Designation: D8110 – 17

Standard Test Method for
Elemental Analysis of Distillate Products by Inductively Coupled Plasma Mass Spectrometry (ICP-MS)[1]

This standard is issued under the fixed designation D8110; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

INTRODUCTION

Certain elements present in distillate petroleum can either adversely or constructively affect the performance of the product and thus impacts its utility and market value. The industry has traditionally relied on inductively coupled plasma atomic emission spectrometry (ICP-AES) or atomic absorption spectrometry (AAS) to determine the concentration of these elements present in the product. As specifications have become more stringent, a need to extend these measurements to lower concentrations by employing more sensitive measurement technologies has arisen. Inductively coupled plasma mass spectrometry is ideal for this application for most distillate petroleum products. By applying ICP-MS for elemental analysis of these products, the concentration range of detectable elements can be extended from low to sub ng/g (ppb mass) to 1000 ng/g (ppb mass) for some elements.

1. Scope

1.1 This test method describes the procedure for the determination of trace elements in light and middle distillate petroleum products using inductively coupled plasma mass spectrometry (ICP-MS).

1.2 This test method should be used by analysts experienced in the use of inductively coupled plasma mass spectrometry (ICP-MS) with knowledge of interpretation of spectral, isobaric, polyatomic, and matrix interferences, as well as procedures for their correction or reduction.

1.3 The table in 6.1 lists elements for which the test method applies along with recommended isotope. Actual working detection limits are sample dependent and, as the sample matrix varies, these detection limits may also vary.

1.4 The concentration range of this test method is typically from low to sub ng/g (ppb mass) to 1000 ng/g (ppb mass), however the precision and bias statement is specified for a smaller concentration range based on test samples analyzed in the ILS, see the table in Section 18. The test method may be used for concentrations outside of this range; however, the precision statements may not be applicable.

1.4.1 This test method shall be further developed to extend that table to include additional elements.

1.5 This test method uses metallo-organic standards (organometallic or organosoluble metal complex) for calibration and does not purport to quantitatively determine insoluble particulates. Analytical results are particle size dependent, and low results are obtained for particles larger than a few micrometers as these particles may settle out in the sample container and are not effectively transported through the sample introduction system.

1.6 Elements present at concentrations above the upper limit of the calibration curves can be determined with additional, appropriate dilutions and with no degradation of precision.

1.7 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.8 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* Specific warning statements are given in 8.2, 8.7, and Section 9.

1.9 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D3605 Test Method for Trace Metals in Gas Turbine Fuels by Atomic Absorption and Flame Emission Spectroscopy

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D4175 Terminology Relating to Petroleum Products, Liquid Fuels, and Lubricants

D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products

D4306 Practice for Aviation Fuel Sample Containers for Tests Affected by Trace Contamination

D4307 Practice for Preparation of Liquid Blends for Use as Analytical Standards

D4628 Test Method for Analysis of Barium, Calcium, Magnesium, and Zinc in Unused Lubricating Oils by Atomic Absorption Spectrometry

D4927 Test Methods for Elemental Analysis of Lubricant and Additive Components—Barium, Calcium, Phosphorus, Sulfur, and Zinc by Wavelength-Dispersive X-Ray Fluorescence Spectroscopy

D4951 Test Method for Determination of Additive Elements in Lubricating Oils by Inductively Coupled Plasma Atomic Emission Spectrometry

D5185 Test Method for Multielement Determination of Used and Unused Lubricating Oils and Base Oils by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)

D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance

D6300 Practice for Determination of Precision and Bias Data for Use in Test Methods for Petroleum Products and Lubricants

D6443 Test Method for Determination of Calcium, Chlorine, Copper, Magnesium, Phosphorus, Sulfur, and Zinc in Unused Lubricating Oils and Additives by Wavelength Dispersive X-ray Fluorescence Spectrometry (Mathematical Correction Procedure)

D6732 Test Method for Determination of Copper in Jet Fuels by Graphite Furnace Atomic Absorption Spectrometry

D6792 Practice for Quality System in Petroleum Products and Lubricants Testing Laboratories

D7111 Test Method for Determination of Trace Elements in Middle Distillate Fuels by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)

D7220 Test Method for Sulfur in Automotive, Heating, and Jet Fuels by Monochromatic Energy Dispersive X-ray Fluorescence Spectrometry

