METHOD 6010C

INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROMETRY

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

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

1.0 SCOPE AND APPLICATION

1.1 Inductively coupled plasma-atomic emission spectrometry (ICP-AES) may be used to determine trace elements in solution. With the exception of groundwater samples, all aqueous and solid matrices need acid digestion prior to analysis. Groundwater samples that were prefiltered and acidified will not need acid digestion. Samples which are not digested need either an internal standard or should be matrix-matched with the standards. If either option is used, instrument software should be programmed to correct for intensity differences of the internal standard between samples and standards. Refer to Chapter Three, "Inorganic Analytes," for a listing of digestion procedures that may be appropriate. The following analytes have been determined by this method:

Element	Symbol	CAS Number	Element	Symbol	CAS Number
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	Strotium	Sr	7440-24-6
Copper	Cu	7440-50-8	Thallium	Tl	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	CAS Number	Element	Symbol	CAS Number
Magnesium	Mg	7439-95-4	Zinc	Zn	7440-66-6
Manganese	Mn	7439-96-5			

CAS Number: Chemical Abstract Service Registry Number.

1.2 Table 1 lists all of the elements for which this method was validated. The sensitivity and the optimum and linear ranges for each element will vary with the wavelength, spectrometer, matrix, and operating conditions. Table 1 lists the recommended analytical wavelengths and estimated instrumental detection limits (IDLs) for the elements in clean aqueous matrices with insignificant background interferences. Other elements and matrices may be analyzed by this method if appropriate performance at the concentrations of interest (see Sec. 9.0) is demonstrated.

1.3 Analysts should clearly understand the data quality objectives prior to analysis and must document and have on file the required initial demonstration performance data described in the following sections prior to using the method for analysis.

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

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

1.5 Use of this method is restricted to use by, or under supervision of, spectroscopists appropriately experienced and trained in the correction of spectral, chemical, and physical interferences described in this method. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis, samples must be 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 (refer to Sec. 1.1).

2.2 This method describes multielemental determinations by ICP-AES using sequential or simultaneous optical systems and axial or radial viewing of the plasma. The instrument measures characteristic emission spectra by optical spectrometry. 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 required 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 occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences identified in Sec. 4.0 should also be recognized and appropriate corrections made; tests for their presence are described in Secs. 9.6 and 9.7. Alternatively, users may choose multivariate calibration methods. In this 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

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

4.2 Spectral interferences are caused by background emission from continuous or recombination phenomena, stray light from the line emission of high concentration elements, overlap of a spectral line from another element, or unresolved overlap of molecular band spectra.

4.2.1 Compensation for background emission and stray light can usually be conducted by subtracting the background emission determined by measurements adjacent to the analyte wavelength peak. Spectral scans of samples or single element solutions in the analyte regions may indicate when alternate wavelengths are 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 on both sides of the wavelength peak or by measured emission on only 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 adequately corrected to reflect the same change in background intensity as 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.

4.2.2 To determine the appropriate location for off-line background correction, the user must scan the area on either side adjacent to the wavelength and record the apparent emission intensity from all other method analytes. This spectral information must be documented and kept on file. The location selected for background correction must be either free of off-line interelement 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 done 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).

4.2.3 Spectral overlaps may be avoided by using an alternate wavelength or can be compensated for by equations that correct for interelement contributions. Instruments that use equations for interelement correction require that the interfering elements be analyzed at the same time as the element of interest. When operative and uncorrected, interferences will produce false positive or positively biased determinations. More extensive information on interferant effects at various wavelengths and resolutions is available in reference wavelength tables and books. Users 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. Some potential spectral interferences observed for the recommended wavelengths are given in Table 2. For multivariate calibration methods using whole spectral regions, spectral interferences are handled by including spectra of the interfering elements in the algorithm. The interferences listed are only those that occur between method analytes. Only interferences of a direct overlap nature are listed. These overlaps were observed with a single instrument having a working resolution of 0.035 nm.

4.2.4 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 2, 100 mg/L of Al will yield a false positive signal for an As level equivalent to approximately 1.3 mg/L. Therefore, 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 user is cautioned that other instruments may exhibit somewhat different levels of interference than those shown in Table 2. These data are provided for guidance purposes only. The interference effects must be evaluated for each individual instrument, since the intensities will vary.

4.2.5 Interelement corrections will vary for the same emission line among instruments because of differences in resolution, as determined by the grating, the 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. Users should continuously note that some samples may contain uncommon elements that could contribute spectral interferences.

4.2.6 The interference 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 is required to determine and document for each wavelength the effect from referenced interferences (Table 2) as well as any other suspected interferences that may be specific to the instrument or matrix. The analyst is encouraged to utilize a computer routine for automatic correction on all analyses.

4.2.7 Users 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 to 220.1 nm. This 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.

