

METHOD 6020A

INDUCTIVELY COUPLED PLASMA - MASS SPECTROMETRY

1.0 SCOPE AND APPLICATION

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

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

<u>Element</u>	<u>CASRN^a</u>
Aluminum (Al)	7429-90-5
Antimony (Sb)	7440-36-0
Arsenic (As)	7440-38-2
Barium (Ba)	7440-39-3
Beryllium (Be)	7440-41-7
Cadmium (Cd)	7440-43-9
Calcium (Ca)	7440-70-2
Chromium (Cr)	7440-47-3
Cobalt (Co)	7440-48-4
Copper (Cu)	7440-50-8
Iron (Fe)	7439-89-6
Lead (Pb)	7439-92-1
Magnesium (Mg)	7439-95-4
Manganese (Mn)	7439-96-5
Mercury (Hg)	7439-97-6
Nickel (Ni)	7440-02-0
Potassium (K)	7440-09-7
Selenium (Se)	7782-49-2
Silver (Ag)	7440-22-4
Sodium (Na)	7440-23-5
Thallium (Tl)	7440-28-0
Vanadium (V)	7440-62-2
Zinc (Zn)	7440-66-6

^aChemical Abstract Service Registry Number

Acceptability of the method for an element was based upon the multi-laboratory performance compared with that of either furnace atomic absorption spectrophotometry or inductively coupled

plasma-atomic emission spectrometry. It should be noted that one multi-laboratory study was conducted in 1988 and advances in ICP-MS instrumentation and software have been made since that time and additional studies have been added with validation and improvements in performance of the method. Performance, in general, exceeds the multi-laboratory performance data for the listed elements. It is expected that current performance will exceed the multi-laboratory performance data for the listed elements (and others) that are provided in Section 13.0. Instrument detection limits, sensitivities, and linear ranges will vary with the matrices, instrumentation, and operating conditions. In relatively simple matrices, detection limits will generally be below 0.1 µg/L. Less sensitive elements (like Se and As) and desensitized major elements may be 1.0 µg/L or higher.

1.3 If Method 6020 is used to determine any analyte not listed in Section 1.2, it is the responsibility of the analyst to demonstrate the accuracy and precision of the method in the waste to be analyzed. The analyst is always required to monitor potential sources of interferences and take appropriate action to ensure data of known quality (see Section 9.4). Other elements and matrices may be analyzed by this method if performance is demonstrated for the analyte of interest, in the matrices of interest, at the concentration levels of interest in the same manner as the listed elements and matrices (see Sec. 9.0).

1.4 Use of this method should be relegated to spectroscopists who are knowledgeable in the recognition and in the correction of spectral, chemical, and physical interferences in ICP-MS.

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

2.0 SUMMARY OF METHOD

2.1 Prior to analysis, samples which require total ("acid-leachable") values must be digested using appropriate sample preparation methods (such as Methods 3005 - 3052).

2.2 Method 6020 describes the multi-elemental determination of analytes by ICP-MS in environmental samples. The method measures ions produced by a radio-frequency inductively coupled plasma. Analyte species originating in a liquid are nebulized and the resulting aerosol is transported by argon gas into the plasma torch. The ions produced by high temperatures are entrained in the plasma gas and introduced, by means of an interface, into a mass spectrometer. The ions produced in the plasma are sorted according to their mass-to-charge ratios and quantified with a channel electron multiplier. Interferences must be assessed and valid corrections applied or the data flagged to indicate problems. Interference correction must include compensation for background ions contributed by the plasma gas, reagents, and constituents of the sample matrix.

3.0 DEFINITIONS

Refer to Chapter One and Chapter Three for a listing of applicable definitions.

4.0 INTERFERENCES

4.1 Isobaric elemental interferences in ICP-MS are caused by isotopes of different elements forming atomic ions with the same nominal mass-to-charge ratio (m/z). A data system must be used to correct for these interferences. This involves determining the signal for another isotope

of the interfering element and subtracting the appropriate signal from the analyte isotope signal. Since commercial ICP-MS instruments nominally provide unit resolution at 10% of the peak height, very high ion currents at adjacent masses can also contribute to ion signals at the mass of interest. Although this type of interference is uncommon, it is not easily corrected, and samples exhibiting a significant problem of this type could require resolution improvement, matrix separation, or analysis using another verified and documented isotope, or use of another method.

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

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

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

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

Similarly,

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

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

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

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

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

mixed gas plasmas have been shown to greatly reduce molecular interferences (Ref. 8). These techniques can be used provided that method detection limits, accuracy, and precision requirements for analysis of the samples can be met.