D7343 Practice for Optimization, Sample Handling, Calibration, and Validation of X-ray Fluorescence Spectrometry Methods for Elemental Analysis of Petroleum Products and Lubricants

D7778 Guide for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

3. Terminology

3.1 *Definitions*—For definitions of other terms used in this test method, refer to Terminology D4175.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *analyte, n*—an element whose concentration is being determined. **D5185**

3.2.2 *calibration, n*—the determination of the values of the significant parameters by comparison with values indicated by a set of reference standards. **D7111**

3.2.3 *calibration curve, n*—the graphical or mathematical representation of a relationship between the assigned (known) values of standards and the measured responses from the measurement system. **D7111**

3.2.4 *calibration blank, n*—a volume of solvent containing the same matrix as the calibration standards (see Section 12).

3.2.5 *calibration standard, n*—a standard having an accepted value (reference value) for use in calibrating a measurement instrument or system (see Section 12). **D7111**

3.2.6 *calibration stock solution, n*—a solution prepared from the stock standard(s) or solution(s) to verify the instrument response with respect to analyte concentration.

3.2.7 *concentric nebulizer, n*—a device that generates an aerosol by flowing a liquid through a central capillary contained within a concentric tube through which gas flows at a high velocity.

3.2.8 *inductively-coupled plasma (ICP), n*—a high-temperature discharge generated by flowing an ionizable gas through a magnetic field induced by a radio frequency coil surrounding the tubes that carry the gas. **D7111**

3.2.9 *inductively coupled plasma mass spectrometry (ICP-MS), n*—an analytical technique that that utilizes ICP to generate elemental ions that are then separated and quantitated by mass spectrometry.

3.2.10 *internal standard, n*—chemical standard having an accepted value (and added to the fuel test specimen and calibration standard) to determine the emission intensity ratio of an element to the internal standard. **D7111**

3.2.10.1 *Discussion*—This is used to measure the relative instrument response to the other analytes that are components of the same solution. The internal standards must be analytes that are not a sample component.

3.2.11 *linear response range, n*—the elemental concentration range over which the calibration curve is a straight line, within the precision of the test method. **D5185**

3.2.12 *mass spectrometry, n*—the analytical process of separating and determining ions according to their mass-to-charge ratio.

3.2.13 *method detection limit (MDL), n*—the minimum concentration of an analyte that can be identified, measured and reported with 99 % confidence that the analyte concentration is greater than background noise.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

3.2.13.1 *Discussion*—This confidence level is determined from analysis of a sample in a given matrix containing the analyte(s).

3.2.14 *method of standard additions, n*—a technique whereby a known amount of the analyte is added to a portion of the sample and measured along with the sample as received; extrapolation of the measurements allows the concentration of the analyte in the original sample to be calculated.

3.2.15 *m/z, n*—mass to charge ratio, the measured signal for an ion determined by mass spectrometry; the charge is typically 1, so that the m/z = the mass.

3.2.16 *quality control reference solution (QCS), n*—a solution with the certified concentration(s) of the analytes (a reference source that is a secondary source to the calibration standards is preferred) and used for a verification of the instrument's calibration.

3.2.17 *radio frequency (RF), n*—the range of frequencies between 3 kHz and 300 GHz. **D7111**

3.2.18 *reagent blank, n*—a volume of solvent containing the same matrix as the samples.

4. Summary of Test Method

4.1 This test method describes the multi-element determination of trace elements by inductively coupled plasma mass spectrometry (ICP-MS). Sample material in solution is introduced by pneumatic nebulization into a radio frequency plasma where energy transfer processes cause desolvation, atomization, and ionization. The ions are extracted from the plasma through a differentially pumped vacuum interface and separated on the basis of their mass-to-charge ratio (m/z) by a mass spectrometer. The ions transmitted through the mass selector are detected by a dynode electron multiplier assembly and the ion information processed by a data handling system. Interferences relating to the technique must be recognized and a correction factor applied or the interferences must be reduced through the use of collision/reaction cell technology or alternatively through mass spectrometers utilizing high resolution or MS/MS modes of operation (see Section 6 on interferences). Such corrections must include compensation for isobaric elemental interferences and interferences from polyatomic ions derived from the plasma gas, reagents, sample matrix, peristaltic pump tubing, sample introduction system, cones, etc. Internal standardization or the method of standard additions must be used to correct for instrumental drift as well as suppressions or enhancements of instrument response caused by the sample matrix.