4.2.8 If the correction routine is operating properly, the determined apparent analyte(s) concentration from analysis of each interference solution should fall within a specific concentration range around the calibration blank. The concentration range is calculated by multiplying the concentration of the interfering element by the value of the correction factor being tested and dividing by 10. If after the subtraction of the calibration blank the apparent analyte concentration falls outside of this range, in either a positive or negative direction, a change in the correction factor of more than 10% should be suspected. The cause of the change should be determined and corrected and the correction factor updated. The interference check solutions should be analyzed more than once to confirm a change has occurred. Adequate rinse time between solutions and before analysis of the calibration blank will assist in the confirmation.

4.2.9 When interelement corrections are applied, their accuracy should be verified daily, by analyzing spectral interference check solutions. The correction factors or multivariate correction matrices tested on a daily basis must be within the 20% criteria for five consecutive days. All interelement spectral correction factors or multivariate correction matrices must be verified and updated every six months or when an instrumentation change occurs, such as one in the torch, nebulizer, injector, or plasma conditions. Standard solutions should be inspected to ensure that there is no contamination that may be perceived as a spectral interference.

4.2.10 When interelement corrections are not used, verification of absence of interferences is required.

4.2.10.1 One method to verify the absence of interferences is to use a computer software routine for comparing the determinative data to established limits for notifying the analyst when an interfering element is detected in the sample at a concentration that will produce either an apparent false positive concentration (i.e., greater than the analyte instrument detection limit), or a false negative analyte concentration (i.e., less than the lower control limit of the calibration blank defined for a 99% confidence interval).

4.2.10.2 Another way to verify the absence of interferences is to analyze an interference check solution which contains similar concentrations of the major components of the samples (>10 mg/L) on a continuing basis to verify the absence of effects at the wavelengths selected. These data must be kept on file with the sample analysis data. If the check solution confirms an operative interference that is $20% of the analyte concentration, the analyte must be determined using (1) analytical and background correction wavelengths (or spectral regions) free of the interference, (2) by an alternative wavelength, or (3) by another documented test procedure.

4.3 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 high acid concentrations. If physical interferences are present, they must be reduced by diluting the sample, by using a peristaltic pump, by using an internal standard, or by using a high solids nebulizer. Another problem that can occur with high dissolved solids is salt buildup at the tip of the nebulizer, affecting aerosol flow rate and causing instrumental drift. The problem can be controlled by wetting the argon prior to nebulization, by using a tip washer, by using a high solids nebulizer, or by diluting the sample. 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 test described in Sec. 9.9 will help determine if a physical interference is present.

4.4 Chemical interferences include molecular compound formation, ionization effects, and solute vaporization effects. Normally, these effects are not significant with the ICP technique, but if observed, can be minimized by careful selection of operating conditions (incident power, observation position, and so forth), by buffering of the sample, by matrix matching, and by standard addition procedures. Chemical interferences are highly dependent on matrix type and the specific analyte element. The analyst is encouraged to review the information in all of Sec. 4.0 to deal with the majority of interferences likely to be encountered when using this method.

4.4.1 The method of standard additions (MSA) can be useful when certain interferences are encountered. Refer to Method 7000 for a more detailed discussion of the MSA.

4.4.2 An alternative to using the method of standard additions is to use the internal standard technique, which involves adding one or more elements that are both not found in the samples and verified to not cause an interelement spectral interference to the samples, standards, and blanks. Yttrium or scandium are often used. The concentration should be sufficient for optimum precision, but not so high as to alter the salt concentration of the matrix. The element intensity is used by the instrument as an internal standard to ratio the analyte intensity signals for both calibration and quantitation. This technique is very useful in overcoming matrix interferences, especially in high solids matrices.

4.5 Memory interferences result when analytes in a previous sample contribute to the signals measured in a new sample. Memory effects can result from sample deposition on the uptake tubing to the nebulizer and from the build up 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 recognized within an analytical run and suitable rinse times should be used to reduce them. The rinse times necessary for a particular element must be estimated prior to analysis. This may be achieved by aspirating a standard containing elements at a concentration ten times the usual amount or at the top of the linear dynamic range. The aspiration time for this sample should be the same as a normal sample analysis period, followed by analysis of the rinse blank at designated intervals. Note the length of time necessary for reducing analyte signals to "equal to" or "less than" the lower limit of quantitation. Until the required rinse time is established, the rinse period should be at least 60 sec between samples and standards. If a memory interference is suspected, the sample must be reanalyzed after a rinse period of sufficient length. Alternate rinse times may be established by the analyst based upon the project-specific DQOs.

4.6 Users 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 interference check solution with the elements of interest at 0.5 to 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 a measurable analyte, overcorrection could go undetected if a negative value is reported as zero.

4.7 The dashes in Table 2 indicate that no measurable interferences were observed even at higher interferant concentrations. Generally, interferences were discernible if they produced peaks, or background shifts, corresponding to 2 to 5% of the peaks generated by the analyte concentrations.