4.3 Additionally, solid phase chelation may be used to eliminate isobaric interferences from both element and molecular sources. An on-line method has been demonstrated for environmental waters such as sea water, drinking water and acid decomposed samples. Acid decomposed samples refer to samples decomposed by methods similar to methods 3052, 3051, 3050 or 3015. Samples with percent levels of iron and aluminum should be avoided. The method also provides a method for preconcentration to enhance detection limits simultaneously with elimination of isobaric interferences. The method relies on chelating resins such as iminodiacetate or other appropriate resins and selectively concentrates the elements of interest while eliminating interfering elements from the sample matrix. By eliminating the elements that are direct isobaric interferences or those that form isobaric interfering molecular masses, the mass region is simplified and these interferences can not occur. The method has been proven effective for the certification of standard reference materials and validated using SRMs (References 13-15). The method has the potential to be used on-line or off-line as an effective sample preparation method specifically designed to address interference problems.

4.4 Physical interferences are associated with the sample nebulization and transport processes as well as with ion-transmission efficiencies. Nebulization and transport processes can be affected if a matrix component causes a change in surface tension or viscosity. Changes in matrix composition can cause significant signal suppression or enhancement (Ref. 9). Dissolved solids can deposit on the nebulizer tip of a pneumatic nebulizer and on the interface skimmers (reducing the orifice size and the instrument performance). Total solid levels below 0.2% (2,000 mg/L) have been currently recommended (Ref. 10) to minimize solid deposition. An internal standard can be used to correct for physical interferences, if it is carefully matched to the analyte so that the two elements are similarly affected by matrix changes (Ref. 11). When intolerable physical interferences are present in a sample, a significant suppression of the internal standard signals (to less than 30 % of the signals in the calibrations standard) will be observed. Dilution of the sample fivefold (1+4) will usually eliminate the problem (see Sec. 9.3).

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

5.0 SAFETY

Refer to Chapter Three for a discussion on safety related references and issues.

6.0 EQUIPMENT AND SUPPLIES

6.1 Inductively coupled plasma-mass spectrometer:

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

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

7.0 REAGENTS AND STANDARDS

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

7.2 Reagent water: All references to water in the method refer to reagent water unless otherwise specified. Refer to Chapter One for a definition of reagent water.

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

7.3.1 Bismuth internal standard stock solution (1 mL = 100 µg Bi): Dissolve 0.1115 g Bi₂O₃ in a minimum amount of dilute HNO₃. Add 10 mL conc. HNO₃ and dilute to 1,000 mL with reagent water.

7.3.2 Holmium internal standard stock solution (1 mL = 100 µg Ho): Dissolve 0.1757 g Ho₂(CO₃)₂·5H₂O in 10 mL reagent water and 10 mL HNO₃. After dissolution is complete, warm the solution to degas. Add 10 mL conc. HNO₃ and dilute to 1,000 mL with reagent water.

7.3.3 Indium internal standard stock solution (1 mL = 100 µg In): Dissolve 0.1000 g indium metal in 10 mL conc. HNO₃. Dilute to 1,000 mL with reagent water.

7.3.4 Lithium internal standard stock solution (1 mL = 100 µg ⁶Li): Dissolve 0.6312 g 95-atom-% ⁶Li, Li₂CO₃ in 10 mL of reagent water and 10 mL HNO₃. After dissolution is complete, warm the solution to degas. Add 10 mL conc. HNO₃ and dilute to 1,000 mL with reagent water.

7.3.5 Rhodium internal standard stock solution (1 mL = 100 µg Rh): Dissolve 0.3593 g ammonium hexachlororhodate (III) (NH₄)₃RhCl₆ in 10 mL reagent water. Add 100 mL conc. HCl and dilute to 1,000 mL with reagent water.

7.3.6 Scandium internal standard stock solution (1 mL = 100 µg Sc): Dissolve 0.15343 g Sc₂O₃ in 10 mL (1+1) hot HNO₃. Add 5 mL conc. HNO₃ and dilute to 1,000 mL with reagent water.

7.3.7 Terbium internal standard stock solution (1 mL = 100 µg Tb): Dissolve 0.1828 g Tb₂(CO₃)₃·5H₂O in 10 mL (1+1) HNO₃. After dissolution is complete, warm the solution to degas. Add 5 mL conc. HNO₃ and dilute to 1,000 mL with reagent water.