4.2 A weighed portion (approximately 1 g is typical) of a thoroughly homogenized light or middle distillate petroleum sample is diluted, by mass with *o*-xylene, or other suitable solvent (10× to 100× is typical) to bring the sample analytes within the measurement range or when necessary or desired. Standards are prepared in the same manner. Internal Standards such as those listed in 8.6 may be added to the solutions and the method of standard addition may be used to compensate for variations in test specimen introduction efficiency and element ionization efficiency in the plasma. In choosing an internal standard, one should consider purity (freedom from analyte),

sensitivity/isotope abundance, interferences (polyatomic and isobaric), quadrupole mass bias, ionization energies (that is, internal standard versus analyte), soluble/compatible with the sample matrix and coexistent species, and so forth. The solutions are introduced to the ICP-MS instrument using a peristaltic pump equipped with appropriate solvent resistant tubing, syringe pump, or alternatively by self-aspiration. By comparing measured m/z peak intensities of elements in the test specimen with m/z peak intensities measured with the standards, the concentrations of elements in the test specimen can be calculated.

5. Significance and Use

5.1 Petroleum products may contain elements either in trace concentrations (for example, ng/g (ppb mass)) or in minor to major levels (ppm to mass %). These elements might be characteristic of the crude petroleum or might originate from specific inclusions of additives for beneficial effect in the refined product. Often, such additives have product specifications which control the quality of a product in commerce. Hence, it is important to determine these elements as accurately as possible. Other elements present at trace levels may be harmful to combustion engines causing wear or reduced performance, may cause poisoning of catalysts, or may be of environmental concern as combustion emissions. ICP-MS instrumentation is well-suited for determining these elements and is particularly useful for the determination of the trace level elements that may not be readily achieved by other techniques.

5.2 Various elemental analytical techniques such as atomic absorption spectrometry (AAS), for example, Test Method D3605 and D4628; inductively coupled plasma atomic emission spectrometry (ICP-AES), for example, Test Methods D7111, D4951, and D5185; X-ray fluorescence (XRF), for example, Practice D7343, Test Method D7220, Test Methods D4927, and Test Method D6443; or graphite furnace atomic absorption spectrometry (GFAAS), for example, Test Method D6732 are used for this purpose. This test method is the first example where ICP-MS is used for elemental analysis of petroleum products.

5.3 This test method covers the rapid determination of seven elements in distillate petroleum products. Test times approximate a few minutes per test specimen, and quantification for most elements is in the low to sub ng/g (ppb mass) range. High analysis sensitivity can be achieved for some elements that are difficult to determine by other techniques.

6. Interferences

6.1 *Mass*—Several analyte elements in Table 1 are subject to polyatomic interferences from plasma or matrix sources. The use of collision/reaction cell (CRC) technology on quadrupole based spectrometers should be applied appropriately in order to minimize these interferences. Follow the manufacturer's operating guide to develop and apply appropriate cell conditions to compensate for the interferences. In the case where a collision/reaction cell is unavailable, mathematical correction may be applied to correct for interferences or alternatively high resolution mass spectrometers may be used,

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TABLE 1 Recommended Analytical Mass, Possible Molecular Ion Interferences and Recommended Collision/Reaction Cell Technology Mode

Element	m/z^A	Possible Molecular Ion Interferences	Suggested Mode^B
Aluminum	**27**	CNH, BO (minor, requires key components in matrix)	no CRC
Calcium	40^C , 43, **44**	Ar (major at ^{40}Ca^A), CNO, CO_2 (major)	CRC^C
Copper	**63**, 65	PO_2, ArNa, TiO (minor, each requires key components in matrix)	CRC
Iron	**56**, 57	ArO, ArOH (major)	CRC
Lead	206, 207, 208	...	no CRC
Magnesium	**24**, 25	C_2 (major), CN (minor, requires N key component in matrix)	CRC
Potassium	**39**	ArH (major), NaO	CRC, no CRC

^{A} Isotopes recommended shown in bold.
^{B} Elements of which CRC is suggested show significant benefit for freedom of spectral interferences, where both modes are listed the benefit is less pronounced.
^{C} ^{40}Ca requires reaction CRC mode, for example, H_2, NH_3, and so forth.

refer to 6.2.1. To apply interference corrections, all concentrations must be within the previously established linear response range of each element listed in Table 1.

