not only with optical resolution, but also with operating conditions (such as power, viewing height and argon-flow rate). When using the recommended wavelengths, the analyst must determine and document for each wavelength the effect from referenced interferences (Table 1) as well as any other suspected interferences that may be specific to the instrument or matrix. The analyst should utilize a computer routine for automatic correction on all analyses.

4.1.3.6 Analysts of sequential instruments must verify the absence of spectral interference by scanning over a range of 0.5 nm, centered on the wavelength of interest, for several samples. The range for lead, for example, would be from 220.6 - 220.1 nm. The procedure must be repeated whenever a new matrix is to be analyzed and when a new calibration curve using different instrumental conditions is to be prepared. Samples that show an elevated background emission across the range may be background-corrected by applying a correction factor equal to the emission adjacent to the line or at two points on either side of the line and interpolating between them. An alternate wavelength that does not exhibit a background shift or spectral overlap may also be used.

4.1.3.7 The accuracy of interelement corrections should be verified daily through the analysis of spectral-interference check (SIC) solutions. See Secs. 7.12 and 9.9 for instructions on the preparation and use of SIC solutions.

4.1.3.8 When interelement corrections are *not* used, the absence of interferences **must** be verified. Procedures for verifying the absence of interferences are given in sections 7.12 and 9.9.

4.2 Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or acid concentrations. If physical interferences are present, they must be reduced through (1) sample dilution, (2) the use of a peristaltic pump; (3) the use of an internal standard; or (4) the use of a high-solids nebulizer.

Another problem that can occur, when high concentrations of dissolved solids are present, is salt buildup at the tip of the nebulizer, thus affecting aerosol flow rate and resulting in instrumental drift. Salt buildup can be controlled through (1) wetting the argon prior to nebulization; (2) use of a tip washer; (3) use of a high-solids nebulizer; or (4) sample dilution. Also, it has been reported that better control of the argon flow rate, especially to the nebulizer, improves instrument performance. This may be accomplished with the use of mass flow controllers. The tests described in Sec. 9.11 will help determine if a physical interference is present.

4.3 Chemical interferences include molecular compound formation, ionization effects, and solute vaporization effects. Normally, these effects are not significant with the ICP technique. However, if observed, they can be minimized by (1) careful selection of operating

conditions (i.e., incident power, observation position, etc.); (2) buffering of the sample through matrix-matching; and (3) standard-addition procedures. Chemical interferences are highly dependent on matrix type and analyte.

4.3.1 The majority of interferences likely to be encountered when using this method can be managed successfully using the techniques discussed throughout Sec. 4.1. However, based on professional judgment, the method of standard additions may be useful when certain specific interferences are encountered. Refer to Method 7000 for a more detailed discussion on the use and application of the method of standard additions.

4.3.2 An alternative to the method of standard additions is the use of an internal standard(s). In the internal standard technique, one or more elements not found in the samples, and verified to not cause an interelement spectral interference, are added to the samples, calibration standards, and blanks. Yttrium or scandium is often used for this purpose. The concentration should be sufficient for optimum precision, but not so high as to alter the salt concentration of the matrix. The internal standard element intensity is used to ratio the analyte intensity signals for both calibration and quantitation. This technique is very useful in overcoming matrix interferences, particularly in high solids matrices.

4.4 Memory interferences result when analytes in a previous sample contribute to the intensity signals measured in a subsequent sample. Memory effects can result from sample deposition on the uptake tubing to the nebulizer and from the buildup of sample material in the plasma torch and spray chamber. The site where these effects occur is dependent on the element and can be minimized by flushing the system with a rinse blank between samples. The possibility of memory interferences should be considered within an analytical run. When recognized, suitable rinse times should be established to reduce them. The rinse times necessary for a particular element must be estimated prior to analysis. The estimation may be made by aspirating a standard containing the element(s) of interest at a concentration level that is ten times the typical or expected amount, or at the upper limit of the linear range. The aspiration time for the rinse time-estimation standard should be the same as a normal sample analysis period, followed by analysis of the rinse blank at a series of designated intervals. The length of the rinse time necessary for reducing the analyte signal(s) to less than or equal to the IDL should be noted. A rinse period of at least 60 seconds should be used between samples and standards until a more suitable rinse time can be established. If a memory interference is determined to be present, the sample must be reanalyzed following use of the newly established rinse period. Alternate rinse times may be established by the analyst based upon the project-specific DQOs.

4.5 Analysts are advised that high salt concentrations can cause analyte signal suppressions and confuse interference tests. If the instrument does not display negative values, fortify the SIC check solution with the elements of interest at 0.5 - 1 mg/L and measure the added standard concentration accordingly. Concentrations should be within 20% of the true spiked concentration or dilution of the samples will be necessary. In the absence of measurable analyte, overcorrection could go undetected if a negative value is reported as zero.

4.6 The calibration blank (Sec. 7.11.2.1) may restrict the quantitation sensitivity, or otherwise degrade the precision and bias of the analysis. Chapter Three should be consulted for clean chemistry methods and procedures for reducing the magnitude and variability of the calibration blank.

4.7 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 safety data sheets (SDSs) 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, such as those of osmium, 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, argon-plasma, optical emission spectrometer

6.1.1 Computer-controlled, emission spectrometer with background correction capability

6.1.2 Radio-frequency generator - compliant with FCC regulations

6.1.3 Optional mass-flow controller for argon nebulizer-gas supply

6.1.4 Optional peristaltic pump

6.1.5 Optional autosampler

6.1.6 Argon gas supply - high purity

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 Hydrochloric acid (concentrated), HCl

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

7.5 Hydrochloric acid (5% [v/v]), HCl - Prepare by adding 50 mL concentrated HCl to 400 mL water and diluting to 1 L.

7.6 Nitric acid (concentrated), HNO_3

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

7.8 Hydrofluoric acid (concentrated), HF - For use in matching the background matrices of the calibrations standards relative to those of the samples.