4.8 The calibration blank (Sec. 7.5.1) may restrict the sensitivity of the quantitation limit or degrade the precision and accuracy of the analysis. Consult Chapter Three for recommended precautions and procedures necessary in reducing the magnitude and variability of the calibration blank.

5.0 SAFETY

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

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

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

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

6.0 EQUIPMENT AND SUPPLIES

6.1 Inductively coupled argon plasma emission spectrometer

6.1.1 Computer-controlled emission spectrometer with background correction.

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 precision and accuracy.

6.3 Volumetric pipets of suitable precision and accuracy.

7.0 REAGENTS AND STANDARDS

7.1 Reagent- or trace metals-grade chemicals must be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. If the purity of a reagent is in question, analyze for contamination. If the concentration of the contamination is less than the lower limit of quantitation, then the reagent is acceptable.

7.1.1 Hydrochloric acid (conc), HCl.

7.1.2 Hydrochloric acid HCl (1:1) -- Add 500 mL concentrated HCl to 400 mL water and dilute to 1 L in an appropriately- sized beaker.

7.1.3 Nitric acid (conc), HNO_3.

7.1.4 Nitric acid, HNO_3 (1:1) -- Add 500 mL concentrated HNO_3 to 400 mL water and dilute to 1 L in an appropriately-sized beaker.

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

7.3 Standard stock solutions may be purchased or prepared from ultra-high purity grade chemicals or metals (99.99% pure or greater). With several exceptions specifically noted, all salts must be dried for 1 hr at 105 EC.

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

Typical stock solution preparation procedures follow. Concentrations are calculated based upon the weight of pure metal added, or with the use of the element fraction and the weight of the metal salt added.

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

NOTE: The weight of the analyte is expressed to four significant figures for consistency with the weights below because rounding to two decimal places can contribute up to 4% error for some of the compounds.

For metals:

$$\text{Concentration (ppm)} = \frac{\text{weight (mg)}}{\text{volume (L)}}$$

For metal salts:

$$\text{Concentration (ppm)} = \frac{\text{weight (mg) x mole fraction}}{\text{volume (L)}}$$

7.3.1 Aluminum solution, stock, 1 mL = 1000 µg of Al

Dissolve 1.000 g of aluminum metal, accurately weighed to at least four significant figures, in an acid mixture of 4.0 mL of HCl (1:1) and 1.0 mL of concentrated $HN0_3$ in a beaker. Warm beaker slowly to dissolve the metal. When dissolution is complete, transfer solution quantitatively to a 1000-mL volumetric flask, add an additional 10.0 mL of HCl (1:1) and dilute to volume with reagent water.

7.3.2 Antimony solution, stock, 1 mL = 1000 µg of Sb

Dissolve 2.6673 g of $K(SbO)C_4H_4O_6$ (element fraction Sb = 0.3749), accurately weighed to at least four significant figures, in reagent water, add 10 mL of HCl (1:1), and dilute to volume in a 1000-mL volumetric flask with reagent water.

7.3.3 Arsenic solution, stock, 1 mL = 1000 µg of As

Dissolve 1.3203 g of As_2O_3 (element fraction As = 0.7574), accurately weighed to at least four significant figures, in 100 mL of reagent water containing 0.4 g of NaOH. Acidify the solution with 2 mL of concentrated HNO_3 and dilute to volume in a 1000-mL volumetric flask with reagent water.

7.3.4 Barium solution, stock, 1 mL = 1000 µg of Ba

Dissolve 1.5163 g of $BaCl_2$ (element fraction Ba = 0.6595), dried at 250 °C for 2 hr, accurately weighed to at least four significant figures, in 10 mL of reagent water with 1 mL of HCl (1:1). Add 10.0 mL of HCl (1:1) and dilute to volume in a 1000-mL volumetric flask with reagent water.

7.3.5 Beryllium solution, stock, 1 mL = 1000 µg of Be

<u>Do not dry</u>. Dissolve 19.6463 g of $BeSO_4 \cdot 4H_2O$ (element fraction Be = 0.0509), accurately weighed to at least four significant figures, in reagent water, add 10.0 mL of concentrated HNO_3, and dilute to volume in a 1000-mL volumetric flask with reagent water.

7.3.6 Boron solution, stock, 1 mL = 1000 µg of B

<u>Do not dry</u>. Dissolve 5.716 g of anhydrous H_3BO_3 (B fraction = 0.1749), accurately weighed to at least four significant figures, in reagent water and dilute in a 1-L

volumetric flask with reagent water. Transfer immediately after mixing in a clean polytetrafluoroethylene (PTFE) bottle to minimize any leaching of boron from the glass container. The use of a non-glass volumetric flask is recommended to avoid boron contamination from glassware.

7.3.7 Cadmium solution, stock, 1 mL = 1000 µg of Cd

Dissolve 1.1423 g of CdO (element fraction Cd = 0.8754), accurately weighed to at least four significant figures, in a minimum amount of (1:1) HNO_3. Heat to increase the rate of dissolution. Add 10.0 mL of concentrated HNO_3 and dilute to volume in a 1000-mL volumetric flask with reagent water.

