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Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air

Compendium Method IO-3.5

DETERMINATION OF METALS IN AMBIENT PARTICULATE MATTER USING INDUCTIVELY COUPLED PLASMA/ MASS SPECTROMETRY (ICP/MS)

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Method IO-3.5

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DETERMINATION OF METALS IN AMBIENT PARTICULATE MATTER USING INDUCTIVELY COUPLED PLASMA/MASS SPECTROMETRY

1. Scope

1.1 Suspended particulate matter (SPM) in air generally is a complex multi-phase system of all airborne solid and low vapor pressure liquified particles having aerodynamic particles sizes from below 0.01-100 µm and larger. Historically, SPM measurement has concentrated on total suspended particulates (TSP), with no preference to size selection.

1.2 On July 1, 1987, the U. S. Environmental Protection Agency (EPA) promulgated a new size-specific air quality standard for ambient particulate matter. This new primary standard applies only to particles with aerodynamic diameters ≤ 10 µm (PM_{10}) and replaces the original standard for TSP. To measure concentrations of these particles, the EPA also promulgated a new federal reference method (FRM). This method is based on the separation and removal of non-PM_{10} particles from an air sample, followed by filtration and gravimetric analysis of PM_{10} mass on the filter substrate.

1.3 The new primary standard (adopted to protect human health) limits PM_{10} concentrations to 150 µg/std m^3, averaged over a 24-h period. These smaller particles are able to reach the lower regions of the human respiratory tract and, therefore, are responsible for most of the adverse health effects associated with suspended particulate pollution. The secondary standard, used to assess the impact of pollution on public welfare, has also been established at 150 µg/std. m^3.

1.4 Ambient air SPM measurements are used (among other purposes) to determine whether defined geographical areas are in attainment or non-attainment with the national ambient air quality standards (NAAQS) for PM_{10}. These measurements are obtained by the states in their state local air monitoring station (SLAMS) networks as required under 40 CFR Part 58. Further, Appendix C of Part 58 requires that the ambient air monitoring methods used in these EPA-required SLAMS networks must be methods that have been designated by EPA as either reference or equivalent methods.

1.5 The procedure for analyzing the elemental metal components in ambient air particulate matter collected on high volume filter material is described in this method. The high volume filter material may be associated with either the TSP or PM_{10} sampler, as delineated in Inorganic Compendium Method IO-2.1.

1.6 Filters are numbered, pre-weighted, field deployed and sampled, returned to the laboratory, extracted using microwave or hot acid, then analyzed by inductively coupled plasma/mass spectrometry (ICP/MS). The extraction procedure is accomplished by following Inorganic Compendium Method IO-3.1. Those metals and their associated method detection limit (MDL) applicable to this technology are listed in Table 1.

1.7 This method should be used by analysts experienced in the use of ICP/MS, the interpretation of spectral and matrix interferences and procedures for their correction. A minimum of 6-months' experience with commercial instrumentation is required.

2. Applicable Documents

2.1 ASTM Standards

- D1356 *Definition of Terms Related to Atmospheric Sampling and Analysis*.
- D1357 *Planning the Sampling of the Ambient Atmosphere*.
- D4096 *Application of the High Volume Sample Method for Collection and Mass Determination of Airborne Particle Matter*.

2.2 Other Documents

- U. S. Environmental Protection Agency, *Quality Assurance Handbook for Air Pollution Measurement Systems, Volume I: A Field Guide for Environmental Quality Assurance*, EPA-600/R-94-038a.
- U. S. Environmental Protection Agency, *Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II: Ambient Air Specific Methods (Interim Edition)*, EPA-600/R-94/038b.
- Reference Method for the Determination of Particulate Matter in the Atmosphere, *Code of Federal Regulations*. 40 CFR 50, Appendix J.
- Reference Method for the Determination of Suspended Particulates in the Atmosphere (High Volume Method), *Code of Federal Regulations*. 40 CFR 50, Appendix B.
- Reference Method for the Determination of Lead in Suspended Particulate Matter Collected from Ambient Air, *Federal Register* 43 (194): 46258-46261.
- U. S. EPA Project Summary Document (1).
- U. S. EPA Laboratory Standard Operating Procedures (2).
- Scientific Publications of Ambient Air Studies (3-14).

3. Summary of Method

3.1 The method describes the multi-element determination of trace elements by ICP/MS. Sample material in solution is introduced by pneumatic nebulization into a radiofrequency plasma where energy transfer processes cause desolvation, atomization, and ionization.

3.2 The ions are extracted from the plasma through a differentially pumped vacuum interface and separated on the basis of their mass-to-charge ratio by a quadrupole mass spectrometer having a minimum resolution capability of 1 amu peak width at 5% peak height.

3.3 The ions transmitted through the quadruple are registered by a continuous dynode electron multiplier or Faraday detector and the ion information processed by a data handling system.

3.4 Interferences relating to the technique (see Section 5) must be recognized and corrected for. Such corrections must include compensation for isobaric elemental interferences and interferences from polyatomic ions derived from the plasma gas, air, reagents, or sample matrix. Instrumental drift as well as suppressions or enhancements of instrument response caused by the sample matrix must be corrected for by internal standardization.

4. Definitions

[Note: Definitions used in this document are consistent with ASTM methods. All pertinent abbreviations and symbols are defined within this document at point of use.]

4.1 Instrument Detection Limit (IDL). The concentration equivalent of the analyte signal, which is equal to three times the standard deviation of the blank signal at the selected analytical mass(es).

4.2 Method Detection Limit (MDL). The minimum concentration of an analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero. MDLs are intended as a guide to instrumental limits typical of a system optimized for multi-element determinations and employing commercial instrumentation and pneumatic nebulization sample introduction. However, actual MDLs and linear working ranges will be dependent on the sample matrix, instrumentation and selected operating conditions.

4.3 Linear Dynamic Range (LDR). The concentration range over which the analytical working curve remains linear.

4.4 Laboratory Reagent Blank (LRB) (Preparation Blank). An aliquot of reagent water that is treated exactly as a sample including exposure to all labware, equipment, solvents, reagents, and internal standards that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents or apparatus.

4.5 Calibration Blank. A volume of ASTM Type I water acidified with the same acid matrix as is present in the calibration standards.

4.6 Internal Standard. Pure analyte(s) added to a solution in known amount(s) and used to measure the relative responses of other method analytes that are components of the same solution. The internal standard must be an analyte that is not a sample component.

4.7 Stock Standards Solutions. A concentrated solution containing one or more analytes prepared in the laboratory using assayed reference compounds or purchased from a reputable commercial source.

4.8 Calibration Standard (CAL). A solution prepared from the stock standard solution(s) which is used to calibrate the instrument response with respect to analyte concentration.

4.9 Tuning Solution. A solution used to determine acceptable instrument performance prior to calibration and sample analyses.

4.10 Quality Control Sample (QCS). A solution containing known concentrations of method analytes which is used to fortify an aliquot of LRB matrix. The QCS is obtained from a source external to the laboratory and is used to check laboratory performance.

4.11 Nebulizer. A device creating a fine spray of sample solution to be carried into the plasma for measurement. Its performance is critical for good analysis.

4.12 Mass Spectrometer (MS). For a quadrupole mass spectrometer, an analytical system which consist of parallel set of four rod electrodes mounted in a square configuration. By coupling composite pairs of rods together and applying radio frequency (RF) and direct current (DC) potentials between the pairs of rods, ions (generated from the ion source of reaction of chemical compound with a high intense beam of electrons) moving through the field, based upon their trajectories, can be separated according to their atomic mass units (amu) and subsequently detected by an electron multiplier detector.

4.13 MS-SCAN. The MS is programmed to SCAN all ions repeatedly over a specified mass range.

4.14 MS-SIM. The MS is programmed to scan a selected number of ions repeatedly [i.e., selected ion monitoring (SIM) mode].

5. Interferences

[Note: Several interference sources may cause inaccuracies in the determination of trace elements by ICP/MS.]