6.1.1 Some mass interference can be avoided by judicious choice of analytical masses. When mass interferences cannot be avoided, the necessary corrections should be made using the computer software supplied by the instrument manufacturer. With any instrument, the analyst must always be alert to the possible presence of unexpected elements producing interfering mass peaks.

6.2 Several types of interference effects may contribute to inaccuracies in the determination of trace elements. These interferences can be summarized as follows:

6.2.1 *Isobaric Elemental Interferences*—Isobaric elemental interferences are caused by isotopes of different elements which form singly or doubly charged ions of the same nominal mass-to-charge ratio and which cannot be resolved by the mass spectrometer in use. If alternative analytical isotopes having higher natural abundance are selected in order 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. In these cases, it is recommended to select target isotopes with abundances much higher than that of the isobar to minimize the effects of the correction factors. It should be noted that such corrections will only be as accurate as the accuracy of the isotope ratio used in the elemental equation for data calculations and that all interference measurements must be within the range of the instrument detector, otherwise a dilution should be performed and the sample reanalyzed. Relevant isotope ratios and instrument bias factors should be established prior to the application of any corrections.

6.2.2 *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 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.

6.2.3 *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 which 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. Many of the common interferences have been identified, and these are listed in Table 1 together with the method elements affected. Such interferences must be recognized, and when they cannot be avoided by the selection of an alternative analytical isotope, appropriate corrections must be made to the data or collision/reaction cell technology utilized. 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.

6.2.4 *Physical Interferences*—Physical interferences are associated with the physical processes that govern the transport of the 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 (for example, viscosity effects), at the point of aerosol formation and transport to the plasma (for example, surface tension), or during excitation and ionization processes within the plasma itself. Similarly, high bias may result if the elemental species in the samples are more volatile than those elemental species used in the formulation of the calibration standards due to enhanced formation and transport of the aerosol in the spray chamber. High levels of dissolved solids in the sample may contribute deposits of material on the cones reducing the effective diameter and shape of the orifices and, therefore, ion transmission. Dissolved solid levels not exceeding 0.2 % (w/v) have been recommended to reduce such effects. Internal standardization or standard addition may be effectively used to compensate for many physical interference effects. Internal standards should have similar analytical behavior to the elements being determined.

6.2.4.1 When analyzing carbon based petroleum solvents/ samples, the argon plasma breaks down the hydrocarbon compounds into ionized carbon, un-ionized carbon and carbon dioxide. Much of the un-ionized carbon deposits on the sampler cone and can very rapidly occlude the sampler cone orifice. This plugging of the sampler cone causes significant

signal drift and more importantly will cause the instrument to shut down or a complete loss of signal. It is necessary to introduce oxygen into the aerosol to encourage the formation of carbon dioxide which will not deposit on the sampler cone. Oxygen is generally introduced into the spray chamber or transfer line between the spray chamber and the plasma. Refer to instrument manufacturer recommendations for details on specific oxygen flow rates and introduction techniques.

6.2.5 *Memory Interferences*—Memory interferences result when isotopes of elements in a previous sample contribute to the signals measured in a subsequently analyzed 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 sample introduction system. The site where these effects occur is dependent on the element and can be minimized by flushing the system with a solvent rinse blank between samples. The possibility of memory interferences should be recognized within an analytical run and suitable rinse times should be used to reduce them. Additionally, blanks should be analyzed periodically to demonstrate freedom from memory effects. The rinse times necessary for a particular element should be estimated prior to analysis. This may be achieved by aspirating a standard representing the highest concentration estimated to be present in the test samples or the highest calibration standard, whichever is higher 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 10 % of the reporting 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 re-analyzed after a long rinse period.

6.2.6 *Viscosity Effects*—Differences in the viscosities of test specimen solutions and standard solutions can cause differences in the uptake rates if self-aspiration is used. These differences can adversely affect the accuracy of the analysis. The effects can be reduced by using a peristaltic pump to deliver solutions to the nebulizer and by the use of internal standardization or standard addition.