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

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

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

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

7.4 Mixed calibration standard solutions are prepared by diluting the stock-standard solutions to levels in the linear range for the instrument in a solvent consisting of 1 percent (v/v) HNO_3 in reagent water. The calibration standard solutions must contain a suitable concentration of an appropriate internal standard for each analyte. Internal standards may be added on-line at the time of analysis using a second channel of the peristaltic pump and an appropriate mixing manifold. Generally, an internal standard should be no more than 50 amu removed from the analyte. Recommended internal standards include 6Li , ^{45}Sc , ^{89}Y , ^{103}Rh , ^{115}In , ^{159}Tb , ^{169}Ho , and ^{209}Bi . Prior to preparing the mixed standards, each stock solution must be analyzed separately to determine possible spectral interferences or the presence of impurities. Care must be taken when preparing the mixed standards that the elements are compatible and stable. Transfer the mixed standard solutions to freshly acid-cleaned FEP fluorocarbon bottles for storage. Fresh mixed standards must be prepared as needed with the realization that concentrations can change on aging. Calibration standards must be initially verified using a quality control standard (see Section 7.7).

7.5 Blanks: Three types of blanks are required for the analysis. The calibration blank is used in establishing the calibration curve. The preparation blank is used to monitor for possible contamination resulting from the sample preparation procedure. The rinse blank is used to flush the system between all samples and standards.

7.5.1 The calibration blank consists of the same concentration(s) of the same acid(s) used to prepare the final dilution of the calibrating solutions of the analytes [often 1 percent HNO_3 (v/v) in reagent water] along with the selected concentrations of internal standards such that there is an appropriate internal standard element for each of the analytes. Use of HCl for antimony and silver is cited in Section 7.1.

7.5.2 The preparation (or reagent) blank must be carried through the complete preparation procedure and contain the same volumes of reagents as the sample solutions.

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

7.6 The interference check solution (ICS) is prepared to contain known concentrations of interfering elements that will demonstrate the magnitude of interferences and provide an adequate test of any corrections. Chloride in the ICS provides a means to evaluate software corrections for chloride-related interferences such as $^{35}Cl^{16}O^+$ on $^{51}V^+$ and $^{40}Ar^{35}Cl^+$ on $^{75}As^+$. Iron is used to demonstrate adequate resolution of the spectrometer for the determination of manganese.

Molybdenum serves to indicate oxide effects on cadmium isotopes. The other components are present to evaluate the ability of the measurement system to correct for various molecular-ion isobaric interferences. The ICS is used to verify that the interference levels are corrected by the data system within quality control limits.

NOTE: The final ICS solution concentrations in Table 1 are intended to evaluate corrections for known interferences on only the analytes in Sec. 1.2. If Method 6020 is used to determine an element not listed in Sec. 1.2, it is the responsibility of the analyst to modify the ICS solutions, or prepare an alternative ICS solution, to allow adequate verification of correction of interferences on the unlisted element (see Section 9.4).

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

7.6.1.1 Mixed ICS solution I may be prepared by adding 13.903 g $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 2.498 g CaCO_3 (dried at 180 °C for 1 hour before weighing), 1.000 g Fe, 1.658 g MgO, 2.305 g Na_2CO_3 , and 1.767 g K_2CO_3 to 25 mL of reagent water. Slowly add 40 mL of (1+1) HNO_3 . After dissolution is complete, warm the solution to degas. Cool and dilute to 1,000 mL with reagent water.

7.6.1.2 Mixed ICS solution II may be prepared by slowly adding 7.444 g 85 % H_3PO_4 , 6.373 g 96% H_2SO_4 , 40.024 g 37% HCl, and 10.664 g citric acid $\text{C}_6\text{O}_7\text{H}_8$ to 100 mL of reagent water. Dilute to 1,000 mL with reagent water.

7.6.1.3 Mixed ICS solution III may be prepared by adding 1.00 mL each of 100- $\mu\text{g}/\text{mL}$ arsenic, cadmium, selenium, chromium, cobalt, copper, manganese, nickel, silver, vanadium, and zinc stock solutions to about 50 mL reagent water. Add 2.0 mL concentrated HNO_3 , and dilute to 100.0 mL with reagent water.

7.6.1.4 Working ICS Solutions

7.6.1.4.1 ICS-A may be prepared by adding 10.0 mL of mixed ICS solution I (Sec. 7.6.1.1), 2.0 mL each of 100- $\mu\text{g}/\text{mL}$ titanium stock solution (Sec. 7.3.9) and molybdenum stock solution (Sec. 7.3.10), and 5.0 mL of mixed ICS solution II (Sec. 7.6.1.2). Dilute to 100 mL with reagent water. ICS solution A must be prepared fresh weekly.