5.1 Isobaric Elemental Interferences

Isobaric elemental interferences are caused by isotopes of different elements that form single- or double-charged ions of the same nominal mass-to-charge ratio and cannot be resolved by mass spectrometer in use. All elements determined by this method have, at a minimum, one isotope free of isobaric elemental interference. Of the analytical isotopes recommended for use with this method, only molybdenum-98 (ruthenium) and selenium-82 (krypton) have isobaric elemental interferences. If alternative analytical isotopes having higher natural abundance are selected to achieve greater sensitivity, an isobaric interference may occur. All data obtained under such conditions must be corrected by measuring the signal from another isotope of the interfering element and subtracting the appropriate signal ratio from the isotope of interest. A record of this correction process should be included with the report of the data. These corrections will only be as accurate as the accuracy of the isotope ratio used in the elemental equation for data calculations. Relevant isotope ratios and instrument bias factors should be established prior to the application of any corrections.

5.2 Abundance Sensitivity

Abundance sensitivity is a property defining the degree to which the wings of a mass peak contribute to adjacent masses. The abundance sensitivity is affected by ion energy and quadruple operating pressure. Wing overlap interferences may result when a small ion peak is being measured adjacent to a large one. The potential for these interferences should be recognized and the spectrometer resolution adjusted to minimize them.

5.3 Isobaric Polyatomic Ion Interferences

Isobaric polyatomic ion interferences are caused by ions consisting of more than one atom that have the same nominal mass-to-charge ratio as the isotope of interest and that cannot be resolved by the mass spectrometer in use. These ions are commonly formed in the plasma or interface system from support gases or sample components. Most of the common interferences have been identified and are listed in Table 2, together with the method elements affected. Such interferences must be recognized, and when they cannot be avoided by the selection of alternative analytical isotopes, appropriate corrections must be made to the data. Equations for the correction of data should be established at the time of the analytical run sequence as the polyatomic ion interferences will be highly dependent on the sample matrix and chosen instrument conditions.

5.4 Physical Interferences

Physical interferences are associated with the physical processes that govern the transport of sample into the plasma, sample conversion processes in the plasma, and the transmission of ions through the plasma-mass spectrometer interface. These interferences may result in differences between instrument responses for the sample and the calibration standards. Physical interferences may occur in the transfer of solution to the nebulizer (e.g., viscosity effects), at the point of aerosol formation and transport to the plasma (e.g., surface tension), or during excitation and ionization processes within the plasma itself. High levels of dissolved solids in the sample may contribute deposits of material on the extraction and/or skimmer cones reducing the effective diameter of the orifices and therefore ion transmission. Internal standardization may be effectively used to compensate for many physical interference effects. Internal standards ideally should have similar analytical behavior to the elements being determined.

5.5 Memory Interferences

Memory interferences result when isotopes of elements in a previous sample contribute to the signals measured in a new sample. Memory effects can result from sample deposition on the sampler and skimmer cones and from the buildup of sample material in the plasma torch and spray chamber. The site where these effects occur is dependent on the element and can be minimized by flushing the system with a rinse blank between samples (see Section 8.6.3). 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 should be estimated prior to analysis. This estimate may be calculated by aspirating a standard containing elements corresponding to 10 times the upper end of the linear range for a normal sample analysis period, followed by analysis of the rinse blank at designated intervals. The length of time required to reduce analyte signals to within a factor of 10 of the method detection limit, should be noted. Memory interferences may also be assessed within an analytical run by using a minimum of three replicate integrations for data acquisition. If the integrated signal values drop consecutively, the analyst should be alerted to the possibility of a memory effect and should examine the analyte concentration in the previous sample to identify if this was high. If a memory interference is suspected, the sample should be reanalyzed after a long rinse period.

6. Safety

6.1 The toxicity or carcinogenicity of reagents used in this method have not been fully established. Each chemical should be regarded as a potential health hazard, and exposure to these compounds should be as low as reasonably achievable. Each laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be available to all personnel involved in the chemical analyses.

6.2 Analytical plasma sources emit radiofrequency radiation in addition to intense UV radiation. Suitable precautions should be taken to protect personnel from such hazards.

7. Apparatus and Equipment

7.1 Inductively Coupled Plasma/Mass Spectrometer (ICP/MS)

7.1.1 ICP/MS Instrument. Capable of scanning the mass 5-250 amu with a minimum resolution capability of 1 amu peak width at 5% peak height. Instrument may be fitted with a conventional or extended dynamic range detection system.

7.1.2 Argon Gas Supply (high-purity grade, 99.99%). Best source.

7.1.3 A Variable-Speed Peristaltic Pump. Required for solution delivery to the nebulizer.

7.1.4 A Mass-Flow Controller. One mass flow controller is required on the nebulizer gas supply. A water-cooled spray chamber may reduce some types of interferences (e.g., from polyatomic oxide species).

7.1.5 Operating Conditions. Because of the diversity of instrument hardware, no detailed instrument operating conditions are provided. The analyst is advised to follow the recommended operating conditions provided by the manufacturer. The analyst must verify that the instrument configuration and operating conditions satisfy the analytical requirements and maintain quality control data verifying instrument performance and analytical results. Instrument operating conditions used to generate precision and recovery data for this method (Section 14) are included in Table 3.

7.1.6 Electron Multiplier Detector. If an electron multiplier detector is being used, precautions should be taken, where necessary, to prevent exposure to high ion flux. Otherwise, changes in instrument response or damage to the multiplier may result. Samples having high concentrations of elements beyond the linear range of the instrument and with isotopes falling within scanning windows should be diluted prior to analysis.

7.2 Labware

To determine trace level elements, contamination and loss are of prime consideration. Potential contamination sources include improperly cleaned laboratory apparatus and general contamination within the laboratory environment from dust, etc. A clean laboratory work area designated for trace element sample handling must be used. Sample containers can introduce positive and negative errors in the determination of trace elements by (1) contributing contaminants through surface desorption or leaching and (2) depleting element concentrations through adsorption processes. All reusable labware (glass, quartz, polyethylene, Teflon®, etc.), including the sample container, should be cleaned prior to use. Labware may be soaked overnight and thoroughly washed with laboratory-grade detergent and water, rinsed with water, and soaked for 4 h in a mixture of dilute nitric and hydrochloric acid (1 + 2 + 9). It should then be rinsed with ASTM type I water and oven-dried.

[Note: Do not use chromic acid to clean glassware.]

7.2.1 Glassware. Volumetric flasks, graduated cylinders, funnels and centrifuge tubes.

7.2.2 Assorted Calibrated Pipettes. Dust sources.

7.2.3 Conical Phillips Beakers, 350-mL with 50-mm Watch Glasses. Griffin beakers, 350-mL with 75-mm watch glasses.

7.2.4 Storage Bottles. Narrow mouth bottles, Teflon® FEP (fluorinated ethylene propylene) with Tefzel ETFE (ethylene tetrafluorethylene) screw closure, 125-mL and 250-mL capacities.

7.3 Sample Processing Equipment

7.3.1 Air Displacement Pipetter. Digital pipet system capable of delivering volumes from 10 to 2,500 µL with an assortment of high quality disposable pipet tips.

7.3.2 Balance. Analytical, capable of accurately weighing to 0.1 mg.

7.3.3 Hot Plate. (Corning PC100 or equivalent).

7.3.4 Centrifuge. Steel cabinet with guard bowl, electric timer and brake.

7.3.5 Drying Oven. Gravity convection oven with thermostatic control capable of maintaining 105EC ± 5EC.

8. Reagents and Consumable Materials

8.1 Reagents

[Note: Owing to the high sensitivity of ICP/MS, high-purity reagents should be used whenever possible. All acids used for this method must be of ultra high-purity grade. Suitable acids are available from a number of manufacturers or may be prepared by sub-boiling distillation. Nitric acid is preferred for ICP/MS to minimize polyatomic ion interferences. Several polyatomic ion interferences result when hydrochloric acid is used (see Table 2). However, hydrochloric acid is required to maintain stability in solutions containing antimony and silver. When hydrochloric acid is used, corrections for the chloride polyatomic ion interferences must be applied to all data. As discussed in Method I0-3.1, a mixture of 3% HNO_3 / 8% HCl is the best extraction matrix for total extraction of metals from quartz filters.]