6.2.7 *Particulates*—Particulates can plug the nebulizer thereby causing low results. Use of a high-solids nebulizer helps to minimize this effect. Also, the sample introduction system can limit the transport of particulates, and the plasma can incompletely atomize particulates, thereby causing low results.

6.2.8 *Contamination and Background Control*—Contamination is a common occurrence in the analytical laboratory, and can be difficult to control unless proper precautions are taken. Xylene, and other diluent solvents such as kerosene, are incompatible with a variety of plastics. Color is added to plastic labware by the addition of metallic pigment. Tinted labware should be avoided. When possible, all lab plasticware should be replaced with FEP (fluorinated ethylene propylene) or PFA (perfluoroalkoxy). To minimize contamination during standard/sample preparation, prepare all aliquots in either PP (polypropylene) or FEP/PFA pre-cleaned containers. The sample introduction system should be cleaned and maintained periodically based on sample volume and analyte concentration to minimize background contamination. The quantification of low level analytes will not be possible if the background for that particular analyte is elevated. The certificate of analysis for each reagent and dilution solvent should be evaluated to determine if the inherent background concentrations are sufficiently low enough for use. Certified concentrations for target analytes can vary greatly from lot number to lot number.

7. Apparatus

7.1 *Balance,* top loading or analytical, with automatic tare, capable of weighing to 0.0001 g, with sufficient capacity to weigh prepared solutions.

7.2 *Inductively Coupled Plasma Mass Spectrometer (ICP-MS)*—The spectrometer system must be capable of scanning the mass range of the elements to be analyzed. Instrument should be capable of scanning the mass range 6 amu to 208 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. See manufacturers' instruction manual for installation and operation.

7.2.1 The instrument should be configured with a nebulizer, a spray chamber and connector tube. Sample uptake is done by self-aspiration, syringe pump, or with a peristaltic pump. A sampling cone and a skimmer cone made of platinum should be used. The use of oxygen addition to the carrier gas to control carbon deposits on the cones can cause serious damage to nickel cones if used. Suggested masses for the determination of the elements in the light and middle distillate petroleum samples are given in Table 1.

7.3 *Spray Chamber*—Many solvents have vapor pressures much higher than that of the aqueous based liquids for which many generic ICP-MS spray chambers are designed. The volatility or high vapor pressure of many solvents can extinguish the argon plasma due to vapor load. Also, the nebulizers can create a more efficient aerosol with volatile solvents than with aqueous liquids. Basically, the plasma may not handle the load placed on it from solvents. The vapor pressure of the solvent can be reduced by cooling the spray chamber in which the aerosol is created. Typically, these cooled spray chambers are cold water jacketed or Peltier-cooled. A cooled spray chamber is necessary for analysis of more volatile solvents such as xylene and gasoline but may not be necessary with less volatile solvents such as diesel fuel and kerosene. Also, the use of a spray chamber designed to limit the transfer of aerosol, such as a Scott double-pass or baffled cyclonic spray chamber, can limit the vapor load and may be adequate for the analysis of less volatile solvents. Alternatively, a low-flow, heated, total consumptive sample introduction system may be used to minimize plasma loading and to eliminate the possibility of elemental species bias.

7.4 *Nebulizer*—A concentric nebulizer is recommended for this analysis. Alternatively, a high-solids nebulizer can be used

if the sample is introduced by means of peristaltic pumping. This type of nebulizer reduces the possibility of clogging and minimizes aerosol particle effects.

7.5 *Mass Flow Controllers*—A mass-flow controller to regulate the nebulizer gas may be used as recommended by the instrument manufacturer.

7.6 *Peristaltic Pump*—The use of a variable speed peristaltic pump for delivering sample solution to the nebulizer is highly recommended. The flow rate is typically in the range 0.05 mL ⁄min to 0.1 mL/min. The pump tubing must be able to withstand exposure to the diluent solvent for the entire run time. Fluoropolymer elastomer (for example, Viton) tubing is typically used with hydrocarbon solvents, and poly-vinyl chloride tubing is typically used with methyl isobutyl ketone. The disadvantage to peristaltic pumping is that many solvent resistant polymers are not sufficiently clean to achieve the best possible detection limits for some elements.

7.7 *Specimen Solution Containers,* of appropriate size, glass or plastic vials or bottles, with screw caps. Glass containers may contribute to contamination issues for some elements. PTFE vials are recommended since some of the other plastics interact with the hydrocarbons to cause nebulizer clogging. Vials should be pre-cleaned to remove contaminates, dust, fibers, and so forth that can clog tubing or nebulizers. See Practice D4306.

7.8 *Ultrasonic Homogenizer, (Recommended)*—A bath-type or probe-type ultrasonic homogenizer to homogenize the sample is sometimes useful.

7.9 *Membrane Filter,* 47 mm diameter, 0.8 μm or 1.0 μm pore size.

7.10 *Membrane Filter Holder Assembly,* for 47 mm diameter filters, with filtration flask.

8. Reagents and Materials

8.1 *Purity of Reagents*—At a minimum, reagent grade or better chemicals shall be used in all tests. Unless otherwise indicated, it is intended that reagents shall conform to the specifications of the committee on analytical reagents of the American Chemical Society,[3] where such specifications are available. The high sensitivity of inductively coupled plasma mass spectrometry will require reagents of higher purity for trace level analyses at the low range noted in the scope.

8.2 *Argon*—High purity grade (99.99%) (**Warning**—Argon may be a compressed gas under high pressure.).

8.3 *Dilution Solvent*—o-xylene, HPLC grade or better or other appropriate solvent.

8.4 *ICP-MS Calibration Standards*—Organic multi-element solutions made up in appropriate solvents are used for calibration of ICP-MS.

8.4.1 *Metallo-organic Standards*—Multi-element standards can be purchased or prepared from the individual concentrates. Refer to Practice D4307 for a procedure for preparation of multicomponent liquid blends. When preparing multi-element standards, be certain that proper mixing is achieved. An ultrasonic bath is recommended.

8.4.2 *Mixed Standard Solutions*—Prepare mixed standard solutions by combining appropriate masses of the stock solutions (see Note 1). Prior to preparing mixed standard solutions, each stock solution that is not commercially prepared and certified needs to be analyzed separately to identify possible interferences with other analytes or to detect the presence of impurities. Care needs to be taken when preparing the mixed standard solutions to ensure that the elements are compatible and stable.

Note 1—Mixed calibration standards will vary, depending on the number of elements being determined. Commercially prepared mixed calibration standards of appropriate quality may be used. In addition, it should be noted that the stability of commercial standards is only applicable to the standard as provided. Once the standard is diluted into a solvent, the stability is no longer assured by the manufacturer. The stability of commercial standards is generally accomplished with additives and these get diluted out when standards are diluted. Stabilizing agents can also be purchased. It is the responsibility of the user to determine the stability and shelf life of diluted standards.

8.5 *Blank Solution*—This solution must contain all the reagents and be the same volume as used in the processing of the samples. Carry blank solution through the complete procedure.

8.6 *Internal Standards*—Internal standards are used to correct for instrument drift and physical interferences. A list of some acceptable internal standards is provided in Table 2. Other elements may be used as required. Add internal standards to blanks, samples, and standards in a like manner.

8.6.1 The internal standards should be added in sufficient concentration to provide a strong and stable signal after any suppression that might be caused by sample matrices. The actual concentration is not critical but the concentration must be consistent among all samples and standards. It may be desirable to include higher concentrations for those internal standard elements with high ionization potentials such as germanium. Where possible, it is more desirable to keep the internal standard signal within the pulse mode of the discrete dynode detector. If it is necessary for the internal standard concentration to be in the analog mode of the detector, make sure that the signal strength is well into the analog mode and that the signal does not drift back and forth between the modes

TABLE 2 Possible Internal Standards and Limitations of Use

Internal Standard[A]	m/z	Cautionary Possible Limitation
Beryllium	9	...
Scandium	45	Molecular ion interference (CO_2H)
Gallium/Yttrium	69	May be present in samples
Yttrium	89	May be present in samples
Indium	115	Isobaric interference by Sn
Lanthanum	139	...
Cerium	140	...
Bismuth	209	May be present in samples

[A] It is strongly recommended when analyzing a new sample matrix that a scan for the presence of internal standards be performed.

[3] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the United States *Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.