7.9 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). When preparing them manually, **except where specifically noted in the following sections**, dry all metal salts for one hour at 105 °C prior to use. Replace stock standards when succeeding dilutions for the preparation of calibration standards cannot be verified.

CAUTION: Many metal salts are extremely toxic if inhaled or swallowed. Wash hands thoroughly after handling.

NOTE: This section does not apply when analyzing samples prepared by Method 3040.

NOTE: The mass of each analyte is expressed to four decimal places, since rounding to two decimal places can contribute up to 4% error for some compounds.

7.9.1 Aluminum standard stock solution (1000 µg/mL Al) - Prepare by dissolving exactly 1.000 g of aluminum metal in a beaker containing an acid mixture of 4.0 mL of 50% HCl and 1.0 mL of concentrated HNO_3. Warm the beaker slowly to aid in dissolution of the metal. Afterwards, equilibrate the solution to ambient temperature. Add an additional 10.0 mL of 50% HCl and dilute to volume in a 1-L volumetric flask with reagent water.

7.9.2 Antimony standard stock solution (1000 µg/mL Sb) - Prepare by dissolving exactly 2.6673 g of dried $K(SbO)C_4H_4O_6$ in reagent water. Add 10 mL 50% HCl and dilute to volume in a 1-L volumetric flask with reagent water.

7.9.3 Arsenic standard stock solution (1000 µg/mL As) - Prepare by dissolving exactly 1.3203 g of dried As_2O_3 in 100 mL reagent water containing 0.4 g NaOH. Acidify the solution with 2 mL concentrated HNO_3 and dilute to volume in a 1-L volumetric flask with reagent water.

7.9.4 Barium standard stock solution (1000 µg/mL Ba) - Prepare by dissolving exactly 1.5163 g $BaCl_2$ (previously dried for two hours at 250 EC) in a mixture of 10 mL of reagent water and 1 mL 50% HCl. Add 10.0 mL 50% HCl and dilute to volume in a 1-L volumetric flask with reagent water.

7.9.5 Beryllium standard stock solution (1000 µg/mL Be) - Prepare by dissolving exactly 19.6463 g of **undried** $BeSO_4 \cdot 4H_2O$ in reagent water. Add 10.0 mL concentrated HNO_3 and dilute to volume in a 1-L volumetric flask with reagent water.

CAUTION: Drying of beryllium salts can lead to a toxic inhalation hazard.

7.9.6 Boron standard stock solution (1000 µg/mL) - Prepare by dissolving exactly 5.716 g of undried, anhydrous H_3BO_3 in reagent water. Dilute to volume in a 1-L volumetric flask with reagent water. The use of a non-glass volumetric flask is recommended in order to avoid boron contamination from glassware. Transfer immediately to an appropriate container for storage.

7.9.7 Cadmium standard stock solution (1000 µg/mL Cd) - Prepare by dissolving exactly 1.1423 g CdO in a minimum amount of 50% HNO_3. Apply heat to aid in dissolution. Following equilibration to ambient temperature, add 10.0 mL of concentrated HNO_3 and dilute to volume in a 1-L volumetric flask with reagent water.

7.9.8 Calcium standard stock solution (1000 µg/mL Ca) - Prepare by suspending exactly 2.4969 g $CaCO_3$ (previously dried for one hour at 180 EC) in reagent water. Dissolve cautiously with a minimum amount of 50% HNO_3. Add 10.0 mL concentrated HNO_3 and dilute to volume in a 1-L volumetric flask with reagent water.

7.9.9 Chromium standard stock solution (1000 µg/mL Cr) - Prepare by dissolving exactly 1.9231 g CrO_3 in reagent water. Following dissolution, acidify the

solution with 10 mL concentrated HNO_3 and dilute to volume in a 1-L volumetric flask with reagent water.

7.9.10 Cobalt standard stock solution (1000 µg/mL Co) - Prepare by dissolving exactly 1.000 g of cobalt metal in a minimum amount of 50% HNO_3. Add 10.0 mL 50% HCl and dilute to volume in a 1-L volumetric flask with reagent water.

7.9.11 Copper standard stock solution (1000 µg/mL Cu) - Prepare by dissolving exactly 1.2564 g CuO in a minimum amount of 50% HNO_3. Add 10.0 mL concentrated HNO_3 and dilute to volume in a 1-L volumetric flask with reagent water.

7.9.12 Iron standard stock solution (1000 µg/mL Fe) - Prepare by dissolving exactly 1.4298 g Fe_2O_3 in a warm mixture of 20 mL 50% HCl and 2 mL of concentrated HNO_3. Following equilibration to ambient temperature, add an additional 5.0 mL of concentrated HNO_3. Dilute the solution to volume in a 1-L volumetric flask with reagent water.

7.9.13 Lead standard stock solution (1000 µg/mL Pb) - Prepare by dissolving exactly 1.5985 g $Pb(NO_3)_2$ in a minimum amount of 50% HNO_3. Add 10 mL 50% HNO_3 and dilute to volume in a 1-L volumetric flask with reagent water.

7.9.14 Lithium standard stock solution (1000 µg/mL Li) - Prepare by dissolving exactly 5.3248 g lithium carbonate in a minimum amount of 50% HCl. Dilute to volume in a 1-L volumetric flask with reagent water.

7.9.15 Magnesium standard stock solution (1000 µg/mL Mg) - Prepare by dissolving exactly 1.6584 g MgO in a minimum amount of 50% HNO_3. Add 10.0 mL 50% HNO_3 and dilute to volume in a 1-L volumetric flask with reagent water.

7.9.16 Manganese standard stock solution (1000 µg/mL Mn) - Prepare by dissolving exactly 1.000 g of manganese metal in an acid mixture of 10 mL concentrated HCl and 1 mL concentrated HNO_3. Dilute to volume in a 1-L volumetric flask with reagent water.