7.6.1.4.2 ICS-AB may be prepared by adding 10.0 mL of mixed ICS solution I (Sec. 7.6.1.1), 2.0 mL each of 100- $\mu\text{g}/\text{mL}$ titanium stock solution (Sec. 7.3.9) and molybdenum stock solution (Sec. 7.3.10), 5.0 mL of mixed ICS solution II (Sec. 7.6.1.2), and 2.0 mL of Mixed ICS solution III (Sec. 7.6.1.3). Dilute to 100 mL with reagent water. Although the ICS solution AB must be prepared fresh weekly, the analyst should be aware that the solution may precipitate silver more quickly.

7.7 The quality control standard is the initial calibration verification solution (ICV), which must be prepared in the same acid matrix as the calibration standards. This solution must be an independent standard near the midpoint of the linear range at a concentration other than that used for instrument calibration. An independent standard is defined as a standard composed of the analytes from a source different from those used in the standards for instrument calibration.

7.8 Mass spectrometer tuning solution. A solution containing elements representing all of the mass regions of interest (for example, 10 µg/L of Li, Co, In, and Tl) must be prepared to verify that the resolution and mass calibration of the instrument are within the required specifications (see Section 10.1). This solution is also used to verify that the instrument has reached thermal stability (see Section 11.4).

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Sample collection procedures should address the considerations described in Chapter Nine.

8.2 See the introductory material in Chapter Three, Inorganic Analytes, for information on sample handling, storage, holding times and preservation. Only polyethylene or fluorocarbon (TFE or PFA) containers are recommended for use in this method.

9.0 QUALITY CONTROL

9.1 All quality control data should be maintained and be available for easy reference or inspection.

9.2 Instrument detection limits (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 must 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 must be determined at least every three months and kept with the instrument log book. Refer to Chapter One for additional guidance.

9.3 The intensities of all internal standards must be monitored for every analysis. If the intensity of any internal standard in a sample falls below 30 percent of the intensity of that internal standard in the initial calibration standard, a significant matrix effect must be suspected. Under these conditions, the detection limit has degraded and the correction ability of the internal standardization technique becomes questionable. The following procedure is followed: First, make sure the instrument has not just drifted by observing the internal standard intensities in the nearest clean matrix (calibration blank, Section 7.5.1). If the low internal standard intensities are also seen in the nearest calibration blank, terminate the analysis, correct the problem, recalibrate, verify the new calibration, and reanalyze the affected samples. If drift has not occurred, matrix effects need to be removed by dilution of the affected sample. The sample must be diluted fivefold (1+4) and reanalyzed with the addition of appropriate amounts of internal standards. If the first dilution does not eliminate the problem, this procedure must be repeated until the internal-standard intensities rise above the 30 percent limit. Reported results must be corrected for all dilutions.

9.4 To obtain analyte data of known quality, it is necessary to measure more than the analytes of interest in order to apply corrections or to determine whether interference corrections are necessary. For example, tungsten oxide moleculars can be very difficult to distinguish from mercury isotopes. If the concentrations of interference sources (such as C, Cl, Mo, Zr, W) are such that, at the correction factor, the analyte is less than the limit of quantification and the concentration of interferences are insignificant, then the data may go uncorrected. Note that monitoring the interference sources does not necessarily require monitoring the interferant itself, but that a molecular species may be monitored to indicate the presence of the interferant. When correction equations are used, all QC criteria must also be met. Extensive QC for interference corrections are

required at all times. The monitored masses must include those elements whose hydrogen, oxygen, hydroxyl, chlorine, nitrogen, carbon and sulfur molecular ions could impact the analytes of interest. Unsuspected interferences may be detected by adding pure major matrix components to a sample to observe any impact on the analyte signals. When an interference source is present, the sample elements impacted must be flagged to indicate (a) the percentage interference correction applied to the data or (b) an uncorrected interference by virtue of the elemental equation used for quantitation. The isotope proportions for an element or molecular-ion cluster provide information useful for quality assurance.

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

9.5 Dilution test (serial dilution): If the analyte concentration is within the linear dynamic range of the instrument and sufficiently high (minimally, a factor of at least 100 times greater than the concentration in the reagent blank, refer to Section 7.5.2), an analysis of a fivefold (1+4) dilution must agree within $\pm 10\%$ of the original determination. If not, an interference effect must be suspected. One dilution test must be included for each twenty samples (or less) of each matrix in a batch.

9.6 Post-digestion spike addition: An analyte spike added to a portion of a prepared sample, or its dilution, should be recovered to within 75 to 125 percent of the known value or within the laboratory derived acceptance criteria. The spike addition should be based on the indigenous concentration of each element of interest in the sample. If the spike is not recovered within the specified limits, the sample must be diluted and reanalyzed to compensate for the matrix effect. Results must agree to within 10% of the original determination. The use of a standard-addition analysis procedure may also be used to compensate for this effect (refer to Method 7000).

9.7 A laboratory control sample (LCS) should be analyzed for each analyte using the same sample preparations, analytical methods and QA/QC procedures employed for the test samples. One LCS should be prepared and analyzed for each sample batch at a frequency of one LCS for each 20 samples or less.

9.8 Check the instrument calibration by analyzing appropriate quality control solutions as follows:

9.8.1 Check instrument calibration using a calibration blank (Section 7.5.1) and the initial calibration verification solution (Sections 7.7 and 11.6).

9.8.2 Verify calibration at a frequency of every 10 analytical samples with the instrument check standard (Section 7.6) and the calibration blank (Section 7.5.1). These solutions must also be analyzed for each analyte at the beginning of the analysis and after the last sample.

9.8.3 The results of the initial calibration verification solution and the instrument check standard must agree within $\pm 10\%$ of the expected value. If not, terminate the analysis, correct the problem, and recalibrate the instrument. Any sample analyzed under an out-of-control calibration must be reanalyzed .

9.8.4 The results of the calibration blank must be less than 3 times the current IDL for each element. If this is not the case, the reason for the out-of-control condition must be found and corrected, and affected samples must be reanalyzed. If the laboratory consistently has concentrations greater than 3 times the IDL, the IDL may be indicative of an estimated IDL and should be re-evaluated.

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

9.10 Analyze one duplicate sample for every matrix in a batch at a frequency of one matrix duplicate for every 20 samples.

9.10.1 The relative percent difference (RPD) between duplicate determinations must be calculated as follows:

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

where:

RPD = relative percent difference.

D_1 = first sample value.

D_2 = second sample value (duplicate)

A control limit of 20% RPD should not be exceeded for analyte values greater than 100 times the instrumental detection limit. If this limit is exceeded, the reason for the out-of-control situation must be found and corrected, and any samples analyzed during the out-of-control condition must be reanalyzed.

9.11 Ultra-trace analysis requires the use of clean chemistry. Several suggestions for reduction on the analytical blank are provided in Chapter Three.

10.0 CALIBRATION AND STANDARDIZATION

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

10.2 Calibrate the instrument for the analytes of interest (recommended isotopes for the analytes in Sec. 1.2 are provided in Table 2), using the calibration blank and at least a single initial calibration standard according to the instrument manufacturer's procedure. Flush the system with the rinse blank (Sec. 7.5.3) between each standard solution. Use the average of at least three integrations for both calibration and sample analyses.

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

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

10.4 Immediately after the calibration has been established, the calibration must be verified and documented for every analyte by the analysis of the calibration verification solution (Section 7.7). When measurements exceed $\pm 10\%$ of the accepted value, the analyses must be terminated, the problem corrected, the instrument recalibrated, and the new calibration verified. Any samples analyzed under an out-of-control calibration must be reanalyzed. During the course of an analytical run, the instrument may be "resloped" or recalibrated to correct for instrument drift but resloping must not be used as an alternative to reanalyzing samples following an unacceptable QC sample, such as a CCV. 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 Solubilization and digestion procedures are presented in Chapter Three (e.g., Methods 3005 - 3052).

NOTE: If mercury is to be analyzed, the digestion procedure must use mixed nitric and hydrochloric acids through all steps of the digestion. Mercury will be lost if the sample is digested when hydrochloric acid is not present. If it has not already been added to the sample as a preservative, Au should be added to give a final concentration of 2 mg/L (use 2.0 mL of 5.3.11 per 100 mL of sample) to preserve the mercury and to prevent it from plating out in the sample introduction system.

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

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

11.4 Operating conditions: The analyst should follow the instructions provided by the instrument manufacturer. Allow at least 30 minutes for the instrument to equilibrate before analyzing any samples. This must be verified by analyzing a tuning solution (Section 7.8) at least four times with relative standard deviations of $\leq 5\%$ for the analytes contained in the tuning solution.