7.3.8 Calcium solution, stock, 1 mL = 1000 µg of Ca

Suspend 2.4969 g of $CaCO_3$ (element Ca fraction = 0.4005), dried at 180 EC for 1 hr before weighing, accurately weighed to at least four significant figures, in reagent water and dissolve cautiously with a minimum amount of (1:1) HNO_3. Add 10.0 mL of concentrated HNO_3 and dilute to volume in a 1000-mL volumetric flask with reagent water.

7.3.9 Chromium solution, stock, 1 mL = 1000 µg of Cr

Dissolve 1.9231 g of CrO_3 (element fraction Cr = 0.5200), accurately weighed to at least four significant figures, in reagent water. When dissolution is complete, acidify with 10 mL of concentrated HNO_3 and dilute to volume in a 1000-mL volumetric flask with reagent water.

7.3.10 Cobalt solution, stock, 1 mL = 1000 µg of Co

Dissolve 1.000 g of cobalt metal, accurately weighed to at least four significant figures, in a minimum amount of (1:1) HNO_3. Add 10.0 mL of HCl (1:1) and dilute to volume in a 1000-mL volumetric flask with reagent water.

7.3.11 Copper solution, stock, 1 mL = 1000 µg of Cu

Dissolve 1.2564 g of CuO (element fraction Cu = 0.7989), accurately weighed to at least four significant figures, in a minimum amount of (1:1) HNO_3. Add 10.0 mL of concentrated HNO_3 and dilute to volume in a 1000-mL volumetric flask with reagent water.

7.3.12 Iron solution, stock, 1 mL = 1000 µg of Fe

Dissolve 1.4298 g of Fe_2O_3 (element fraction Fe = 0.6994), accurately weighed to at least four significant figures, in a warm mixture of 20 mL HCl (1:1) and 2 mL of concentrated HNO_3. Cool, add an additional 5.0 mL of concentrated HNO_3, and dilute to volume in a 1000-mL volumetric flask with reagent water.

7.3.13 Lead solution, stock, 1 mL = 1000 µg of Pb

Dissolve 1.5985 g of $Pb(NO_3)_2$ (element fraction Pb = 0.6256), accurately weighed to at least four significant figures, in a minimum amount of (1:1) HNO_3. Add 10 mL (1:1) HNO_3 and dilute to volume in a 1000-mL volumetric flask with reagent water.

7.3.14 Lithium solution, stock, 1 mL = 1000 µg of Li

Dissolve 5.3248 g of lithium carbonate (element fraction Li = 0.1878), accurately weighed to at least four significant figures, in a minimum amount of HCl (1:1) and dilute to volume in a 1000-mL volumetric flask with reagent water.

7.3.15 Magnesium solution, stock, 1 mL = 1000 µg of Mg

Dissolve 1.6584 g of MgO (element fraction Mg = 0.6030), accurately weighed to at least four significant figures, in a minimum amount of (1:1) HNO_3. Add 10.0 mL of (1:1) concentrated HNO_3 and dilute to volume in a 1000-mL volumetric flask with reagent water.

7.3.16 Manganese solution, stock, 1 mL = 1000 µg of Mn

Dissolve 1.00 g of manganese metal, accurately weighed to at least four significant figures, in acid mixture (10 mL of concentrated HCl and 1 mL of concentrated HNO_3) and dilute to volume in a 1000-mL volumetric flask with reagent water.

7.3.17 Mercury solution, stock, 1 mL = 1000 µg of Hg

WARNING: Do not dry, **mercury is a highly toxic element**.

Dissolve 1.354 g of $HgCl_2$ (Hg fraction = 0.7388) in reagent water. Add 50.0 mL of concentrated HNO_3 and dilute to volume in 1000-mL volumetric flask with reagent water.

7.3.18 Molybdenum solution, stock, 1 mL = 1000 µg of Mo

Dissolve 1.7325 g of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (element fraction Mo = 0.5772), accurately weighed to at least four significant figures, in reagent water and dilute to volume in a 1000-mL volumetric flask with reagent water.

7.3.19 Nickel solution, stock, 1 mL = 1000 µg of Ni

Dissolve 1.000 g of nickel metal, accurately weighed to at least four significant figures, in 10.0 mL of hot concentrated HNO_3, cool, and dilute to volume in a 1000-mL volumetric flask with reagent water.

7.3.20 Phosphate solution, stock, 1 mL = 1000 µg of P

Dissolve 4.3937 g of anhydrous KH_2PO_4 (element fraction P = 0.2276), accurately weighed to at least four significant figures, in water. Dilute to volume in a 1000-mL volumetric flask with reagent water.