7.9.17 Mercury standard stock solution (1000 µg/mL Hg) - Prepare by dissolving exactly 1.354 g of **undried** $HgCl_2$ in reagent water. Add 50.0 mL concentrated HNO_3 and dilute to volume in 1-L volumetric flask with reagent water.

CAUTION: Drying of mercury salts can lead to a toxic inhalation hazard.

7.9.18 Molybdenum standard stock solution (1000 µg/mL Mo) - Prepare by dissolving exactly 1.7325 g $(NH_4)_6Mo_7O_{24}•4H_2O$ in reagent water and dilute to volume in a 1-L volumetric flask with reagent water.

7.9.19 Nickel standard stock solution (1000 µg/mL Ni) - Prepare by dissolving exactly 1.000 g of nickel metal in 10.0 mL of hot, concentrated HNO_3. Following equilibration to ambient temperature, dilute the solution to volume in a 1-L volumetric flask with reagent water.

7.9.20 Phosphate standard stock solution (1000 µg/mL P) - Prepare by dissolving exactly 4.3937 g of anhydrous KH_2PO_4 in reagent water. Dilute to volume in a 1-L volumetric flask with reagent water.

7.9.21 Potassium standard stock solution (1000 µg/mL K) - Prepare by dissolving exactly 1.9069 g KCl (dried to a constant weight at 110EC) in reagent water. Dilute to volume in a 1-L volumetric flask with reagent water.

7.9.22 Selenium standard stock solution (1000 µg/mL Se) - Prepare by dissolving exactly 1.6332 g of **undried** H_2SeO_3 in reagent water and dilute to volume in a 1-L volumetric flask with reagent water.

7.9.23 Silica standard stock solution (1000 µg/mL SiO_2) - Prepare by dissolving exactly 2.964 g of **undried** $(NH4)_2SiF6$ in 200 mL of 1:20 HCl. Heat solution to 85 °C to aid in dissolution. After allowing the solution to equilibrate to ambient temperature, dilute to volume in a 1-L volumetric flask with reagent water. Transfer immediately to an appropriate container for storage. Protect standard from light during storage.

7.9.24 Silver standard stock solution (1000 µg/mL Ag) - Prepare by dissolving exactly 1.5748 g of $AgNO_3$ in a reagent water mixture of 10 mL concentrated HNO_3. Dilute to volume in a 1-L volumetric flask with reagent water. Protect standard from light during storage.

7.9.25 Sodium standard stock solution (1000 µg/mL Na) - Prepare by dissolving exactly 2.5419 g of NaCl in reagent water. Add 10.0 mL of concentrated HNO_3 and dilute to volume in a 1-L volumetric flask with reagent water.

7.9.26 Strontium standard stock solution (1000 µg/mL Sr) - Prepare by dissolving exactly 2.4154 g of $Sr(NO_3)_2$ in a 1-L volumetric flask containing 10 mL of concentrated HCl and 700 mL of reagent water. Dilute to volume with reagent water.

7.9.27 Thallium standard stock solution (1000 µg/mL Tl) - Prepare by dissolving exactly 1.3034 g $TlNO_3$ in reagent water. Add 10.0 mL of concentrated HNO_3 and dilute to volume in a 1-L volumetric flask with reagent water.

7.9.28 Tin standard stock solution (1000 µg/mL Sn) - Prepare by dissolving exactly 1.000 g Sn shot in 200 mL of 50% HCl. Apply heat to aid in dissolution. After allowing the solution to equilibrate to ambient temperature, dilute to volume in a 1-L volumetric flask with 50% HCl.

7.9.29 Vanadium standard stock solution (1000 µg/mL V) - Prepare by dissolving exactly 2.2957 g NH_4VO_3 in a minimum amount of concentrated HNO_3. Apply heat to aid in dissolution. After allowing the solution to equilibrate to ambient temperature, add 10.0 mL of concentrated HNO_3 and dilute to volume in a 1-L volumetric flask with reagent water.

7.9.30 Zinc standard stock solution (1000 µg/mL Zn) - Prepare by dissolving exactly 1.2447 g ZnO in a minimum amount of dilute HNO_3. Add 10.0 mL of concentrated HNO_3 and dilute to volume in a 1-L volumetric flask with reagent water.

7.9.31 Yttrium internal standard stock solution (1000 µg/mL Y) - Prepare by dissolving exactly 4.3081 g $Y(NO_3)_3 \cdot 6H_2O$ in a minimum amount of concentrated HNO_3. Add 10.0 mL concentrated HNO_3 and dilute to volume in a 1-L volumetric flask with reagent water.

7.10 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.

7.11 Working-level standard solutions and blanks

NOTE: Following the preparation of all intermediate- and working-level standard solutions, blanks, and QC standards (Sec. 9.0) immediately transfer to an appropriate container for storage. For all intermediate and working standards, especially low-level standards (i.e., < 1 µg/mL metal), the stability must be demonstrated prior to use. Working-level standards should be prepared as needed, recognizing the fact that low-level metal standards can degrade rapidly over time (Refer to Sec. 10.6 for guidance on determining the integrity of standards).

7.11.1 Mixed-calibration standard solutions — Prepare by combining proper volumes of the standard stock solutions in 100-mL volumetric flasks. Add the appropriate types and volumes of acids so that the matrices of the standards are matched, relative to those of the sample digestates. Store all mixed-calibration standards in an appropriate container and protect from light. Prior to preparing the mixed standards, each standard stock solution should be analyzed, separately, in order to determine possible spectral interferences and/or the presence of impurities. 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. Refer to Table 2 for recommendations in selecting the most appropriate stock standards (Sec. 7.9) to combine for the preparation of working-level, mixed–calibration standards.