8.1.1 Nitric Acid, Concentrated (sp.gr. 1.41). Best source.

8.1.2 Nitric Acid (1+1). Add 500 mL conc. nitric acid to 400 mL of ASTM type I water and dilute to 1 L.

8.1.3 Nitric Acid (1+9). Add 100 mL conc. nitric acid to 400 mL of ASTM type I water and dilute to 1 L.

8.1.4 Hydrochloric Acid, Concentrated (sp.gr. 1.19). Best source.

8.1.5 Hydrochloric Acid (1+1). Add 500 mL conc. hydrochloric acid to 400 mL of ASTM type I water and dilute to 1 L.

8.1.6 Hydrochloric Acid (1+4). Add 200 mL conc. hydrochloric acid to 400 mL of ASTM type I water and dilute to 1 L.

8.1.7 Ammonium Hydroxide, Concentrated (sp.gr. 0.902). Best source.

8.1.8 Tartaric Acid (CASRN 87-69-4). Best source.

8.2 Water

For all sample preparation and dilutions, ASTM type I water (ASTM D1193) is required. Suitable water may be prepared by passing distilled water through a mixed bed of anion and cation exchange resins.

8.3 Standard Stock Solutions

Standard stock solutions may be purchased from a reputable commercial source or prepared from ultra high-purity grade chemicals or metals (99.99 - 99.999% pure). All salts should be dried for 1 h at 105EC, unless otherwise specified. Stock solutions should be stored in Teflon® bottles. Use the following procedures for preparing standard stock solutions:

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

[Note: Some metals, particularly those that form surface oxides, require cleaning prior to being weighed, which requires pickling the surface of the metal in acid. An amount in excess of the desired weight should be pickled repeatedly, rinsed with water, dried, and weighed until the desired weight is achieved.]

8.3.1 Aluminum Solution, Stock. 1 mL = 1,000 µg Al: Pickle aluminum metal in warm (1 + 1) HCl to an exact weight of 0.100 g. Dissolve in 10 mL conc. HCl and 2 mL conc. nitric acid, heat to dissolve. Continue heating until volume is reduced to 4 mL. Cool and add 4 mL ASTM type I water. Heat until the volume is reduced to 2 mL. Cool and dilute to 100 mL with ASTM type I water.

8.3.2 Antimony Solution, Stock. 1 mL = 1,000 µg Sb: Dissolve 0.100 g antimony powder in 2 mL (1 + 1) nitric acid and 0.5 mL conc. hydrochloric acid, heat to dissolve. Cool and add 20 mL ASTM type I water and 0.15 g tartaric acid. Warm the solution to dissolve the white precipitate. Cool and dilute to 100 mL with ASTM type I water.

8.3.3 Arsenic Solution, Stock. 1 mL = 1,000 µg As: Dissolve 0.1320 g As_2O_3 in a mixture of 50 mL ASTM type I water and 1 mL conc. ammonium hydroxide. Heat gently to dissolve. Cool and acidify the solution with 2 mL conc. nitric acid. Dilute to 100 mL with ASTM type I water.

8.3.4 Barium Solution, Stock. 1 mL = 1,000 µg Ba: Dissolve 0.1437 g $BaCO_3$ in a solution mixture of 10 mL ASTM type I water and 2 mL conc. nitric acid. Heat and stir to dissolve and degassing. Dilute to 100 mL with ASTM type I water.

8.3.5 Beryllium Solution, Stock. 1 mL = 1,000 µg Be: Dissolve 1.965 g $BeSO_4 4H_2O$ (DO NOT DRY) in 50 mL ASTM Type I water. Add 1 mL conc. nitric acid. Dilute to 100 mL with ASTM type I water.

8.3.6 Bismuth Solution, Stock. 1 mL = 1,000 µg Bi: Dissolve 0.1115 g Bi_2O_3 in 5 mL conc. nitric acid. Heat to dissolve. Cool and dilute to 100 mL with ASTM type I water.

8.3.7 Cadmium Solution, Stock. 1 mL = 1,000 µg Cd: Pickle cadmium metal in (1 + 9) nitric acid to an exact weight of 0.100 g. Dissolve in 5 mL (1 + 1) nitric acid, heating to dissolve. Cool and dilute to 100 mL wit ASTM type I water.

8.3.8 Chromium Solution, Stock. 1 mL = 1,000 µg Cr: Dissolve 0.1923 g CrO_3 in a solution mixture of 10 mL ASTM type I water and 1 mL conc. nitric acid. Dilute to 100 mL with ASTM type I water.

8.3.9 Cobalt Solution, Stock. 1 mL = 1,000 µg Co: Pickle cobalt metal in (1 + 9) nitric acid to an exact weight of 0.100 g. Dissolve in 5 mL (1 + 1) nitric acid, heating to dissolve. Cool and dilute to 100 mL with ASTM type I water.

8.3.10 Copper Solution, Stock. 1 mL = 1,000 µg Cu: Pickle copper metal in (1 + 9) nitric acid to an exact weight of 0.100 g. Dissolve in 5 mL (1 + 1) nitric acid, heating to dissolve. Cool and dilute to 100 mL with ASTM type I water.

8.3.11 Indium Solution, Stock. 1 mL = 1,000 µg In: Pickle indium metal in (1 + 1) nitric acid to an exact weight of 0.100 g. Dissolve in 10 mL (1 + 1) nitric acid, heating to dissolve. Cool and dilute to 100 mL with ASTM type I water.

8.3.12 Lead Solution, Stock. 1 mL = 1,000 µg Pb: Dissolve 0.1599 g $PbNO_3$ in 5 mL (1 + 1) nitric acid. Dilute to 100 mL with ASTM type I water.

8.3.13 Magnesium Solution, Stock. 1 mL = 1,000 µg Mg: dissolve 0.1658 g MgO in 10 mL (1 + 1) nitric acid, heating to dissolve. Cool and dilute to 100 mL with ASTM type I water.

8.3.14 Manganese Solution, Stock. 1 mL = 1,000 µg Mn: Pickle manganese flake in (1 + 9) nitric acid to an exact weight of 0.100 g. Dissolve in 5 mL (1 + 1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with ASTM type I water.

8.3.15 Molybdenum Solution, Stock. 1 mL = 100 µg Mo: Dissolve 0.1500 g MoO_3 in a solution mixture of 10 mL ASTM type I water and 1 mL conc. ammonium hydroxide, heating to dissolve and 1 mL conc. ammonium hydroxide, heating to effect solution. Cool and dilute to 100 mL with ASTM type I water.

8.3.16 Nickel Solution, Stock. 1 mL = 1,000 µg Ni: Dissolve 0.100 g nickel powder in 5 mL conc. nitric acid, heating to dissolve. Cool and dilute to 100 mL with ASTM type I water.

8.3.17 Scandium Solution, Stock. 1 mL = 1,000 µg Sc: Dissolve 0.1534 g sc_2O_3 in 5 mL (1 + 1) nitric acid, heating to dissolve. Cool and dilute to 100 mL ASTM type I water.

8.3.18 Selenium Solution, Stock. 1 mL = 1,000 µg Se: Dissolve 0.1405 g SeO_2 in 20 mL ASTM type I water. Dilute to 100 mL with ASTM type I water.

8.3.19 Silver Solution, Stock. 1 mL = 100 µg Ag: Dissolve 0.100 g silver metal in 5 mL (1 + 1) nitric acid, heating to dissolve. Cool and dilute to 100 mL with ASTM type I water. Store in dark container.

8.3.20 Terbium Solution, Stock. 1 mL = 1,000 µg Tb: Dissolve 0.1176 g Tb_4O_7 in 5 mL conc. nitric acid, heating to dissolve. Cool and dilute to 100 mL with ASTM type I water.

8.3.21 Thallium Solution, Stock. 1 mL = 1,000 µg T1: Dissolve 0.1303 g $TlNO_3$ in a solution mixture of 10 mL ASTM type I water and 1 mL conc. nitric acid. Dilute to 100 mL with ASTM type I water.

8.3.22 Thorium Solution, Stock. 1 mL = 1,000 µg Th: Dissolve 0.2380 g $Th(NO_3)_4 \cdot 4H_2O$ (DO NOT DRY) in 20 mL ASTM type I water. Dilute to 100 mL with ASTM type I water.

8.3.23 Uranium Solution, Stock. 1 mL = 1,000 µg U: Dissolve 0.2110 g $UO_2(NO_3)_2 \cdot 6H_2O$ (DO NOT DRY) in 20 mL ASTM type I water and dilute to 100 mL with ASTM type I water.

8.3.24 Vanadium Solution, Stock. 1 mL = 1,000 µg V: Pickle vanadium metal in (1 + 9) nitric acid to an exact weight of 0.100 g. Dissolve in 5 mL (1 + 1) nitric acid, heating to dissolve. Cool and dilute to 100 mL with ASTM type I water.

8.3.25 Yttrium Solution, Stock. 1 mL = 1,000 µg Y: Dissolve 0.1270 g Y_2O_3 in 5 mL (1 + 1) nitric acid, heating to dissolve. Cool and dilute to 100 mL with ASTM type I water.

8.3.26 Zinc Solution, Stock. 1 mL = 1,000 µg Zn: Pickle zinc metal in (1 + 9) nitric acid to an exact weight of 0.100 g. Dissolve in 5 mL (1 + 1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with ASTM type I water.

8.4 Multi-Element Stock Standard Solutions

Care must be taken in the preparation of multi-element stock standards so that the elements are compatible and stable. Originating element stocks should be checked for impurities that might influence the accuracy of the standard. Freshly prepared standards should be transferred to acid-cleaned, not previously used FEP fluorocarbon bottles for storage and monitored periodically for stability. Suggested element combinations are:

Standard Solution A		Standard Solution B
Aluminum	Manganese	Barium
Antimony	Molybdenum	Silver
Arsenic	Nickel	
Beryllium	Selenium	
Cadmium	Thallium	
Chromium	Thorium	
Cobalt	Uranium	
Copper	Vanadium	
Lead	Zinc	

Multi-element stock standard solutions A and B (1 mL = 10 µg) may be prepared by diluting 1 mL of each single element stock in the combination list to 100 mL with ASTM type I water containing 1% (v/v) nitric acid.

Fresh multi-element calibration standards should be prepared every 2 weeks, or as needed. Dilute each of the stock multi-element standard solutions A and B to levels appropriate to the operating range of the instrument using ASTM type I water containing 1% (v/v) nitric acid. The element concentrations in the standards should be sufficiently high to produce good measurement precision and to accurately define the slope of the response curve. Concentrations of 200 µg/L are suggested. If the direct addition procedure and internal standards (see Section 8.5) to the calibration standards are being used, store in Teflon® bottles. Calibration standards should be verified initially using a quality control sample (see Section 8.8).

8.5 Internal Standards Stock Solution, 1 mL = 100 µg

Dilute 10 mL of scandium, yttrium, indium, terbium and bismuth stock standards (Section 8.3) to 100 mL with ASTM type I water and store in Teflon® bottle. Use this solution concentrate to add to blanks, calibration standards, and samples or dilute by an appropriate amount using 1% (v/v) nitric acid, if the internal standards are being added by peristaltic pump.

8.6 Blanks

Three types of blanks are required for this method. A calibration blank establishes the analytical calibration curve. The laboratory reagent blank assesses possible contamination from the sample preparation procedure and spectral background. The rinse blank flushes the instrument between samples to reduce memory interferences.

8.6.1 Calibration blank consists of 1% (v/v) nitric acid in ASTM type I water. If the direct addition procedure is being used, add internal standards.

8.6.2 Laboratory reagent blank (LRB) must contain all the reagents in the same volumes as used in processing the samples. The LRB must be carried through the entire sample digestion and preparation scheme. If the direct addition procedure is being used, add internal standards to the solution after preparation is complete.

8.6.3 Rinse blank consists of 2% (v/v) nitric acid in ASTM type I water.

8.7 Tuning Solution

This solution is used for instrument tuning and mass calibration prior to analysis. The solution is prepared by mixing beryllium, magnesium, cobalt, indium and lead stock solutions (see Section 8.3) in 1% (v/v) nitric acid to produce a concentration of 100 µg/L of each element. Internal standards are not added to this solution.

8.8 Quality Control Sample (QCS)

The QCS should be obtained from a source outside the laboratory. Dilute an appropriate aliquot of analytes (concentrations not to exceed 1,000 µg/L) in 1% (v/v) nitric acid. If the direct addition procedure is being used, add internal standards after dilution, mix, and store in a Teflon® bottle.

8.9 Laboratory Fortified Blank (LFB)

To an aliquot of LFB, add aliquots from multi-element stock standards A and B (see Section 8.4) to produce the LFB with a final concentration of 100 µg/L for each analyte. The LFB must be carried through the entire sample digestion and preparation scheme. If the direct addition procedure is being used, add internal standards to this solution after preparation.

9. Sample Receipt in the Laboratory

9.1 The sample should be received from the extraction laboratory as documented in Inorganic Compendium Method IO-3.1.

9.2 No additional preservation is needed at this time. Sample is ready for ICP/MS analysis. However, the samples contain hydrochloric acid, and the calibration standards do not. Correction for interferences for chloride must be made (see Section 13.4).

10. Calibration and Standardization

10.1 Calibration

[Note: Demonstration and documentation of acceptable initial calibration is required before samples are analyzed and periodically throughout sample analysis as dictated by results of continuing calibration checks. After initial calibration is successful, a calibration check is required at the beginning and end of each period during which analyses are performed and at requisite intervals.]

10.1.1 Allow a period of not less than 30 min for instrument warm up. During this process, conduct mass calibration and resolution checks using the tuning solution. Resolution at low mass is indicated by magnesium isotopes 24, 25, and 26. Resolution at high mass is indicated by lead isotopes 206, 207, and 208. For good performance, adjust spectrometer resolution to produce a peak width of approximately 0.75 amu at 5% peak height. Adjust mass calibration if it has shifted by more than 0.1 amu from unit mass.

10.1.2 Instrument stability must be demonstrated by running the tuning solution (see Section 8.7) a minimum of five times with resulting relative standard deviations of absolute signals for all analytes of less than 5%.

10.1.3 Prior to initial calibration, set up proper instrument software routines for quantitative analysis. The instrument must be calibrated for the analytes to be determined using the calibration blank (see Section 8.6.1) and calibration standards A and B (see Section 8.4) prepared at one or more concentration levels. A minimum of three replicate integrations are required for data acquisition. Use the average of the integrations for instrument calibration and data reporting.

10.1.4 The rinse blank should be used to flush the system between solution changes for blanks, standards, and samples. Allow sufficient rinse time to remove traces of the previous sample or a minimum of 1 min. Solutions should be aspirated for 30 s prior to the acquisition of data to establish equilibrium.

10.2 Internal Standardization

10.2.1 Internal standardization must be used in all analyses to correct for instrument drift and physical interferences. A list of acceptable internal standards is provided in Table 4.

10.2.2 For full mass range scans, a minimum of three internal standards must be used. Procedures described in this method for general application detail five internal standards: scandium, yttrium, indium, terbium, and bismuth. These standards were used to generate the precision and recovery data attached to this method. Internal standards must be present in all samples, standards, and blanks at identical levels.

10.2.3 This may be achieved by directly adding an aliquot of the internal standards to the CAL standard, blank, or sample solution or alternatively by mixing with the solution prior to nebulization using a second channel of the peristaltic pump and a mixing coil. The concentration of the internal standard should be sufficiently high to obtain a precise measurement of the isotope used for data correction and to minimize the possibility of correction errors if the internal standard is naturally present in the sample.

10.2.4 A concentration of 200 µg/L of each internal standard is recommended. Internal standards should be added to blanks, samples, and standards in a like manner so that dilution effects from the addition may be disregarded.

10.3 Instrument Performance

[Note: Check the performance of the instrument and verify the calibration using data gathered from analyses of calibration blanks, calibration standards and the QCS.]

10.3.1 After establishing calibration, it must be initially verified for all analytes by analyzing the QCS (see Section 8.8). If measurements exceed ± 10% of the established QCS value, terminate the analysis, identify and correct the problem, recalibrate the instrument, and reverify the calibration reverified before continuing analyses.

10.3.2 To verify that the instrument is properly calibrated on a continuing basis, run the calibration blank and calibration standards as surrogate samples after every 10 analyses. The results of the analyses of the standards will indicate whether the calibration remains valid. If the indicated concentration of any analyte deviates from the true concentration by more than 10%, reanalyze the standard. If the analyte is again outside the 10% limit, the instrument must be recalibrated and the previous ten samples reanalyzed. The instrument responses from the calibration check may be used for recalibration purposes. If the sample matrix is responsible for the calibration drift, the previous 10 samples should be reanalyzed in groups of five between calibration checks to prevent a similar drift situation from occurring.

11. Quality Control (QC)

11.1 Laboratory

Each laboratory using this method is required to operate a formal QC program. The minimum requirements of this program are an initial demonstration of laboratory capability and the analysis of laboratory reagent blanks, fortified blanks, and samples as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of the data thus generated.

11.2 Initial Demonstration of Performance

11.2.1 The initial demonstration of performance is used to characterize instrument performance (method detection limits and linear calibration ranges) for analyses conducted by this method.

11.2.2 Method detection limits (MDL) should be established for all analytes, using reagent water (blank) fortified at a concentration of two to five times the estimated detection limit. To determine MDL values, take seven replicate aliquots of the fortified reagent water and process through the entire analytical method. Perform all calculations defined in the method and report the concentration values in the appropriate units. Calculate the MDL as follows:

$$MDL = (t) \times (S)$$

where:

t = Student's t value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom [t = 3.14 for seven replicates].
S = standard deviation of the replicate analyses.

MDLs should be determined every 6 months or whenever a significant change in background or instrument response is expected (e.g., detector change).

11.2.3 Linear calibration ranges are primarily detector limited. The upper limit of the linear calibration range should be established for each analyte by determining the signal responses from a minimum of three different concentration standards, one of which is close to the upper limit of the linear range. Avoid damage to the detector during this process. The linear calibration range, which may be used for the analysis of samples, should be judged by the analyst from the resulting data. Linear calibration ranges should be determined every 6 months or whenever a significant change in instrument response is expected (e.g., detector change).

11.3 General Quality Control

[Note: The required general quality control requirements for ICP analysis are discussed below and summarized in Table 8.]

11.3.1 Initial Calibration. At least two calibration standards and a calibration blank are analyzed at the beginning of an analysis run. The standards used to calibration are diluted from certified stock standards and are used within the expiration dates. The calibration standards and blanks are prepared in the same matrix as the samples.

11.3.2 Initial Calibration Verification (ICV). The QCS is analyzed immediately following initial calibration to verify the initial calibration. The QCS is prepared at the midpoints of the calibration curves. It is prepared from certified stocks having a different manufacturer than the calibration standards. The measured concentration should be within 90% to 110% of the actual concentration.

11.3.3 Initial Calibration Blank (ICB). The ICB is analyzed immediately following ICV and prior to the high standard verification. The acceptance criteria for the ICB is the same as for continuing calibration blank (CCB) verification.

11.3.4 High Standard Verification (HSV). Immediately after the analysis of the ICB, and prior to the analysis of samples, the HSVs are reanalyzed. The measured concentration should be within 95% to 105% of actual concentration.

11.3.5 Interference Check Standards (ICS). The ICSs are analyzed at the beginning and end of the run and for every 8 hours of continuous operation. The results for the analytes should be within 80% and 120% of the actual concentration. Samples containing levels of interferences above the levels in the ICS should be considered for dilution.

11.3.6 Continuing Calibration Verification (CCV). CCV standards are prepared from the calibration standard stocks at the midpoint of the calibration curve. The CCV standards are analyzed at the beginning of the run prior to samples, after every 10 samples, and at the end of the run prior to the last continuing calibration blank (CCB) analysis. The measured concentration should be within 90% and 110% of the actual concentration.

11.3.7 Continuing Calibration Blanks (CCBs). The CCBs are analyzed following each CCV. The results of the CCBs are evaluated as follows:

- The CCBs are compared to the method detection limits.
- The absolute value of the instrument response must be less than the method detection limits.
- If not, then sample results for analyses < 5 times the amount of the blank must be flagged or analysis must be repeated.

11.3.8 Method Blank (MB). A MB sample is prepared and analyzed with each sample batch. This analysis is used to determine if concentrations reflect background levels from sample digestion. If the instrument measured response is greater than the method detection limits, then the sample results for the affected analyte(s) must be flagged. Samples may be considered candidates for redigestion and reanalysis for that analyte.

11.3.9 Laboratory Control Spike (LCS). An LCS is the same as a laboratory fortified blank. An LCS is prepared and analyzed with each sample batch (or 1 per 20 samples). The results for the analytes should be within 80% to 120% of actual concentration. If the results are not within this criterion, then the results must be qualified.

11.3.10 Matrix Spike (MS). A MS sample is prepared and analyzed with each sample batch (or 1 per 20 samples). These samples are used to provide information about the effect of the sample matrix on the digestion and measurement methodology. The spike is added before the digestion, (i.e., prior to the addition of other reagents). The percent recovery for the analyte as part of the MS should be between 75% and 125% for all analytes.

11.3.11 Duplicate and/or Spike Duplicate. Duplicate samples and/or matrix spike duplicates are prepared and analyzed with each sample batch. These samples are used to estimate method precision,

expressed as relative percent difference (RPD). The RPD between the duplicate and/or matrix spike duplicate final concentrations should be <20%.

11.3.12 Serial Dilution. The ICP serial dilution analysis must be performed on one sample per batch. After a fivefold serial dilution, the analyte concentration must be within 90% and 110% of the undiluted sample results.

11.3.13 Sample Dilution. Dilute and reanalyze samples that are more concentrated than the linear calibration limit.

11.4 Assessing Analyte Recovery - Laboratory Fortified Sample Matrix

11.4.1 The laboratory must add a known amount of analyte to a minimum of 5% of the routine samples or one sample per sample set, whichever is greater.

11.4.2 Calculate the percent recovery for each analyte, corrected for background concentrations measured in the unfortified sample and compare these values to the control limits established in Section 11.3.3 for the analyses of LFBs. Recovery calculations are not required if the concentration of the analyte added is less than 10% of the sample background concentration. Percent recovery may be calculated in units appropriate to the matrix using the following equation:

$$R = (C_s - C)/s \times 100$$

where:

R = percent recovery, %.

C_s = fortified sample concentration, ng/L.

C = sample background concentration, ng/L.

s = concentration equivalent of fortifier added to sample, ng/L.

11.4.3 If recovery of any analyte falls outside the designated range and laboratory performance for that analyte is shown to be in control (see Section 11.3), the recovery problem encountered with the fortified sample is judged to be matrix-related, not system-related. The analyte in the unfortified sample must be labeled "suspect/matrix" to inform the user that the results are suspect due to matrix effects.

11.5 Internal Standards Responses

The analyst is expected to monitor the responses from the internal standards throughout the sample set being analyzed. Ratios of the internal standards responses against each other should also be monitored routinely. This information may be used to detect potential problems caused by mass dependent drift, errors incurred in adding the internal standards, or increases in the concentrations of individual internal standards caused by background contributions from the sample. The absolute response of any one internal standard should not deviate more than 60-125% of the original response in the calibration blank. If deviations greater than this are observed, use the following test procedure:

11.5.1 Flush the instrument with the rinse blank and monitor the responses in the calibration blank. If the responses of the internal standards are now within the limit, take a fresh aliquot of the sample, dilute by a further factor of two, add the internal standards and reanalyze.