7.3.21 Potassium solution, stock, 1 mL = 1000 µg of K

Dissolve 1.9069 g of KCl (element fraction K = 0.5244) dried at 110 EC, accurately weighed to at least four significant figures, in reagent water, and dilute to volume in a 1000-mL volumetric flask with reagent water.

7.3.22 Selenium solution, stock, 1 mL = 1000 µg of Se

Do not dry. Dissolve 1.6332 g of H_2SeO_3 (element fraction Se = 0.6123), accurately weighed to at least four significant figures, in reagent water and dilute to volume in a 1000-mL volumetric flask with reagent water.

7.3.23 Silica solution, stock, 1 mL = 1000 µg SiO_2

Do not dry. Dissolve 2.964 g of NH_4SiF_6, accurately weighed to at least four significant figures, in 200 mL (1:20) HCl with heating at 85 EC to dissolve the solid. Let solution cool and dilute to volume in a 1000-mL volumetric flask with reagent water. Store in a PTFE container and protect from light.

7.3.24 Silver solution, stock, 1 mL = 1000 µg of Ag

Dissolve 1.5748 g of $AgNO_3$ (element fraction Ag = 0.6350), accurately weighed to at least four significant figures, in water and 10 mL of concentrated HNO_3. Dilute to volume in a 1000-mL volumetric flask with reagent water.

7.3.25 Sodium solution, stock, 1 mL = 1000 µg of Na

Dissolve 2.5419 g of NaCl (element fraction Na = 0.3934), accurately weighed to at least four significant figures, in reagent water. Add 10.0 mL of concentrated HNO_3 and dilute to volume in a 1000-mL volumetric flask with reagent water.

7.3.26 Strontium solution, stock, 1 mL = 1000 µg of Sr

Dissolve 2.4154 g of strontium nitrate ($Sr(NO_3)_2$) (element fraction Sr = 0.4140), accurately weighed to at least four significant figures, in a 1000-mL flask containing 10 mL of concentrated HCl and 700 mL of reagent water. Dilute to volume with reagent water.

7.3.27 Thallium solution, stock, 1 mL = 1000 µg of Tl

Dissolve 1.3034 g of $TlNO_3$ (element fraction Tl = 0.7672), accurately weighed to at least four significant figures, in reagent water. Add 10.0 mL of concentrated HNO_3 and dilute to volume in a 1000-mL volumetric flask with reagent water.

7.3.28 Tin solution, stock, 1 mL = 1000 µg of Sn

Dissolve 1.000 g of Sn shot, accurately weighed to at least 4 significant figures, in 200 mL of HCl (1:1) with heating to dissolve the metal. Let solution cool and dilute with HCl (1:1) in a 1000-mL volumetric flask.

7.3.29 Vanadium solution, stock, 1 mL = 1000 µg of V

Dissolve 2.2957 g of NH_4VO_3 (element fraction V = 0.4356), accurately weighed to at least four significant figures, in a minimum amount of concentrated HNO_3. Heat to dissolve the metal. Add 10.0 mL of concentrated HNO_3 and dilute to volume in a 1000-mL volumetric flask with reagent water.

7.3.30 Zinc solution, stock, 1 mL = 1000 µg of Zn

Dissolve 1.2447 g of ZnO (element fraction Zn = 0.8034), accurately weighed to at least four significant figures, in a minimum amount of dilute HNO_3. Add 10.0 mL of concentrated HNO_3 and dilute to volume in a 1000-mL volumetric flask with reagent water.

7.3.31 Yttrium solution, stock, 1 mL = 1000 µg of Y

Dissolve 4.3081 g of $Y(NO_3)_3C6H_20$ (element fraction Y = 0.2321), accurately weighed to at least four significant figures, in a minimum amount of dilute HNO_3. Add 10.0 mL of concentrated HNO_3 and dilute to volume in a 1000-mL volumetric flask with reagent water.

7.4 Mixed calibration standard solutions

Prepare mixed calibration standard solutions (see Table 3) by combining appropriate volumes of the stock solutions above in volumetric flasks. Add the appropriate types and volumes of acids so that the standards are matrix-matched with the sample digestates. Prior to preparing the mixed standards, each stock solution should be analyzed separately to determine possible spectral interference or the presence of impurities. Care should be taken when preparing the mixed standards to ensure that the elements are compatible and stable together. Transfer the mixed standard solutions to FEP fluorocarbon or previously unused polyethylene or polypropylene bottles for storage. For all intermediate and working standards, especially low level standards (i.e., <1 ppm), stability must be demonstrated prior to use. Freshly-mixed standards should be prepared, as needed, with the realization that concentration can change with age. (Refer to Sec. 10.3.1 for guidance on determining the viability of standards.) Some typical calibration standard combinations are listed in Table 3.

NOTE: If the addition of silver to the recommended acid combination initially results in a precipitate, then add 15 mL of water and warm the flask until the solution clears. Cool and dilute to 100 mL with water. For this 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 require additional HCl.