NOTE: Care should be taken when preparing the calibration standards to ensure that the elements are compatible and stable when mixed together.

NOTE: Depending on the acid combination of the resulting mixed-standard solution, the formation of a precipitate may occur upon addition of the silver standard stock solution. If this happens, add 15 mL of reagent water and apply heat to the volumetric flask until the solution clears. Equilibrate the flask to ambient temperature following dissolution and dilute to volume with reagent water. For such an acid combination, the silver concentration should be limited to 2 mg/L. Silver is stable under these conditions in a water matrix for 30 days if protected from the light. Higher concentrations of silver necessitate the use of additional HCl.

7.11.2 Blanks - Two types of blanks are necessary for the analysis of samples prepared by any method, other than Method 3040: (1) the calibration blank is used in establishing the analytical curve; and (2) the method blank contains all of the exact same reagents, and in the same proportions, as those used for the processing of samples, and

is thus used to identify possible contamination resulting from either the reagents (namely, acids) or equipment (including even filters) used during sample processing.

7.11.2.1 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. 7.11.1). Prepare a sufficient quantity, such that it may be used to flush the system in between standards and samples. The calibration blank will also be used for all initial calibration blank (ICB) and continuing calibration blank (CCB) determinations.

7.11.2.2 Method blank - Prepare by 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-OES determinations in samples. These steps may include, but are not limited to, pre-filtering, digestion, dilution, filtering, and analysis (refer to Sec. 9.7.1).

7.11.3 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 (Sec. 7.11.1); or otherwise, purchase an already-prepared, second-source reference material from a different commercial lot or vendor. The ICV should be prepared so as to contain metal concentrations equal or nearly equivalent to the midpoint concentration level of the calibration curve (see Sec. 10.8 for use).

7.11.4 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 (see Sec. 10.8 for use).

7.12 SIC solutions - The SIC solutions must be used regardless of whether or not interelement corrections are applied. They evaluate both potential spectral interferences and the accuracy of any correction equations.

7.12.1 Individual element SIC solutions - Individual element SIC solutions are used to evaluate possible spectral interferences and to set interelement corrections if necessary. A solution of each element is prepared at the highest concentration in the linear range likely to be observed in samples. The acid strength should be equivalent to that of the calibration standards. See section 9.9.1 for use of the individual element SIC solutions. SIC solutions should be tested to verify that they are not contaminated with elements of interest. The verification of purity can be done by analysis using an alternate technology, such as ICP-MS. For ICP-OES instruments with solid-state detectors, the verification might also be done by examining alternate wavelengths. If the SIC solutions are purchased ready-made, the vendor should provide details of any contaminants. In some cases, it may not be possible to obtain solutions completely free of contaminants, in which case the known, verified concentration can be subtracted from the instrument result before assessing any interferences.

7.12.2 Mixed element SIC solution - The mixed element SIC solution is used as an ongoing daily check of freedom from spectral interferences. The mixed element SIC

solution contains the following elements and is made up in an acid solution equivalent to the calibration standards. See Sec. 9.9.2 for use of the mixed element SIC solution. As for the single element solutions described in 7.12.1 known and documented contaminants are subtracted from the observed values in the mixed element SIC check.

Mixed element SIC solution: Aluminum, 500mg/L; Calcium, 500mg/L; Iron, 200mg/L; Magnesium, 500mg/L

8.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

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 QA 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

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 results plus three times the standard 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.

NOTE: Many of the alkali- and alkaline-earth metals have second-order response curves due to ionization and self-absorption effects. These effects can be minimized by using an easily ionized element in excess in the internal standard or standards themselves. Lithium or cesium are good candidates. Second-order calibration curves may be used for alkali or alkaline earth metals if the instrumentation and software can accommodate them. However, the effective range must be checked and the second-order curve fit should have a correlation coefficient of 0.995 or better. Third-order calibration fits are not acceptable. Second-order response curves should be revalidated and recalculated at least every six months. These curves are much more sensitive to changes in

operating conditions than the first-order curves and should be checked whenever there have been moderate equipment changes.

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 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. All method blanks, LCSs, MS samples, and duplicate samples should be subjected to the same preparatory and instrumentation procedures (Sec. 11.0) as those used on actual samples.

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 lower limit of quantitation (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, 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, 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, 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% recovery of the target element spike values for accuracy, 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. 1.1.4 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. 9.11 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.

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

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:
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, 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 after the last acceptable method blank 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 appropriately similar mediums 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% recovery (see Sec. 9.7.3) of the reported manufacturers' target element values may not be achievable. Refer to Chapters One and Three for additional information.

9.8 Lower Limit of Quantitation 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 $\leq$ 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 that is 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 Spectral interference checks

Two types of SIC checks are used. Individual element SIC checks are performed when the instrument is initially setup, and periodically (at least once every 6 months) thereafter. The mixed element SIC solution is used daily to check that the instrument is free from interference from elements typically observed in high concentration and to check that and interference corrections applied are still valid.

9.9.1 Single element interference checks - At a minimum, single element SIC checks must be performed for the following elements:

Aluminum 500mg/L; Boron 50mg/L, Barium, 50mg/L, Calcium 500mg/L; Copper 50mg/L; Iron 200mg/L; Magnesium 500mg/L; Manganese 50mg/L; Molybdenum 20mg/L; Sodium 1000mg/L; Nickel 20mg/L; Selenium 20mg/L; Silicon 200mg/L; Tin 20mg/L; Vanadium 20mg/L; Zinc 20mg/L

The absolute value of the concentration observed for any unspiked analyte in the single element SIC checks must be less than two times the analytes' LLOQ. The concentration of the SIC checks are suggested, but become the highest concentration allowed in a sample analysis and cannot be higher than the highest established linear range. Samples with concentrations of elements higher than the SIC check must be diluted until the concentration is less than the SIC check solution. Note that reanalysis of a diluted sample is required even if the high concentration element is not required to be

reported for the specific sample, since the function of the SIC check is to evaluate spectral interferences on other elements.

The single element SIC checks are performed when the instrument is setup and periodically (at least once every 6 months) thereafter.

9.9.2 Mixed element interference check - The mixed element SIC solution (see section 7.12.2) is analyzed at least once per day, immediately after the initial calibration. The concentration measured for any target analytes must be less than +/- the LLOQ. If this criterion is not met then sample analysis may not proceed until the problem is corrected, or alternatively the LLOQ may be raised to twice the concentration observed in the SIC solution. The only exceptions are those elements that have been demonstrated to be contaminants in the SIC solutions (see Section 7.12.1). These may be present up to the concentration documented plus the LLOQ.

9.10 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.

9.11 If less than acceptable bias and precision data are generated for the MS(s), the additional QC protocols in sections 9.11.1 and/or 9.11.2 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).

9.11.1 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 should be suspected. The MS 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.

CAUTION: If spectral overlap is suspected, then the use of computerized compensation, an alternate wavelength, or comparison with an alternate method is recommended.

9.11.2 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 MS 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.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Before using this procedure for quantitation, ensure that initial demonstration of performance data is available for viewing. Such data must document:

- The selection criteria for background correction points;
- analytical dynamic ranges, including the applicable equations, and upper limits of ranges;
- IDLs and method LLOQs; and
- The determination and verification of interelement correction equations, or other routines for correcting spectral interferences. These data must be generated using the same instrument, operating conditions, and calibration routine to be used for sample analysis. The data must be kept on file and available for review by the data user or auditor.

10.2 Set up the instrument using the appropriate operating conditions. Follow the instructions provided by the instrument manufacturer unless other conditions provide similar or better results. Specific wavelengths for use in quantitation should be selected from the manufacturer's instructions. Other wavelengths may be substituted if they can provide the needed sensitivity and are corrected for spectral interferences. Because of differences among various makes and models of 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 based on the specific program and end user. Operating conditions for aqueous solutions usually vary from:

- 1100-1500-watts forward power;
- 14-18-mm viewing height;
- 15-19-L/min argon-coolant flow;
- 0.6-1.5-L/min argon-nebulizer flow; and
- 1.0-1.8-mL/min sample-pumping rate; with a 1-min pre-flush time and measurement time near 1 sec/wavelength peak for sequential instruments and 10 sec/sample for simultaneous instruments.

One recommended way in which to achieve repeatable interference correction factors is to adjust the argon-aerosol flow to reproduce the Cu/Mn intensity ratio at the wavelengths 324.754 nm and 257.610 nm.

10.3 Plasma optimization

Optimize the plasma operating conditions prior to use of the instrument. The purpose of plasma optimization is to provide a maximum signal-to-background ratio for some of the least sensitive elements in the analytical array. The use of a mass-flow controller to regulate the nebulizer gas flow or source optimization software greatly facilitates the procedure. This routine

is not needed on a daily basis, but only is necessary when first setting up a new instrument or following a change in operating conditions. The following procedure is recommended; otherwise follow the manufacturer's guidelines.

10.3.1 Ignite the radial plasma and select an appropriate incident RF power. Allow the instrument to become thermally stable before beginning; approximately 30 - 60 minutes of operation. Optimize the ICP per manufacturer's instructions or alternatively by the following procedure: While aspirating a 1000-µg/L solution of yttrium, follow the instrument manufacturer's instructions and adjust the aerosol carrier gas-flow rate through the nebulizer, so that a definitive blue emission region of the plasma extends approximately 5 - 20 mm above the top of the load coil. Record the nebulizer gas-flow rate or pressure setting for future reference. The yttrium solution can also be used for coarse optical alignment of the torch, by observing the overlay of the blue light over the entrance slit to the optical system. If yttrium is an analyte of interest in samples, be aware it may take some time to rinse out 1000 µg/L yttrium solution.

10.3.2 After establishing the nebulizer gas-flow rate, determine the solution-uptake rate of the nebulizer in mL/min, by aspirating a known volume of a calibration blank for a period of at least one minute. Divide the volume (mL) aspirated by the time (min) and record the uptake rate. Set the peristaltic pump to deliver this rate.

10.3.3 Profile the instrument per manufacturer's directions to align it optically, as it will be used during analysis.

10.3.4 Complete the following procedure for vertical optimization or follow manufacturer's directions:

NOTE: This procedure can be used for both vertical and horizontal optimization.

Aspirate a solution containing 10 µg/L of several selected elements. As, Se, Tl, and Pb are the least sensitive of the elements and most in need of optimization. However, other elements may be used, based on the professional judgment of the analyst (V, Cr, Cu, Li and Mn have also been used with success). Collect intensity data at the wavelength peak for each analyte at 1mm intervals from 14 – 18 mm above the load coil. (This region of the plasma is referred to as the "analytical zone".) Repeat this process using the calibration blank. Determine the net signal-to-blank-intensity ratio for each analyte for each viewing height setting. Choose the height for viewing the plasma that provides the best net intensity ratios for the elements analyzed or the highest intensity ratio for the least sensitive element.

For optimization in the axial mode, follow the instrument manufacturer's instructions.

10.3.5 The instrument operating conditions finally selected as being optimum should provide the lowest reliable IDLs.

10.3.6 If the instrument operating conditions, such as incident power or nebulizer gas-flow rate, are changed, or if a new torch injector with a different orifice internal diameter is installed, then the plasma and viewing height should be re-optimized.

10.3.7 After completing the initial optimization of operating conditions, and before analyzing samples, establish and initially verify an interelement spectral interference correction routine to be used during sample analysis. A general description of spectral interferences and the analytical specifications for background correction, in particular, are discussed in Sec. 4.0. Directions for verification of freedom from interference are given in Sections 7.12 and 9.9. The criterion for determining that an interelement spectral interference is present is an apparent positive or negative concentration for the analyte that falls beyond ± the LLOQ from zero. The upper control limit is the analyte LLOQ. Once established, verify the entire routine at least once every six months. Only a portion of the correction routine must be verified more frequently or on a daily basis. Initial and periodic verifications of the routine should be kept on file.

10.3.8 Before daily calibration, and after the instrument warm-up period, the nebulizer gas-flow rate must be reset to the determined optimized flow. If a mass-flow controller is being used, it should be set to the recorded optimized flow rate. In order to maintain valid spectral interelement correction routines, the nebulizer gas-flow rate should be the same (< 2% change) from day to day.

10.4 For operation with organic solvents, the use of the auxiliary argon inlet is recommended, as is the use of solvent-resistant tubing, increased plasma (coolant) argon flow, decreased nebulizer flow, and increased radio frequency (RF) power, in order to obtain a robust plasma, stable operating conditions, and precise measurements.

10.5 At a minimum, the elements required for the project plus any required for interference correction must be calibrated. Recommended wavelengths for the analytes in Sec. 1.1 should be obtained from the instrument manufacturer. Flush the system in between each standard and sample using the rinse blank. The rinse time needs to be sufficient to ensure that analytes present at the linear range are effectively cleaned out prior to analysis of the subsequent sample. Use the average of at least three integrations for both calibration standard and sample analyses.

10.6 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, 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.

10.7 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 are recommended in order to minimize curve fitting errors at the low end of the calibration curve.

10.8 After the calibration is completed it is verified using several checks.

10.8.1 Initial Calibration Verification - The ICV is a standard prepared from a separate 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.

10.8.2 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 the LLOQ is analyzed and should recover within 80-120% of the true value.

10.8.3 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.

10.8.4 Initial Calibration blank - 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.

10.8 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. 7.11.4 and a CCB (Sec. 7.11.2.1). 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 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.

NOTE: During the course of an analytical run, the instrument may be recalibrated to correct for instrument drift. A recalibration must then be followed immediately by a new analysis of a CCV and CCB before any further samples may be analyzed.

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.

11.2 Profile and calibrate the instrument according to the instrument manufacturer's recommended procedures, using the typical mixed-calibration standard solutions described in Sec. 7.11.1. Prepare the calibration curve as detailed in Sec. 10.7. Flush the system between each standard using the calibration blank (Sec. 7.11.2.1), or as the manufacturer recommends. In order to reduce random error, use the average intensity of multiple exposures for both standardization and sample analysis.

11.3 For all analytes and determinations, the laboratory must analyze an ICV (Secs 7.11.3 and 10.8.1) and a CCV (Secs. 7.11.4 and 10.8.5) and CCB (Secs. 7.11.2.1 and 10.8.5) after every ten samples and at the end of the analysis batch run.

11.4 Analyze the samples and record the results. In between each sample or standard, rinse the system using the calibration blank solution (Sec. 7.11.2.1). Use a minimum rinse time of one minute. Each laboratory may establish a reduction in the rinse time following a suitable demonstration.

11.5 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.

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

11.5.2 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 dilution factors to the respective sample values. Report results up to three significant figures.

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:

$$\text{Concentration}_{DW} = \frac{C \times V}{W \times S}$$

where:

$\text{Concentration}_{DW}$ = 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

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.

13.1 In an EPA round-robin study, seven laboratories applied the ICP-OES technique to water matrices spiked with various metal concentrates and acid-digested. Table 3 lists the true values, the mean reported results, and the mean percent relative standard deviations. These data are provided for guidance purposes only.

13.2 Performance data for aqueous solutions and solid samples from a multi-laboratory study are provided in Tables 5 and 6. 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: http://www.acs.org/content/dam/acsorg/about/governance/committees/chemicalsafety/publications/less-is-better.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 Waste Management Manual for Laboratory Personnel* available at: http://www.labsafety.org/FreeDocs/WasteMgmt.pdf.

16.0 REFERENCES

1. C.L. Jones, *et al*., "An Interlaboratory Study of Inductively Coupled Plasma Atomic Emission Spectroscopy Method 6010 and Digestion Method 3050," EPA-600/4-87-032, U.S. Environmental Protection Agency, Las Vegas, NV, 1987.

2. Taylor, J. K., “Quality Assurance of Chemical Measurements”, Lewis Publishers (1987).

3. Federal Advisory Committee on Detection and Quantitation Approaches and Uses in Clean Water Act Programs, Final Report, http://water.epa.gov/scitech/methods/cwa/det/index.cfm (December 28, 2007).