11.5.2 If the test is not satisfied or if it is a blank or calibration standard that is out of limits, terminate the analysis and determine the cause of the drift. Possible causes may be a partially blocked sampling cone or a change in the tuning condition of the instrument.

12. Procedure

12.1 Samples should be received from the extraction laboratory in a 10-mL centrifuge tube. The samples contain a mixture of nitric and hydrochloric acids. This is not the most appropriate solution for ICP/MS determination. Therefore, corrections described in Section 13.4 must be applied.

12.2 For every new or unusual matrix, a semi-quantitative analysis should be carried out to screen for high element concentrations. Information gained from this procedure may be used to prevent potential damage to the detector during sample analysis and to identify elements that may be higher than the linear range. Matrix screening may be carried out by using intelligent software, if available, or by diluting the sample by a factor of 500 and analyzing in a semi-quantitative mode. The sample should also be screened for background levels of all elements chosen for use as internal standards to prevent bias.

12.3 Initiate instrument operating configuration. Tune and calibrate the instrument for the analytes of interest (see Section 10).

12.4 Establish instrument software run procedures for quantitative analysis. For all sample analyses, a minimum of three replicate integrations are required for data acquisition. Discard any integrations considered to be statistical outliers and use the average of the integrations for data reporting.

12.5 Monitor all masses that might affect data quality during the analytical run. At a minimum, those masses prescribed in Table 5 must be monitored in the same scan as is used for the collection of the data. This information should be used to correct the data for identified interferences.

12.6 Use the rinse blank to flush the system between samples. Allow sufficient time to remove traces of the previous sample or a minimum of 1 min. Aspirate the samples for 30 s prior to the collection of data.

12.7 Samples having concentrations higher than the established linear dynamic range should be diluted into range and reanalyzed. First, analyze the sample for trace elements, protecting the detector from the high concentration elements, if necessary, by selecting appropriate scanning windows. Then dilute the sample to determine the remaining elements. Alternatively, the dynamic range may be adjusted by selecting an alternative isotope of lower natural abundance, provided quality control data for that isotope have been established. Do not adjust the dynamic range by altering instrument conditions to an uncharacterized state.

13. Calculations

13.1 Elemental equations recommended for sample data calculations are listed in Table 6. Sample data should be reported in units of ng/m^3.

13.1.1 Calculate the air volume sampled, corrected to EPA-reference conditions:

$$V_{std} = V_s \left(\frac{T_{std}}{T_m}\right)\left(\frac{P_{bar}}{P_{std}}\right)$$

where:

V_{std} = volume of ambient air sampled at EPA-reference conditions, m^3

V_s = volume of ambient air pulled through the sampler, m^3.

T_{std} = absolute EPA-reference temperature, 298EK.

T_m = average ambient temperature, EK.

P_{bar} = barometric pressure during sampling measurement condition, mm Hg.

P_{std} = EPA-reference barometric pressure, 760 mm Hg.

13.1.2 Metal concentration in the air sample can then be calculated as follows:

$$C = [(\mu g \text{ metal/mL}) \times (\text{Digestion volume (i.e., 20 mL) mL/strip})(9) - F_m]/V_{std}$$

where:

C = concentration, µg metal/m^3.

µg metal/mL = metal concentration determined from Section 12.

final extract volume (mL)/strip = total sample extraction volume from extraction procedure (i.e., 20 mL).

$$9 = \frac{\text{Useable filter area, [20 cm x 23 cm (8" x 9")]}}{\text{Exposed area of one strip, [2.5 cm x 20 cm (1" x 8")].}}$$

F_m = average concentration of blank filters, µg.

V_{std} = standard air volume pulled through filter, std. m^3 (25EC and 760 mm Hg).

Do not report element concentrations below the determined MDL.

13.2 For data values less than 10, use two significant figures to report element concentrations. For data values greater than or equal to 10, three significant figures.

13.3 Reported values should be calibration blank subtracted (see Inorganic Compendium Method IO-3.1).

13.4 Correct data values for instrument drift or sample matrix induced interferences by applying internal standardization. Corrections for characterized spectral interferences should be applied to the data. Chloride interference corrections should be made on all samples, because of the addition of hydrochloric acid during filter extraction, as the chloride ion is a common constituent of environmental samples.

13.5 If an element has more than 1 monitored isotope, examine the concentration calculated for each isotope, or the isotope ratios, to detect a possible spectral interference. Consider both primary and secondary isotopes when evaluating the element concentration. In some cases, secondary isotopes may be

less sensitive or more prone to interferences that the primary recommended isotopes; therefore, differences between the results do not necessarily indicate a problem with data calculated for the primary isotopes.

13.6 The QC data obtained during the analyses provide an indication of the quality of the sample data and should be provided with the sample results.

14. Precision and Accuracy

14.1 Instrument operating conditions for single laboratory testing of the method are summarized in Table 3.

14.2 Data obtained from single laboratory testing of the method for three solid samples consisting of SRM 1645 River Sediment, EPA Hazardous Soil, and EPA Electroplating Sludge are summarized in Table 7. For each method element, the sample background concentration, mean percent recovery, standard deviation of the percent recovery, and relative percent difference between the duplicate fortified samples were determined. Data for matrices other than air are presented because only very limited data on air samples was available when this method was written.

14.3 Activities required to be performed using ICP/MS to validate method precision and accuracy are summarized in Table 8.

15. References

1. "Standard Operating Procedures for the ICP-DES Determination of Trace Elements in Suspended Particulate Matter Collected on Glass-Fiber Filters," EMSL/RTP-SOP-EMO-002, Revision, October, 1983.

2. "Reference Method for the Determination of Suspended Particulates in the Atmosphere (High Volume Method)," *Code of Federal Regulations*, Title 40, Part 50, Appendix B, pp. 12-16 (July 1, 1975).

3. "Reference Method for the Determination of Lead in Suspended Particulate Matter Collected from Ambient Air.," *Federal Register* 43 (194): 46262-3, 1978.

4. Rhodes, R.C., 1981, "Special Extractability Study of Whatman and Schleicher and Schuell Hi-Vol Filters," Memo to file, August 5, 1981, Quality Assurance Division, Environmental Monitoring Systems Laboratory, U. S. Environmental Protection Agency, Research Triangle Park NC.

5. Ward, A. F., *The Jarrell-Ash Plasma Newsletter*, Volumes I, II, and III.

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7. "Simplex Optimization of Multielement Ultrasonic Extraction of Atmospheric Particulates," Harper, et. al., *Analytical Chemistry*, Vol 55(9), August 1983.

8. A. L. Gray and A. R. Date, *Analyst*, Vol 108:1033.

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10. R. S. Houk, *Anal. Chem*. Vol. 58(97A).

11. J. J. Thompson and R. S. Houk, *Appl. Spec.*, Vol. 41:801, 1987.

12. "OSHA Safety and Health Standards, General Industry," (29 CFR 1910), Occupational Safety and Health Administration, OSHA 2206, revised January 1976.

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14. *Code of Federal Regulations* 40, Ch. 1, Pt. 136 Appendix B.

TABLE 1. ESTIMATED METHOD DETECTION[a] LIMITS

Element	Recommended analytical mass	Estimated Method Detection Limits (MDLs)[b]	
		µg/L	ng/m^3
Aluminum	27	0.05	0.01
Antimony	121	0.08	0.01
Arsenic	75	0.9	0.30
Barium	137	0.5	0.10
Beryllium	9	0.1	0.02
Cadmium	111	0.1	0.02
Chromium	52	0.07	0.01
Cobalt	59	0.03	0.01
Copper	63	0.03	0.01
Lead	206,207,208	0.08	0.01
Manganese	55	0.1	0.02
Molybdenum	98	0.1	0.02
Nickel	60	0.2	0.02
Selenium	82	5	1.10
Silver	107	0.05	0.01
Thallium	205	0.09	0.01
Thorium	232	0.03	0.01
Uranium	238	0.02	0.01
Vanadium	51	0.02	0.01
Zinc	66	0.2	0.04

[a]Instrument detection limits (3F) estimated from seven replicate integrations of the blank (1% v/v nitric acid) following calibration of the instrument with three replicate integrations of a multi-element standard.

[b]Based upon sampling rate of 1.13 m^3/min for 24-h for a total sample volume of 1,627.2 m^3, factor of 9 for partial filter analysis; digestion of 0.040 L/filter.

TABLE 2. COMMON POLYATOMIC ION INTERFERENCES IN ICP-MS

BACKGROUND MOLECULAR IONS		
Molecular Ion	**Mass**	**Element Interference**[1]
NH^+	15	
OH^+	17	
OH_2^+	18	
C_2^+	24	
CN^+	26	
CO^+	28	
N_2^+	28	
N_2H^+	29	
NO^+	30	
NOH^+	31	
O_2^+	32	
OH^+	33	
$^{36}ArH^+$	37	
$^{38}ArH^+$	39	
$^{40}ArH^+$	41	
CO_2^+	44	
CO_2H^+	45	Sc
ArC^+, ArO^+	52	Cr
ArN^+	54	Cr
$ArNH^+$	55	Mn
ArO^+	56	
$ArOH^+$	57	
$^{40}Ar^{36}Ar^+$	76	Se
$^{40}Ar^{38}Ar^+$	78	Se
$^{40}Ar_2$	80	Se

TABLE 2. (continued)

MATRIX MOLECULAR IONS		
CHLORIDE **Polyatomic Ion**	**Mass**	**Element Interference**
$^{35}ClO^+$	51	V
$^{35}ClOH^+$	52	Cr
$^{37}ClO^+$	53	Cr
$^{37}ClOH^+$	54	Cr
$Ar^{35}Cl^+$	75	As
$Ar^{37}Cl^+$	77	Se
SULFATE **Polyatomic Ion**	**Mass**	**Element Interference**
$^{32}SO^+$	48	T_i
$^{32}SOH^+$	49	T_i
$^{34}SO^+$	50	V, Cr
$^{34}SOH^+$	51	V
SO_2, S_2^+	64	Zn
$Ar^{32}S^+$	72	
$Ar^{34}S^+$	74	
PHOSPHATE **Polyatomic Ion**	**Mass**	**Element Interference**
PO^+	47	
POH^+	48	
PO_2^+	63	Cu
ArP^2	71	
GROUP I, II METALS **Polyatomic Ion**	**Mass**	**Element Interference**
$ArNa^+$	63	Cu
ArK^+	79	
$ArCa^+$	80	
MATRIX OXIDES[2] **Polyatomic Ion**	**Masses**	**Element Interference**
TiO	62-66	Ni, Cu, Zn
ZrO	106-112	Ag, Cd
MoO	108-116	Cd

[1]Method elements or internal standards affected by the polyatomic ions.

[2]Oxide interferences will normally be very small and will only impact the method elements when present at relatively high concentrations. Some examples of matrix oxides are listed of which the analyst should be aware. It is recommended that Ti and Zr isotopes are monitored in solid waste samples, which are likely to contain high levels of these elements. Mo is monitored as a method analyte.

TABLE 3. EXAMPLE INSTRUMENT OPERATING CONDITIONS

Instrument	VG PlasmaQuad Type I
Plasma forward power	1.35 kW
Coolant flow rate	13.5 L/min
Auxiliary flow rate	0.6 L/min
Nebulizer flow rate	0.78 L/min
Solution uptake rate	0.6 mL/min
Spray chamber temperature	15EC
Data Acquisition	
Detector mode	Pulse counting
Replicate integrations	3
Mass range	8 - 240 amu
Dwell time	320 µs
Number of MCA channels	2048
Number of scan sweeps	85
Total acquisition time	3 min per sample

TABLE 4. INTERNAL STANDARDS AND LIMITATIONS OF USE

Internal Standard	Mass	Possible Limitation
Lithium	6	a
Scandium	45	polyatomic ion interference
Yttrium	89	a,b
Rhodium	103	
Indium	115	isobaric interference by Sn
Terbium	159	
Holmium	165	
Lutetium	175	
Bismuth	209	a

[a]May be present in environmental samples.
[b]In some instruments yttrium may form measurable amounts of YO^+ (105 amu) and YOH^+ (106 amu). If this is the case, care should be taken in the use of the cadmium elemental correction equation.

TABLE 5. RECOMMENDED ANALYTICAL ISOTOPES AND ADDITIONAL MASSES WHICH MUST BE MONITORED

Isotope	Element of Interest
27	Aluminum
121,123	Antimony
75	Arsenic
135,137	Barium
9	Beryllium
106,108,111,114	Cadmium
52,53	Chromium
59	Cobalt
63,65	Copper
206,207,208	Lead
55	Manganese
95,97,98	Molybdenum
60,62	Nickel
77,82	Selenium
107,109	silver
203,205	Thallium
232	Thorium
238	Uranium
51	Vanadium
66,67,68	Zinc
83	Krypton
99	Ruthenium
105	Palladium
118	Tin

NOTE: Isotopes recommended for analytical determination are underlined.

TABLE 6. RECOMMENDED ELEMENTAL EQUATIONS FOR DATA CALCULATIONS

Element	Element Equation	Note
A1	$(1.000)(^{27}C)$	
Sb	$(1.000)(^{121}C)$	
As	$(1.000)(^{75}C)-(3.127)[(^{77}C)-(0.815)(^{82}C)]$	(1)
Ba	$(1.000)(^{137}C)$	
Be	$(1.000)(^{9}C)$	
Cd	$(1.000)(^{111}C)-(1.073)[(^{108}C)-(0.712)(^{106}C)]$	(2)
Cr	$(1.000)(^{52}C)$	(3)
Co	$(1.000)(^{59}C)$	
Cu	$(1.000)(^{63}C)$	
Pb	$(1.000)(^{206}C)+(1.000)(^{207}C)+(1.000)(^{208}C)$	(4)
Mn	$(1.000)(^{55}C)$	
Mo	$(1.000)(^{98}C)-(0.146)(^{99}C)$	(5)
Ni	$(1.000)(^{60}C)$	
Se	$(1.000)(^{82}C)$	(6)
Ag	$(1.000)(^{107}C)$	
Tl	$(1.000)(^{205}C)$	
Th	$(1.000)(^{232}C)$	
U	$(1.000)(^{238}C)$	
V	$(1.000)(^{51}C)-(3.127)[(^{53}C)-(0.113)(^{52}C)]$	(7)
Zn	$(1.000)(^{66}C)$	
Bi	$(1.000)(^{209}C)$	
In	$(1.000)(^{115}C)-(0.016)(^{118}C)$	(8)
Sc	$(1.000)(^{45}C)$	
Tb	$(1.000)(^{159}C)$	
Y	$(1.000)(^{89}C)$	

C - calibration blank subtracted counts at specified mass.
(1) - correction for chloride interference with adjustment for Se77. ArCl 75/77 ratio may be determined from the reagent blank.
(2) - correction for MoO interference. An additional isobaric elemental correction should be made if palladium is present.
(3) - in 0.4% v/v HCl, the background from ClOH will normally be small. However, the contribution may be estimated from the reagent blank.
(4) - allowance for isotopic variability of lead isotopes.
(5) - isobaric elemental correction for ruthenium.
(6) - some argon supplies contain krypton as an impurity. Selenium is corrected for Kr82 by background subtraction.
(7) - correction for chloride interference with adjustment for Cr53 ratio may be determined from the reagent blank.
(8) - isobaric elemental correction for tin.

TABLE 7. PRECISION AND RECOVERY DATA

EPA HAZARDOUS SOIL #884

Element	Sample Concn. (µg/L)	Low Spike (µg/L)	Average Recovery R (%)	S(R)	RPD	High Spike (µg/L)	Average Recovery R (%)	S(R)	RPD
Al	5170	20	*	*	-	100	*	*	-
Sb	5.4	20	69.8	2.5	4.7	100	70.4	1.8	6.5
As	8.8	20	104.7	5.4	9.1	100	102.2	2.2	5.4
Ba	113	20	54.9	63.6	18.6	100	91.0	9.8	0.5
Be	0.6	20	100.1	0.6	1.5	100	102.9	0.4	1.0
Cd	1.8	20	97.3	1.0	1.4	100	101.7	0.4	1.0
Cr	83.5	20	86.7	16.1	8.3	100	105.5	1.3	0.0
Co	7.1	20	98.8	1.2	1.9	100	102.9	0.7	1.8
Cu	115	20	86.3	13.8	3.4	100	102.5	4.2	4.6
Pb	152	20	85.0	45.0	13.9	100	151.7	25.7	23.7
Mn	370	20	*	*	12.7	100	85.2	10.4	2.2
Mo	4.8	20	95.4	1.5	2.9	100	95.2	0.7	2.0
Ni	19.2	20	101.7	3.8	1.0	100	102.3	0.8	0.8
Se	< 3.2	20	79.5	7.4	26.4	100	100.7	9.4	26.5
Ag	1.1	20	96.1	0.6	0.5	100	94.8	0.8	2.3
Tl	0.24	20	94.3	1.1	3.1	100	97.9	1.0	2.9
Th	1.0	20	69.8	0.6	1.3	100	76.0	2.2	7.9
U	1.1	20	100.1	0.2	0.0	100	102.9	0.0	0.0
V	17.8	20	109.2	4.2	2.3	100	106.7	1.3	2.4
Zn	128	20	87.0	27.7	5.5	100	113.4	12.9	14.1

S(R) Standard deviation of percent recovery.
RPD Relative percent difference between duplicate spike determinations.
< Sample concentration below established method detection limit.
* Spike concentration < 10% of sample background concentration.
- Not determined.
+ Equivalent.

TABLE 7. PRECISION AND RECOVERY DATA (continued)

NBS 1645 RIVER SEDIMENT

Element	Sample Concn. (µg/L)	Low Spike (µg/L)	Average Recovery R (%)	S(R)	RPD	High Spike (µg/L)	Average Recovery R (%)	S(R)	RPD
Al	5060	20	*	*	-	100	*	*	-
Sb	21.8	20	73.9	6.5	9.3	100	81.2	1.5	3.9
As	67.2	20	104.3	13.0	7.6	100	107.3	2.1	2.9
Ba	54.4	20	105.6	4.9	2.8	100	98.6	2.2	3.9
Be	0.59	20	88.8	0.2	0.5	100	87.9	0.1	0.2
Cd	8.3	20	92.9	0.4	0.0	100	95.7	1.4	3.9
Cr	29100	20	*	*	-	100	*	*	-
Co	7.9	20	97.6	1.3	2.6	100	103.1	0.0	0.0
Cu	112	20	121.0	9.1	1.5	100	105.2	2.2	1.8
Pb	742	20	*	*	-	100	-	-	-
Mn	717	20	*	*	-	100	-	-	-
Mo	17.1	20	89.8	8.1	12.0	100	98.4	0.7	0.9
Ni	41.8	20	103.7	6.5	4.8	100	102.2	0.8	0.0
Se	< 3.2	20	108.3	14.3	37.4	100	93.9	5.0	15.1
Ag	1.8	20	94.8	1.6	4.3	100	96.2	0.7	1.9
Tl	1.2	20	91.2	1.3	3.6	100	94.4	0.4	1.3
Th	0.90	20	91.3	0.9	2.6	100	92.3	0.9	2.8
U	0.79	20	95.6	1.8	5.0	100	98.5	1.2	3.5
V	21.8	20	91.8	4.6	5.7	100	100.7	0.6	0.8
Zn	1780	20	*	*	-	100	*	*	-

S(R) Standard deviation of percent recovery.
RPD Relative percent difference between duplicate spike determinations.
< Sample concentration below established method detection limit.
* Spike concentration < 10% of sample background concentration.
- Not determined.
+ Equivalent.

TABLE 7. PRECISION AND RECOVERY DATA (continued)

EPA ELECTROPLATING SLUDGE #286

Element	Sample Concn. (µg/L)	Low Spike (µg/L)	Average Recovery R (%)	S(R)	RPD	High Spike (µg/L)	Average Recovery R (%)	S(R)	RPD
Al	5110	20	*	*	-	100	*	*	-
Sb	8.4	20	55.4	1.5	4.1	100	61.0	0.2	0.9
As	41.8	20	91.0	2.3	1.7	100	94.2	0.8	1.5
Ba	27.3	20	1.8	7.1	8.3	100	0	1.5	10.0
Be	0.25	20	92.0	0.9	2.7	100	93.4	0.3	0.9
Cd	112	20	85.0	5.2	1.6	100	88.5	0.8	0.5
Cr	7980	20	*	*	-	100	*	*	-
Co	4.1	20	89.2	1.8	4.6	100	88.7	1.5	4.6
Cu	740	20	*	*	6.0	100	61.7	20.4	5.4
Pb	1480	20	*	*	-	100	*	*	-
Mn	295	20	*	*	-	100	-	-	-
Mo	13.3	20	82.9	1.2	1.3	100	89.2	0.4	1.0
Ni	450	20	*	*	6.8	100	83.0	10.0	4.5
Se	3.5	20	89.7	3.7	4.2	100	91.0	6.0	18.0
Ag	5.9	20	89.8	2.1	4.6	100	85.1	0.4	1.1
Tl	1.9	20	96.9	0.9	2.4	100	98.9	0.9	2.4
Th	3.6	20	91.5	1.3	3.2	100	97.4	0.7	2.0
U	2.4	20	107.7	2.0	4.6	100	109.6	0.7	1.8
V	21.1	20	105.6	1.8	2.1	100	97.4	1.1	2.5
Zn	13300	20	*	*	-	100	*	*	-

S(R) Standard deviation of percent recovery.
RPD Relative percent difference between duplicate spike determinations.
< Sample concentration below established method detection limit.
* Spike concentration < 10% of sample background concentration.
- Not determined.
+ Equivalent.

TABLE 8. EXAMPLE OF QUALITY CONTROL REQUIREMENTS FOR ICP/MS ANALYSIS

QC procedure	Typical frequency	Criteria
Initial calibration (IC)	At the beginning of the analysis	None
Initial calibration verification (ICV) using the QCS	Immediately after initial calibration	90%-110% of the actual concentration
Initial calibration blank (ICB)	Immediately after initial calibration verification	May be less than project detection limits (MDLs)
High standard verification (HSV)	Following the initial calibration blank analysis	95%-105% of the actual concentration
Interference check standard (ICS)	Following the high standard verificatino, every 8 hours, and at the end of a run	80%-120% of the actual concentration
Continuing calibration verification (CCV)	Analyzed before the first sample, after every 10 samples, and at the end of the run	90%-110% of the actual concentration
Continuing clarification blanks (CCBs)	Analyzed following each continuing calibration verification	Must be less than project detection limits (MDLs)
Reagent blank (RB) or Method blank (MB)	1 per 40 samples, a minimum of 1 per batch	Must be less than project detection limits (MDLs)
Laboratory control spike (LCS) or Laboratory fortified blanks (LFB)	1 per 20 samples, a minimum of 1 per batch	80%-120% recovery, with the exception of Ag and Sb
Duplicate and/or spike duplicate	1 per sample batch	RPD $\leq$ 20%
Matrix spike (MS)	1 per 20 samples per sample batch	Percent recovery of 75%-125%
Serial dilution	1 per sample batch	90%-110% of undiluted sample
Sample dilution	Dilute sample beneath the upper calibration limit but no lower than at least 5X the MDL	As needed