7.5 Blanks

Two types of blanks are required for the analysis of samples prepared by any method other than Method 3040. The calibration blank is used in establishing the analytical curve and the method blank is used to identify possible contamination resulting from either the reagents (acids) or the equipment used during sample processing including filtration.

7.5.1 The calibration blank is prepared by acidifying reagent water to the same concentrations of the acids found in the standards and samples. Prepare a sufficient quantity to flush the system between standards and samples. The calibration blank will also be used for all initial (ICB) and continuing calibration blank (CCB) determinations.

7.5.2 The method blank must contain all of the reagents in the same volumes as used in the processing of the samples. The method blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis (refer to Sec. 9.5).

7.6 The initial calibration verification (ICV) standard is prepared by the analyst (or a purchased second source reference material) by combining compatible elements from a standard source different from that of the calibration standard, and at concentration near the midpoint of the calibration curve (see Sec. 10.3.3 for use). This standard may also be purchased.

7.7 The continuing calibration verification (CCV) standard should be prepared in the same acid matrix using the same standards used for calibration, at a concentration near the mid-point of the calibration curve (see Sec. 10.3.4 for use).

7.8 The interference check solution is prepared to contain known concentrations of interfering elements that will provide an adequate test of the correction factors. Spike the sample with the elements of interest, particularly those with known interferences at 0.5 to 1 mg/L. In the absence of measurable analyte, overcorrection could go undetected because a negative value could be reported as zero. If the particular instrument will display overcorrection as a negative number, this spiking procedure will not be necessary.

8.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

See the introductory material to Chapter Three, "Inorganic Analytes."

9.0 QUALITY CONTROL

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

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

9.3 Instrument detection limits (IDLs) are 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. 10.0.

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

9.4 Initial demonstration of proficiency

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

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

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

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

9.7 Laboratory control sample (LCS)

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

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

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

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

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

Refer to Chapter One for definitions of bias and precision, and for the proper data reduction protocols. MS/MSD samples should be spiked at the same level, and with the same spiking material, as the corresponding laboratory control sample that is at the project-specific action level or, when lacking project-specific action levels, at approximately mid-point of the linear dynamic range. Acceptance criteria should either be defined in the project-specifc planning documents or set at a laboratory-derived limit developed through the use of historical analyses per matrix type analyzed. In the absence of project-specific or historical data generated criteria, these limits should be set at ± 25% of the spiked value for accuracy and 20 relative percent difference (RPD) for precision. Acceptance limits derived from historical data should be no wider that ± 25% for accuracy and 20% for precision. Refer to Chapter One for additional guidance. If the bias and precision indicators are outside the laboratory control limits, if the percent recovery is less than 75% or greater than 125%, or if the relative percent difference is greater than 20%, then the interference test discussed in Sec. 9.9 should be conducted.

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

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

where:

RPD = relative percent difference.
D_1 = first sample value.
D_2 = second sample value (spiked or unspiked duplicate).

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

9.9 If less than acceptable accuracy and precision data are generated, additional quality control tests (Secs. 9.9.1 and 9.9.2) are recommended prior to reporting concentration data for the elements in this method. At a minimum, these tests should be performed with each batch of samples prepared/analyzed with corresponding unacceptable data quality results. These tests will then serve to ensure that neither positive nor negative interferences are affecting the measurement of any of the elements or distorting the accuracy of the reported values. If matrix effects are confirmed, the laboratory should consult with the data user when feasible for possible corrective actions which may include the use of alternative or modified test procedures so that the analysis is not impacted by the same interference.

9.9.1 Post digestion spike addition

If the MS/MSD recoveries are unacceptable, the same sample from which the MS/MSD aliquots were prepared should also be spiked with a post digestion spike. Otherwise, another sample from the same preparation should be used as an alternative. An analyte spike is added to a portion of a prepared sample, or its dilution, and should be recovered to within 80% to 120% of the known value. The spike addition should produce a minimum level of 10 times and a maximum of 100 times the lower limit of quantitation. If this spike fails, then the dilution test (Sec. 9.9.2) should be run on this sample. If both the MS/MSD and the post digestion spike fail, then matrix effects are confirmed.

9.9.2 Dilution test

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

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

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

10.0 CALIBRATION AND STANDARDIZATION

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

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

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

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

10.1.3.1 Lower limit of quantitation check sample

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

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

10.1.4 Specific recommended wavelengths are listed in Table 1. Other wavelengths may be substituted if they can provide the needed sensitivity and are corrected for spectral interference. Because of differences among various makes and models of spectrometers, specific instrument operating conditions are not provided. The instrument and operating conditions utilized for determination must be capable of providing data of acceptable quality for the specific project and data user. The analyst should follow the instructions provided by the instrument manufacturer unless other conditions provide similar or better performance for a given task.