17.0 TABLES, DIAGRAMS, FLOW CHARTS, AND VALIDATION DATA

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

TABLE 1

POTENTIAL INTERFERENCES AND ANALYTE CONCENTRATION EQUIVALENTS (mg/L) ARISING FROM INTERFERENCE AT THE 100-mg/L LEVEL

		Interferent[a,b]									
Analyte	Wavelength[c] (nm)	Al	Ca	Cr	Cu	Fe	Mg	Mn	Ni	Ti	V
Aluminum	308.215	--	--	--	--	--	--	0.21	--	--	1.4
Antimony	206.833	0.47	--	2.9	--	0.08	--	--	--	0.25	0.45
Arsenic	193.696	1.3	--	0.44	--	--	--	--	--	--	1.1
Barium	455.403	--	--	--	--	--	--	--	--	--	--
Beryllium	313.042	--	--	--	--	--	--	--	--	0.04	0.05
Cadmium	226.502	--	--	--	--	0.03	--	--	0.02	--	--
Calcium	317.933	--	--	0.08	--	0.01	0.01	0.04	--	0.03	0.03
Chromium	267.716	--	--	--	--	0.003	--	0.04	--	--	0.04
Cobalt	228.616	--	--	0.03	--	0.005	--	--	0.03	0.15	--
Copper	324.754	--	--	--	--	0.003	--	--	--	0.05	0.02
Iron	259.940	--	--	--	--	--	--	0.12	--	--	--
Lead	220.353	0.17	--	--	--	--	--	--	--	--	--
Magnesium	279.079	--	0.02	0.11	--	0.13	--	0.25	--	0.07	0.12
Manganese	257.610	0.005	--	0.01	--	0.002	0.002	--	--	--	--
Molybdenum	202.030	0.05	--	--	--	0.03	--	--	--	--	--
Nickel	231.604	--	--	--	--	--	--	--	--	--	--
Selenium	196.026	0.23	--	--	--	0.09	--	--	--	--	--
Sodium	588.995	--	--	--	--	--	--	--	--	0.08	--
Thallium	190.864	0.30	--	--	--	--	--	--	--	--	--
Vanadium	292.402	--	--	0.05	--	0.005	--	--	--	0.02	--
Zinc	213.856	--	--	--	0.14	--	--	--	0.29	--	--

NOTE: [a] Dashes indicate that no interference was observed even when interferents were introduced at the following levels:

Al at 1000 mg/L	Cu at 200 mg/L	Mn at 200 mg/L
Ca at 1000 mg/L	Fe at 1000 mg/L	Ti at 200 mg/L
Cr at 200 mg/L	Mg at 1000 mg/L	V at 200 mg/L

[b] The figures shown above as analyte concentration equivalents are not the actual observed concentrations. To obtain those figures, add the listed concentration to the interferent figure.

[c] Interferences will be affected by background and wavelength choice and other interferences may be present.

TABLE 2

MIXED STANDARD SOLUTIONS

Solution	Elements
I	Be, Cd, Mn, Pb, Se and Zn
II	Ba, Co, Cu, Fe, and V
III	As and Mo
IV	Al, Ca, Cr, K, Na, Ni, Li, and Sr
V	Ag[a], Mg, Sb, and Tl
VI	P

[a] See second note in Sec. 7.10.1.

TABLE 3

ICP PRECISION AND BIAS DATA[a]

	Sample No. 1				Sample No. 2				Sample No. 3			
Element	True Conc. (μg/L)	Mean Conc. (μg/L)	RSD[b] (%)	Accuracy[d] (%)	True Conc. (μg/L)	Mean Conc. (μg/L)	RSD[b] (%)	Accuracy[d] (%)	True Conc. (μg/L)	Mean Conc. (μg/L)	RSD[b] (%)	Accuracy[d] (%)
Be	750	733	6.2	98	20	20	9.8	100	180	176	5.2	98
Mn	350	345	2.7	99	15	15	6.7	100	100	99	3.3	99
V	750	749	1.8	100	70	69	2.9	99	170	169	1.1	99
As	200	208	7.5	104	22	19	23	86	60	63	17	105
Cr	150	149	3.8	99	10	10	18	100	50	50	3.3	100
Cu	250	235	5.1	94	11	11	40	100	70	67	7.9	96
Fe	600	594	3.0	99	20	19	15	95	180	178	6.0	99
Al	700	696	5.6	99	60	62	33	103	160	161	13	101
Cd	50	48	12	96	2.5	2.9	16	116	14	13	16	93
Co	700	512	10	73	20	20	4.1	100	120	108	21	90
Ni	250	245	5.8	98	30	28	11	93	60	55	14	92
Pb	250	236	16	94	24	30	32	125	80	80	14	100
Zn	200	201	5.6	100	16	19	45	119	80	82	9.4	102
Se[c]	40	32	21.9	80	6	8.5	42	142	10	8.5	8.3	85

NOTE: [a] Not all elements were analyzed by all laboratories.

[b] RSD = relative standard deviation.

[c] Results for Se are from two laboratories.

[d] Accuracy is expressed as the mean concentration divided by the true concentration times 100.

TABLE 4

EXAMPLE ICP-OES PRECISION AND BIAS FOR AQUEOUS SOLUTIONS

Element	Mean Concentration (mg/L)	n	RSD (%)	Accuracy (%)
Al	14.8	8	6.3	100
Sb	15.1	8	7.7	102
As	14.7	7	6.4	99
Ba	3.66	7	3.1	99
Be	3.78	8	5.8	102
Cd	3.61	8	7.0	97
Ca	15.0	8	7.4	101
Cr	3.75	8	8.2	101
Co	3.52	8	5.9	95
Cu	3.58	8	5.6	97
Fe	14.8	8	5.9	100
Pb	14.4	7	5.9	97
Mg	14.1	8	6.5	96
Mn	3.70	8	4.3	100
Mo	3.70	8	6.9	100
Ni	3.70	7	5.7	100
K	14.1	8	6.6	95
Se	15.3	8	7.5	104
Ag	3.69	6	9.1	100
Na	14.0	8	4.2	95
Tl	15.1	7	8.5	102
V	3.51	8	6.6	95
Zn	3.57	8	8.3	96

NOTE: 1. These performance values are independent of sample preparation because the labs analyzed portions of the same solutions and are provided for illustrative purposes only.
2. n = Number of measurements.3. Accuracy is expressed as a percentage of the nominal value for each analyte in acidified, multi-element solutions.

TABLE 5

EXAMPLE ICP-OES PRECISION AND BIAS FOR SOLID WASTE DIGESTS

	Spiked Coal Fly Ash (NIST-SRM 1633a)				Spiked Electroplating Sludge			
Element	Mean Conc. (mg/L)	n	RSD (%)	Bias (% AA)	Mean Conc. (mg/L)	n	RSD (%)	Bias (% AA)
Al	330	8	16	104	127	8	13	110
Sb	3.4	6	73	96	5.3	7	24	120
As	21	8	83	270	5.2	7	8.6	87
Ba	133	8	8.7	101	1.6	8	20	58
Be	4.0	8	57	460	0.9	7	9.9	110
Cd	0.97	6	5.7	101	2.9	7	9.9	90
Ca	87	6	5.6	208	954	7	7.0	97
Cr	2.1	7	36	106	154	7	7.8	93
Co	1.2	6	21	94	1.0	7	11	85
Cu	1.9	6	9.7	118	156	8	7.8	97
Fe	602	8	8.8	102	603	7	5.6	98
Pb	4.6	7	22	94	25	7	5.6	98
Mg	15	8	15	110	35	8	20	84
Mn	1.8	7	14	104	5.9	7	9.6	95
Mo	891	8	19	105	1.4	7	36	110
Ni	1.6	6	8.1	91	9.5	7	9.6	90
K	46	8	4.2	98	51	8	5.8	82
Se	6.4	5	16	73	8.7	7	13	101
Ag	1.4	3	17	140	0.75	7	19	270
Na	20	8	49	130	1380	8	9.8	95
Tl	6.7	4	22	260	5.0	7	20	180
V	1010	5	7.5	100	1.2	6	11	80
Zn	2.2	6	7.6	93	266	7	2.5	101

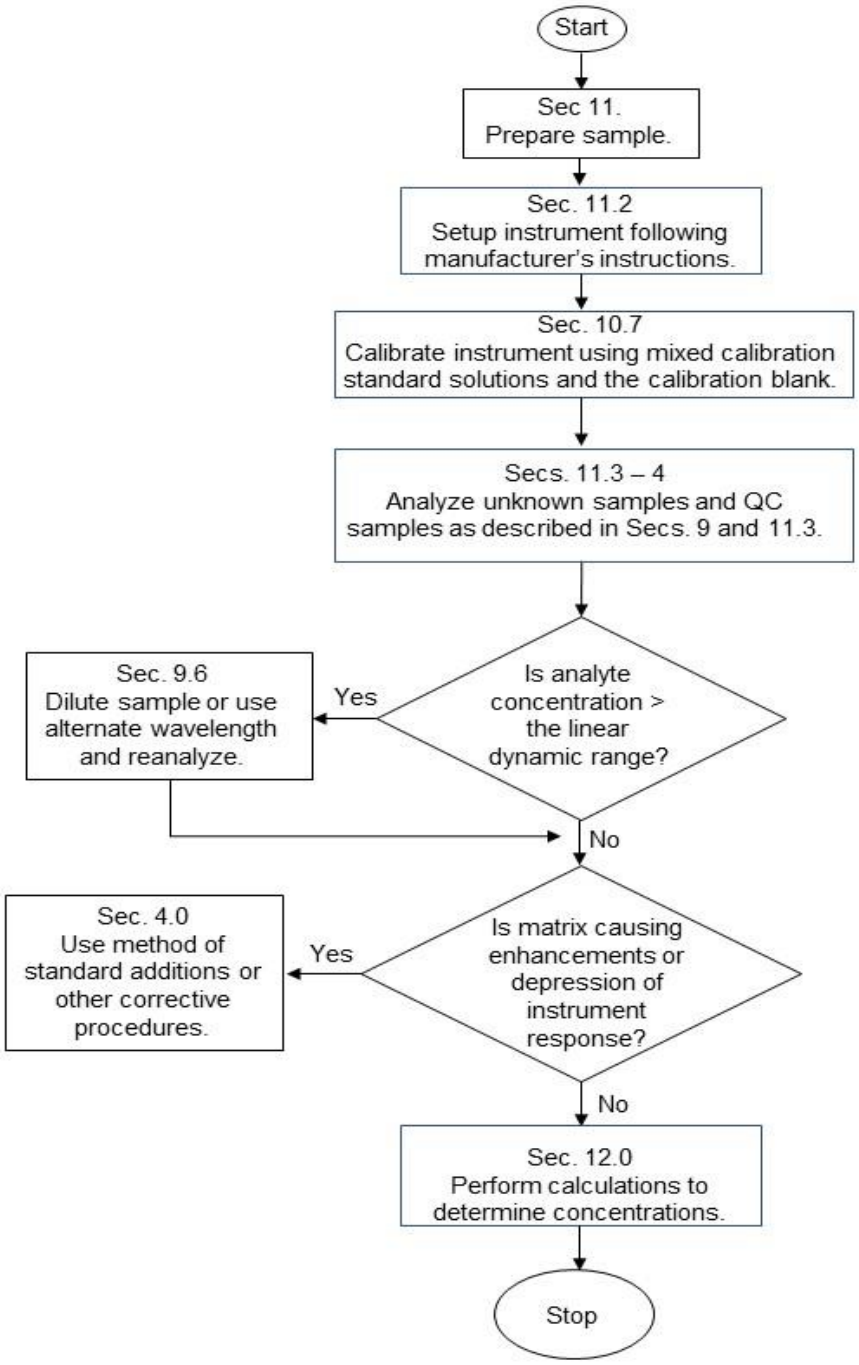
NOTE: 1. These performance values are independent of sample preparation because the labs analyzed portions of the same digests and are provided for illustrative purposes only.

2. n = Number of measurements.

3. Bias for the ICP-OES data is expressed as a percentage of atomic absorption spectroscopy (AA) data for the same digests.

FIGURE 1

INDUCTIVELY COUPLED PLASMA-OPTICAL EMISSION SPECTROMETRY



APPENDIX A

Summary of Revisions to Method 6010D (From Revision 4, July 2013):

1. The revision number was changed to 5 and the footer date updated to July 2018. A table of contents was added.

2. Sec. 9.7.2 was updated to show a reference to Chapter One, Sec 1.1.4.

3. Tables and graphics in this method were updated to be 508 compliant.

5. The ACS document in Sec. 14 was updated.

6. The reference in Sec. 15 was updated.