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

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

11.6 Flush the system with the rinse blank solution (Sec. 7.5.3) until the signal levels return to the DQO or method's levels of quantitation (usually about 30 seconds) before the analysis of each sample (see Section 10.3). Nebulize each sample until a steady-state signal is achieved (usually about 30 seconds) prior to collecting data. Analyze the calibration verification solution (Section 7.6) and the calibration blank (Section 7.5.1) at a frequency of at least once every 10 analytical samples. Flow-injection systems may be used as long as they can meet the performance criteria of this method.

11.7 Dilute and reanalyze samples that are more concentrated than the linear range for an analyte (or species needed for a correction) or measure an alternate but less-abundant isotope. The linearity at the alternate mass must be confirmed by appropriate calibration (see Sec. 10.2 and 10.4). Alternatively apply solid phase chelation chromatography to eliminate the matrix as described in Sec. 4.3.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 The quantitative values shall be reported in appropriate units, such as micrograms per liter ($\mu\text{g/L}$) 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.

12.1.1 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 Section 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).

13.0 METHOD PERFORMANCE

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

13.2 Table 5 summarizes the method performance data for aqueous and sea water samples with interfering elements removed and samples preconcentrated prior to analysis. Table 6 summarizes the performance data for a simulated drinking water standard.

14.0 POLLUTION PREVENTION

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

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions consult *Less is Better: Laboratory Chemical management for Waste Reduction* available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St., N.W. Washington, D.C. 20036, (202) 872-4477.

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

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17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

The pages to follow contain Tables 1 through 7, and a flow diagram of the method procedure.

TABLE 1
RECOMMENDED INTERFERENCE CHECK SAMPLE COMPONENTS
AND CONCENTRATIONS

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

TABLE 2
RECOMMENDED ISOTOPES FOR SELECTED ELEMENTS

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

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

^a These masses are also useful for interference correction (Section 4.2).

^b Internal standard must be enriched in the ⁶Li isotope. This minimizes interference from indigenous lithium.

TABLE 3

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

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

Data obtained from reference 12.

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

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

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

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

TABLE 4

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

Element	Comparability ^a Range	%RSD Range	N ^b	S ^c
Aluminum	83 - 101	11 - 39	13 - 14	7
Antimony	d	12 - 21	15 - 16	2
Arsenic	79 - 102	12 - 23	16 - 16	7
Barium	100 - 102	4.3 - 17	15 - 16	7
Beryllium	50 - 87	19 - 34	12 - 14	5
Cadmium	93 - 100	6.2 - 25	19 - 20	5
Calcium	95 - 109	4.1 - 27	15 - 17	7
Chromium	77 - 98	11 - 32	17 - 18	7
Cobalt	43 - 102	15 - 30	17 - 18	6
Copper	90 - 109	9.0 - 25	18 - 18	7
Iron	87 - 99	6.7 - 21	12 - 12	7
Lead	90 - 104	5.9 - 28	15 - 18	7
Magnesium	89 - 111	7.6 - 37	15 - 16	7
Manganese	80 - 108	11 - 40	16 - 18	7
Nickel	87 - 117	9.2 - 29	16 - 18	7
Potassium	97 - 137	11 - 62	10 - 12	5
Selenium	81	39	12	1
Silver	43 - 112	12 - 33	15 - 15	3
Sodium	100 - 146	14 - 77	8 - 10	5
Thallium	91	33	18	1
Vanadium	83 - 147	20 - 70	6 - 14	7
Zinc	84 - 124	14 - 42	18 - 18	7

Data obtained from reference 12.

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

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

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

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

TABLE 5

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

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

Data obtained from reference 12.

^A The dilution of the sea-water during the adjustment of pH produced 10 mL samples containing 9 mL of sea-water and 30 mL samples containing 27 mL of sea-water. Samples containing 9.0 mL of CASS-2, n=5; samples containing 27.0 mL of CASS-2, n=3.

^B Concentration (ng/mL) ± 95% confidence limits.

TABLE 6

ANALYSIS OF NIST SRM 1643b, TRACE METALS IN WATER^A

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

Data obtained from reference 12.

^A 5.0 mL samples, n=5.

^B Concentration (ng/mL) ± 95% confidence limits.

TABLE 7

COMPARISON OF TOTAL MERCURY RESULTS IN HEAVILY CONTAMINATED SOILS

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

Source: Reference 16.

METHOD 6020A

INDUCTIVELY COUPLED PLASMA - MASS SPECTROMETRY