For radial viewed plasma, operating conditions for aqueous solutions usually vary from:

- 1100 to 1200 watts forward power,
- 14 to 18 mm viewing height,
- 15 to 19 L/min argon coolant flow,
- 0.6 to 1.5 L/min argon nebulizer flow,
- 1 to 1.8 mL/min sample pumping rate with a 1 minute preflush time and measurement time near 1 sec per wavelength peak for sequential instruments and a rinse time of 10 sec per replicate with a 1 sec per replicate read time for simultaneous instruments.

For an axial viewed plasma, the conditions will usually vary from:

- 1100 to 1500 watts forward power,
- 15 to 19 L/min argon coolant flow,
- 0.6 to 1.5 L/min argon nebulizer flow,
- 1 to 1.8 mL/min sample pumping rate with a 1 minute preflush time and measurement time near 1 sec per wavelength peak for sequential instruments and a rinse time of 10 sec per replicate with a 1 sec per replicate read time for simultaneous instruments.

One recommended way to achieve repeatable interference correction factors is to adjust the argon aerosol flow to reproduce the Cu/Mn intensity ratio at 324.754 nm and 257.610 nm respectively. This can be performed before daily calibration and after the instrument warm-up period.

10.1.5 Plasma optimization

The plasma operating conditions need to be optimized 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 required on a daily basis, it is only required when first setting up a new instrument, or following a change in operating conditions. The following procedure is recommended, or follow the manufacturer’s recommendations.

10.1.5.1 Ignite the radial plasma and select an appropriate incident radio frequency (RF) power. Allow the instrument to become thermally stable before beginning, about 30 to 60 minutes of operation. 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 a definitive blue emission region of the plasma extends approximately from 5 to 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.

10.1.5.2 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 three minutes. Divide the volume aspirated by the time in minutes and record the uptake rate. Set the peristaltic pump to deliver that rate in a steady even flow.

10.1.5.3 Profile the instrument to align it optically as it will be used during analysis. The following procedure is written for vertical optimization in the radial mode, but it also can be used for 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 judgement of the analyst or project-specific protocols. (V, Cr, Cu, Li and Mn also have been used with success.) Collect intensity data at the wavelength peak for each analyte at 1 mm intervals from 14 to 18 mm above the load coil. (This region of the plasma is referred to as the analytical zone.) Repeat the 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.

10.1.5.4 The instrument operating conditions finally selected as being optimum should provide the most appropriate instrument responses that correlate to the desired target analyte sensitivity while meeting the minimum quality control criteria noted in this method or as specified in the project-specific planning documents.

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

10.1.5.6 After completing the initial optimization of operating conditions, and before analyzing samples, the laboratory should establish and initially verify an interelement spectral interference correction routine to be used during sample analysis with interference check standards that closely match the anticipated properties of the expected sample matrices, i.e., for saltwater type matrices the interference check standard should contain components that match the salinities of the proposed sample matrix. A general description of spectral interferences and the analytical requirements for background correction, in particular, are discussed in Sec. 4.2.

10.1.5.7 Before daily calibration, and after the instrument warmup period, the nebulizer gas flow rate should 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.

10.2 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 RF power, to obtain stable operation and precise measurements.

10.3 All analyses require that a calibration curve be prepared to cover the appropriate concentration range based on the intended application and prior to establishing the linear dynamic range. Usually, this means the preparation of a calibration blank and mixed calibration standard solutions (Sec. 7.4), the highest of which would not exceed the anticipated linear dynamic range of the instrument. Check the instrument calibration by analyzing appropriate QC samples as follows.

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

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

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

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

10.3.2 For the initial and daily instrument operation, calibrate the system according to the instrument manufacturer's guidelines using the mixed calibration standards as noted in Sec. 7.4. The calibration curve should be prepared daily with a minimum of a calibration blank and a single standard at the appropriate concentration to effectively outline the desired quantitation range. The resulting curve should then be verified with mid-level and low-level initial calibration verification standards as outlined in Sec. 10.3.3.

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

NOTE: Regardless of whether the instrument is calibrated using only a minimum number of standards or with a multi-point curve, the upper limit of the quantitation range may exceed the highest concentration calibration point and can be defined as the "linear dynamic" range, while the lower limit can be identified as the "lower limit of quantitation limit" (LLQL) and will be either the concentration of the lowest calibration standard (for multi-point curves) or the concentration of the low level ICV/CCV check standard. Results reported outside these limits would not be recommended unless they are qualified as estimated. See Sec. 10.4 for recommendations on how to determine the linear dynamic range. The guidance in this section and Sec. 10.3.3 provide options for defining the lower limit of quantitation.

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

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

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

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

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

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

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

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

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

11.0 PROCEDURE

11.1 Preliminary treatment of most matrices is necessary because of the complexity and variability of sample matrices. Groundwater and other aqueous samples designated for a dissolved metal determination which have been prefiltered and acidified will not need acid digestion. However, all associated QC samples (i.e., method blank, LCS and MS/MSD) must undergo the same filtration and acidification procedures. Samples which are not digested must either use an internal standard or be matrix-matched with the standards. 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. 7.4. Flush the system with the calibration blank (Sec. 7.5.1) between each standard or as the manufacturer recommends. (Use the average intensity of multiple exposures for both standardization and sample analysis to reduce random error.) The calibration curve should be prepared as detailed in Sec. 10.3.2.

11.3 Regardless of whether the initial calibration is performed using a single high standard and the calibration blank or the multi-point option, the laboratory should analyze an LLCCV (Sec. 10.3.4). For all analytes and determinations, the laboratory must analyze an ICV and LLICV (Sec. 10.3.3) immediately following daily calibration. It is recommended that a CCV LLCCV, and CCB (Sec. 10.3.4) be analyzed after every ten samples and at the end of the analysis batch.

11.4 Rinse the system with the calibration blank solution (Sec. 7.5.1) before the analysis of each sample. The rinse time will be one minute. Each laboratory may establish a reduction in this rinse time through a suitable demonstration. Analyze the samples and record the results.

12.0 DATA ANALYSIS AND CALCULATIONS

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

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

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

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

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

Where,

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

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

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

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

13.0 METHOD PERFORMANCE

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

13.2 In an EPA round-robin study, seven laboratories applied the ICP technique to acid-digested water matrices that had been spiked with various metal concentrates. Table 4 lists the true values, the mean reported values, and the mean percent relative standard deviations. These data are provided for guidance purposes only.

13.3 Performance data for aqueous solutions and solid samples from a multilaboratory 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 operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions consult *Less is Better: Laboratory Chemical Management for Waste*

Reduction available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St. NW, Washington, D.C. 20036, http://www.acs.org.

15.0 WASTE MANAGEMENT

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

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.

17.0 TABLES, DIAGRAMS, FLOW CHARTS, AND VALIDATION DATA

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

TABLE 1

RECOMMENDED WAVELENGTHS AND ESTIMATED INSTRUMENTAL DETECTION LIMITS

Element	Wavelength[a] (nm)	Estimated IDL[b] (µg/L)
Aluminum	308.215	30
Antimony	206.833	21
Arsenic	193.696	35
Barium	455.403	0.87
Beryllium	313.042	0.18
Boron	249.678 x2	3.8
Cadmium	226.502	2.3
Calcium	317.933	6.7
Chromium	267.716	4.7
Cobalt	228.616	4.7
Copper	324.754	3.6
Iron	259.940	4.1
Lead	220.353	28
Lithium	670.784	2.8
Magnesium	279.079	20
Manganese	257.610	0.93
Mercury	194.227 x2	17
Molybdenum	202.030	5.3
Nickel	231.604 x2	10
Phosphorus	213.618	51
Potassium	766.491	See note c
Selenium	196.026	50
Silica (SiO_2)	251.611	17
Silver	328.068	4.7
Sodium	588.995	19
Strontium	407.771	0.28
Thallium	190.864	27
Tin	189.980 x2	17
Titanium	334.941	5.0
Vanadium	292.402	5.0
Zinc	213.856 x2	1.2

TABLE 1
(continued)

[a] The wavelengths listed (where x2 indicates second order) are recommended because of their sensitivity. Other wavelengths may be substituted (e.g., in the case of an interference) if they provide the needed sensitivity and are treated with the same corrective techniques for spectral interference.

[b] The estimated instrumental detection limits shown are provided for illustrative purposes only. Each laboratory must determine IDLs and MDLs, as necessary, for their specific application of the method. These IDLs represent radial plasma data and axial plasma IDLs may be lower.

[c] Highly dependent on operating conditions and plasma position.

TABLE 2

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

Analyte	Wavelenth (nm)	Interferant[a,b]									
		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	--	--

[a] Dashes indicate that no interference was observed even when interferents were introduced at the following levels:
Al at 1000 mg/L
Ca at 1000 mg/L
Cr at 200 mg/L
Cu at 200 mg/L
Fe at 1000 mg/L
Mg at 1000 mg/L
Mn at 200 mg/L
Ti at 200 mg/L
V at 200 mg/L

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

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

TABLE 3

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 the note in Sec. 7.4.

TABLE 4

EXAMPLE ICP PRECISION AND ACCURACY DATA[a]

Element	Sample No. 1				Sample No. 2				Sample No. 3			
	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

These data are provided for guidance purposes only.

[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 5

EXAMPLE ICP-AES PRECISION AND ACCURACY FOR AQUEOUS SOLUTIONS

Element	Mean Conc. (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

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

TABLE 6

EXAMPLE ICP-AES 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

These performance values are independent of sample preparation because the labs analyzed portions of the same digests and are provided for illustrative purposes only.
n = Number of measurements.
Bias for the ICP-AES data is expressed as a percentage of atomic absorption spectroscopy (AA) data for the same digests.
These data are provided for guidance purposes only.

METHOD 6010C

INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROMETRY