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.*

[1] This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants and is the direct responsibility of Subcommittee D02.03 on Elemental Analysis.

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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

[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. 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.

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,

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.

resulting in increased signal error. The actual concentration of internal standards can vary a great deal and ranges from 2 ng/g to 100 ng/g (ppb mass) are typical.

8.7 *Oxygen Gas,* 99.999% minimum purity. (**Warning—** Strong oxidizer; promotes combustion.)

8.8 *Isopropyl Alcohol,* Reagent grade or better.

8.9 *Quality Control (QC) Samples,* preferably are portions of one or more distillate products that are stable and representative of the samples of interest. These QC samples can be used to check the validity of the testing process as described in Appendix X1. If a suitable QC sample is not available, use a stable standard solution, and dilute it with the blank solution to the trace level required as described in 12.4 on the day of the QC check. Use plastic bottles to contain concentrated metallo-organic solutions.

NOTE 2—HDPE can allow lighter materials such as naphtha to migrate into the polymer thereby reducing the sample volume and potentially concentrating the analytes over time.

9. Hazards

9.1 The toxicity or carcinogenicity of each reagent used in this test method has not been precisely defined; however, each chemical should be treated as a potential health hazard. Adequate precautions should be taken to minimize exposure of personnel to chemicals used in this test method.

9.2 Gases under high pressure are used in this test method. Use only apparatus rated for handling the high gas pressures that occur in this test method.

10. Preparation of Apparatus

10.1 *Instrument*—Consult the manufacturer's instructions for operating the instrument with organic solvents. Set up the instrument for use with the particular dilution solvent chosen. Most lens parameters may be optimized by the auto-tuning function of the instrument.

10.2 *Peristaltic Pump*—If a peristaltic pump is used, inspect the pump tubing and replace it, if necessary, before starting each day. Verify the solution uptake rate and adjust it to the desired rate.

10.3 *ICP Excitation Source*—Plasma is ignited with isopropyl alcohol (IPA), *o*-xylene, or appropriate solvent. A tuning solution is typically used for optimization of plasma and ion lens parameters. Initiate the plasma source at least 30 min before performing analysis. During this warm up period, nebulize dilution solvent. Inspect the torch and sampling cone for carbon buildup during the warm up period. If carbon buildup occurs, replace the torch immediately and consult the manufacturer's operating guide to take proper steps to remedy the situation.

NOTE 3—Select oxygen injection flow, gas flows, power, sample introduction temperature, and other parameters so as to minimize carbon build up on torch, cones, and inside of spectrometer with the particular sample and solvent to be analyzed.

NOTE 4—Some manufacturers recommend even longer warm-up periods to minimize changes in the slopes of calibration curves.

10.4 *Operating Parameters*—Assign the appropriate operating parameters to the instrument task file so that the desired elements can be determined. Parameters to be included are element, mass, integration time, CRC mode if used, and internal standard correction if used. A minimum of three replicate measurements, reported as an average with a maximum relative standard deviation (RSD) of 20 % for analytes reported within the calibration range, are required for each measurement, and the total integration time is typically 1 s or 2 s.

11. Sample Handling

11.1 Samples shall be taken in accordance with procedures described in Practice D4057 or D4177. Suitable sample containers for aviation fuels are described in Practice D4306.

11.2 *Homogenization*—It is extremely important to homogenize samples in the sample container in order to obtain a representative test sample.

11.2.1 *Hand Shaking*—Vigorously shake the sample container for about 30 s immediately prior to taking the aliquot for analysis.

11.2.2 *Ultrasonic Homogenization*—Place the sample (in the sample container) into the ultrasonic bath. Leave the sample in the bath until immediately before dilution.

11.3 If particulate matter is observed in the sample, filter it through a 0.45 µm, 0.8 µm, or 1.0 µm (nylon, TFE-fluorocarbon, cellulose acetate/cellulose nitrate, or other compatible material) membrane filter into an acid-cleaned flask and retain the filtrate for analysis. Follow the same filtration procedure for the blank solution used for the analysis of these samples.

12. Preparation of Test Samples and Standards

12.1 *External Calibration Standard Solution*—On an analytical balance, tare a clean, appropriately sized container for dilution of calibration standards to cover the range needed for the samples to be analyzed. Weigh approximately one gram of the calibration standard into the container and record the mass. Add sufficient dilution solvent to bring the concentration of the elements to the highest level expected for the samples and record this mass. Seal the container and mix the solution well. Calculate the element concentrations as shown in 12.2.3. Make further dilutions in the same manner as required. The stability of the calibration standard solution should be determined in order define the useful life of the solutions.

12.1.1 *Internal Standard Stock Selection*—The analyst's selection of the internal standard element(s) may be influenced by the capabilities (mass availability, sensitivity) of the ICP instrument available. The element(s) chosen for the internal standard should not be a component of the test specimen or calibration standard (see Table 1 and Table 2). In addition, elements selected for internal standards should reflect both the mass and ionization potential of the target elements. While it is not always practical, it is suggested to try and keep the internal standard within approximately 30 amu of the target isotopes.

12.1.2 *Internal Standard Stock Solution*—Weigh a sufficient amount of internal standard concentrate solution into an appropriately sized tared container to last for approximately one week. Add a sufficient amount of dilution solvent so that the concentration of the internal standard will be at least 100×

its detection limit when added to the test specimen solution. Prepare fresh, at least weekly, and store this solution in a tightly capped container.

NOTE 5—Cleaned plastic containers are preferred to avoid contamination issues.

12.1.3 *Method of Standard Addition*—This technique, where the standard is added directly to the aliquots of analyzed sample, may be used as an alternative to external standards (see 12.1). The procedure involves preparing several solutions containing the same amount of the sample, but different amounts of standard. The total concentration of the analyte is then the combination of the unknown quantity in the sample plus the quantity added by the standard. If the signal response is linear over the concentration range, extrapolation of the line formed by the measurements to the xaxis intercept will be the unknown concentration.

12.2 *Calibration Standards:*

12.2.1 *Calibration Stock Solution*—The calibration stock standard is prepared from the stock standard(s) or solutions(s) (see Section 8). The calibration intermediate stock standard is prepared by weighing one gram of a thoroughly homogenized stock standard(s) or solutions(s) into the container and record the mass. Add sufficient dilution solvent to bring the concentration of the elements to the highest level needed to prepare calibration standards for the samples and record this mass. to be prepared as often as determined by the lab, after determining the stability of the standards. (See X2.4.)

12.2.2 *Calibration Standard Solutions*—On an analytical balance, tare a clean, appropriately sized container for dilution of calibration standards to cover the range needed for the samples to be analyzed. Weigh needed amount of the calibration stock standard into the container and record the mass. If using internal standard method, you will need to spike the same amount of internal standard stock solution as you plan to add to your samples. Add sufficient dilution solvent to bring the concentration of the elements to the highest level expected for the samples and record this mass. Seal the container and mix the solution well. Calculate the element concentrations as shown in 12.2.3. Make further dilutions of the calibration stock solution in the same manner to make a few lower calibration standards. The stability of the calibration standard solutions should be determined in order to define the useful life of the solutions. A minimum of three (3) calibration standards and a blank are required for external calibrations. Its recommended that the first calibration standard be near the reporting limit.

12.2.3 Calculate the concentrations of the elements in the calibration standard solution as follows:

$$C_{CS} = [(M_{100} / M_{CS}) C_{100}] \quad (1)$$

where:

C_{CS} = the concentration (ng/g (ppb mass)) of element *e* in the calibration standard solution,
C_{100} = the concentration (ng/g (ppb mass)) of element *e* in the organometallic standard,
M_{100} = the mass (g) of the organometallic standard, and
M_{CS} = the mass (g) of the prepared solution of the organometallic standard and blank solution.

12.3 *Check Standards*—Prepare instrument check standards in the same manner as the calibration standards such that the concentrations of elements in the check standards are similar to the expected concentrations of elements in the specimens. It is advisable to prepare the check standard from an alternative source of certified organometallic standard. (Performance criterion are noted in Section 16, Data Validation.)

12.4 *Test Samples using Internal Standard*—Weigh a portion of the well-homogenized sample into a suitable container. Add internal standard stock solution as described in 8.6.1 and reweigh. Add *o*-xylene, or other suitable solvent to bring the sample analytes within the measurement range (10× to 100× is typical) and reweigh. (Performance criterion are noted in Section 16, Data Validation.)

12.5 *Test Samples using Standard Additions*—Weigh equal portions of the well-homogenized sample into two or more suitable containers depending on the number of calibration points to be used. Add varying amounts of the calibration solution to each container except the first one and reweigh. Add *o*-xylene, or other suitable solvent to bring the sample analytes within the measurement range (10× to 100× is typical) and reweigh.

12.5.1 Calculate the concentrations of each element in the sample by extrapolating the m/z intensities for each element in each solution versus the known amounts of that element added to the sample from the calibration solution to the x-axis intercept which will be the concentration in the sample. A spreadsheet template is often used for this purpose. The minimum precision for the calibration must have $r^2 \geq 0.995$. The calibration must be repeated if this acceptance criterion is not fulfilled. Or use the instrument vendor software to calculate concentrations.

12.5.2 To use a single curve for multiple samples of similar matrix type, convert the standard calibration curve to an external calibration. Use the external calibration curve for analysis of the diluted samples and corresponding sample with the standard addition. Standard recovery for each element for each sample must be between 70 % to 130 % of the accepted value to demonstrate validity of the calibration curve. Create a new standard additions curve if the standard element recovery does not meet the acceptance criterion.

13. Calibration

13.1 *Calibration Standards*—At the beginning of the analysis of each batch of samples, perform a calibration consisting of the blank and all calibration standards appropriate for the range. Use the check standard to determine if each element is in calibration When the results obtained with the check standard are within 10 % of the expected concentrations for all elements to be analyzed, proceed with test specimen analyses. Otherwise, make any adjustments to the instrument that are necessary and repeat the calibration for those elements that failed the QC check. Repeat this procedure with the check standard every 10 to 20 samples.

13.2 Aspirate solvent blank between standard (and test specimen) runs to purge the system of elements prior to the next run. If high element concentrations have been run, check

the element signal intensity after the solvent blank purge to ensure that it has been adequately removed.

13.3 Most ICP-MS instruments have software that automatically performs the calculations to establish the calibration curve when using an internal standard. Element m/z intensities are ratioed to the internal standard m/z intensities. The calibration curve is a plot of the m/z ratio for an element e in the working standard (Rws) versus the concentration of element e in the calibration standard (Ccs), and

$$R_{ws} = (I_{ws} - I_b)/I_{ints} \quad (2)$$

where:

I_{was} = m/z intensity for element *e* in the working standard,
I_b = m/z intensity for element *e* in the solution blank, and
I_{ints} = m/z intensity of the internal standard in the working standard solution.

13.4 When analyzing elements at very low levels it is necessary to determine the actual detection limits for these elements. Determine the ICP-MS detection limits for all elements of interest as follows: Prepare a blank solution with an internal standard. Seal the container and mix well. Perform seven consecutive analyses of this solution for all elements of interest under the same conditions/parameters that the calibration standards were run. With the ICP instrument software, determine the standard deviation of the seven results for each element of interest. The MDL is calculated as in 16.7.1.

14. Analysis

14.1 Differences between various makes and models of instruments make it impractical to provide all instrumental operating instructions. Instead, the analyst shall refer to the instructions provided by the manufacturer of the particular instrument. Sensitivity, instrumental detection limit, linear dynamic range, interference effects, and appropriate background correction shall be investigated and established for each individual analyte on that particular instrument.

14.2 Analyze the test sample solutions in the same manner as the calibration standards (that is, same integration time, CRC conditions, plasma conditions, and so forth). Between test samples, nebulize dilution solvent for sufficient time to eliminate any memory effects due to carry over from previous sample. Calculation of concentrations can be performed manually or by computer when such a feature is available.

15. Calculation

15.1 In a manner similar to that described in 13.3 for the calibration, the analysis of the sample generates an m/z ratio as follows:

$$R_f = I_f/I_{intf} \quad (3)$$

where:

R_f = m/z ratio for an element *e* in the sample,
I_f = m/z intensity of element *e* in the sample, and
I_{intf} = m/z intensity of internal standard added to the sample.

Thus, by comparison with the calibration curve, the ICP-MS instrument software determines the element concentrations as follows:

$$C_f = (R_f \times C_{CS})/R_{ws} \quad (4)$$

where:

C_f = concentration (ng/g (ppb mass)) of element *e* in the sample,
C_{CS} = concentration (ng/g (ppb mass)) of element *e* in the calibration standard,
R_f = mass ratio of element *e* in the sample, and
R_{ws} = mass ratio of element *e* in the working standard.

16. Data Validation

16.1 When using external calibration solutions the instrument shall be calibrated using a minimum of three calibration standards and a calibration blank. The calibration correlation coefficient shall be equal to or greater than 0.995.

16.2 A blank shall be analyzed at a minimum frequency of every 10 samples and at the beginning and end of the batch run to ensure contamination was not a problem during the batch analysis. The measured values should not exceed ±10 % of the reporting limit.

16.3 A working standard (12.4) or QC sample (see 8.9 and Appendix X1) shall be analyzed with each batch of samples to verify the instrument's calibration. If the working standard is used, the measured value must be within 10 % of the certified value. If the QC sample is used, the measurement must be within the limits of the control chart.

16.4 The internal standard area counts in each sample should be within 50 % to 150 % of area in calibration blank.

16.5 If the QC for the sample batch is not within the established control limits, reanalyze the samples or qualify the results with the appropriate flags, or both (Practice D6792).

16.6 See Appendix X1 for additional information on quality control.

16.7 *Method Performance:*

16.7.1 Determine detection limits annually or whenever a significant change in background or instrument response is expected (see 13.4).

$$\text{MDL} = (t) \times (\text{s}) \quad (5)$$

where:

t = students' t value for a 99 % confidence level and with n–1 degrees of freedom (t=3.14 for seven replicates), and
s = standard deviation of the replicate analyses.

16.7.2 Reagent blanks can vary from manufacture lot number to lot number so they should be subtracted from the samples, if the concentration of the element is greater than the reporting limit.

16.7.3 Calculate the concentration of the element in the sample as follows:

$$C = A(D / W) \quad (6)$$

where:

C = mass fraction of the element in the sample,
A = ng/g (ppb mass) of element in the analyzed aliquot,
D = mass of the diluent in grams, and
W = mass of sample in grams.

17. Report

17.1 Report ng/g for each element measured.

18. Precision and Bias

18.1 *Precision*—The precision of this test method was determined by statistical analysis of laboratory results as detailed in Practice D6300. In this study, the dilution solvent was limited to *o*-xylene. The precision of this test method for the determination of various elements in distillate petroleum products is shown in Table 3. The precision characterized by the repeatability is described in this table.

18.1.1 *Repeatability Limit (r)*—The value below which the absolute difference between two test results of separate and consecutive test determinations, carried out on the same sample in the same laboratory by the same operator using the same apparatus on samples taken at random from a single quantity of homogeneous material, may be expected to occur with a probability of approximately 95 %.

TABLE 3 Precision of ICP-MS Determination of Trace Elements in Petroleum Middle Distillate Products

Element	Range, (ppb) ng/g	Repeatability	Repeatability at 5 ng/g Level
Aluminum	3 to 400	$0.5140 * X^{1.0338}$	2.7
Calcium	2 to 240	$0.3836 * X^{1.2133}$	2.7
Copper	2 to 20	$1.1919 * X^{0.6436}$	3.4
Iron	1 to 90	$0.2974 * X^{1.1227}$	1.81
Lead	1 to 5	$0.7597 * X^{1.0203}$	3.93
Magnesium	1 to 230	$0.5225 * X^{0.9727}$	2.5
Potassium	7 to 50	$0.1342 * X^{1.558}$	1.65

18.1.2 *Reproducibility*—The value below which the absolute difference between two test results, carried out in different laboratories using samples taken at random from a single quantity of material that is as nearly homogeneous as possible, may be expected to occur with a probability of approximately 95 %.

18.1.3 The precision characterized by the repeatability is shown in Table 3. The reproducibility is not known at present. A second ILS will be conducted within the 5-year limit allowed by ASTM to produce necessary data.

18.2 An interlaboratory study, designed consistent with Practice D7778, was conducted among 11 laboratories using 16 samples of naphtha, diesel, and gasoline. Four different brands of ICP-MS instruments were utilized (Agilent, PerkinElmer, Spectro, and Thermo). The details of the study and supporting data are given in ASTM Research Report RR:D02-1858.[4]

18.2.1 Based on the repeatability found in the ILS, calculated repeatability values for each element at 5 ng/g level are also shown in Table 3.

19. Keywords

19.1 aluminum; calcium; copper; diesel; distillates; gasoline; inductively coupled plasma mass spectrometry; iron; lead; magnesium; naphtha; potassium

[4] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1858. Contact ASTM Customer Service at service@astm.org.

APPENDIXES

(Nonmandatory Information)

X1. HELPFUL HINTS FOR QUALITY CONTROL MONITORING

X1.1 Quality Control Monitoring

X1.1.1 Confirm the performance of the instrument or the test procedure by analyzing a QC sample.

X1.1.2 Prior to monitoring the measurement process, the user of the test method needs to determine the average value and control limits of the QC sample. See Practice D6299 and MNL 7.[5]

X1.1.3 Record the QC results and analyze by control charts or other statistically equivalent techniques to ascertain the statistical control status of the total testing process. See Practice D6299, Guide D6792, and MNL 7. Investigate any out-of-control data for root cause(s). The results of this investigation may, but not necessarily, result in instrument recalibration.

X1.1.4 In the absence of explicit requirements given in the test method, the frequency of QC testing is dependent on the criticality of the quality being measured, the demonstrated stability of the testing process, and customer requirements. Generally, a QC sample is analyzed each testing day with routine samples. The QC frequency should be increased if a large number of samples are routinely analyzed. However, when it is demonstrated that the testing is under statistical control, the QC testing frequency may be reduced. The QC sample precision should be checked against the ASTM test method precision to ensure data quality.

X1.1.5 It is recommended that, if possible, the type of QC sample that is regularly tested be representative of the material routinely analyzed. An ample supply of QC sample material should be available for the intended period of use, and must be homogenous and stable under the anticipated storage conditions. See Practice D6299, Guide D6792, and MNL 7, or a combination thereof, for further guidance on QC and control charting techniques.

[5] ASTM MNL 7: Manual on Presentation of Data Control Chart Analysis, 6th Ed, Section 3.

X2. HELPFUL HINTS FOR THE OPERATION OF THE TEST METHOD

X2.1 Check the temperature and humidity controls of the laboratory containing the ICP-MS instruments, and verify adequacy for performing accurate and precise analyses. Ensure that stable environmental conditions exist throughout the period of use.

X2.2 Check the accuracy of elemental concentrations of commercially obtained calibration standards before use, either by comparing against suitable primary standards or by an independent analytical method.

X2.3 Verify the absence of analytes in all solvents and reagents used by performing a semi-quantitative scan. The net intensity should be less than the reporting limit for each analyte element.

X2.4 Establish the preparation frequency of calibration standards by experiment. Prepare fresh working and check standards based upon the stability of the solutions as indicated by the data.

X2.5 Inspect torches before use for cracks, and discard or repair as appropriate.

X2.6 Use clean torches that are free of carbon buildup.

X2.7 Check for carbon buildup on the torch while nebulizing the working standard. Make the necessary adjustments to eliminate buildup. These adjustments may consist of the following:

X2.7.1 Reducing the pump rate.

X2.7.2 Increasing the auxiliary gas flow.

X2.7.3 Using a chilled spray chamber.

X2.7.4 Diluting the sample.

X2.7.5 Making other adjustments described in the instrument manual.

X3. HELPFUL HINTS FOR THE ANALYSTS

X3.1 Follow good laboratory practice when handling samples. Some samples may have very low levels of analytes. All samples should be handled with extreme care to avoid contamination. The sample containers should be opened only when ready for analysis.

X3.2 Work in a well-ventilated hood, and adequate protection as prescribed in the appropriate safety practices.

X3.3 Check the temperature and humidity controls of the laboratory containing the ICP-MS instrument, and verify adequacy for performing accurate and precise analyses. Ensure that stable environmental conditions exist throughout the period of use.

X3.4 Contamination is a common occurrence in the analytical laboratory and can be difficult to control unless proper precautions are taken. Ensure that all glassware and so forth that contacts samples and standards do not contaminate the analyses. Soak the glassware in warm dilute (5 %) pure nitric acid for several hours, and then rinse thoroughly with deionized water. Xylene, kerosene, and other diluent solvents used are incompatible with a variety of plastics. Tinted or colored lab-ware should be avoided. When possible, all plastic-ware should be replaced with FEP or PFA materials.

X3.5 To minimize contamination during standard/sample preparation, prepare all aliquots in either PP or FEP/PFA precleaned containers. The sample introduction system should be cleaned and maintained periodically based on sample volume and analyte concentration.

X3.6 Select solvents and other reagents that do not contain significant levels of the analytes being determined.

X3.7 It is extremely important to homogenize samples in the original sample container in order to obtain a representative test sample. Employ adequate mixing and sampling procedures, especially for heavier samples. Heat heavy oil samples sufficiently obtain good liquidity, and then shake the sample vigorously on a shaking machine if necessary. If using hand shaking, vigorously shake the sample container for about 30 sec immediately prior to taking an aliquot for analysis. Ultrasonic homogenizers and vortex mixers can help in making the samples uniform in their content.

X3.8 If particulates are observed in the sample, filter through a 0.45 µm, 0.8 µm, or 1.0 µm (nylon, TFE-fluorocarbon, cellulose acetate/cellulose nitrate, or other compatible material) membrane filter into an acid-cleaned container and retain the filtrate for analysis. Follow the same procedure for the blank solution used for the analysis of these samples.

X3.9 Testing should be performed under normal laboratory conditions using an operator with good experience in ICP-MS technology, and with knowledge of interpretation of spectral and matrix interferences, and procedures for their correction or reduction.

X3.10 The instrument measurement capability is affected by instrument maintenance quality, laboratory environment/protocols, equipment age, and other factors.

X3.11 Inspect the torch for cracks. Discard defective torches. Use clean torches that do not have carbon deposits.

X3.12 Inspect the nebulizer tubing daily for kinks or cracks, and replace if necessary. Measure the nebulizer uptake rate

daily to check for plugging. Clean it if the rate is not normal.

X3.13 Adjust the variations due to buildup of deposits on the nebulizer during the course of determinations by frequently nebulizing the check standard.

X3.14 When the carbon build-up in the torch is problematic, adjust the experimental conditions to eliminate the problem. Such adjustments can include (*1*) reducing the sample intake rate, (*2*) increasing the auxiliary argon gas flow rate, (*3*) use a jacketed, chilled spray chamber, (*4*) lowering the torch relative to the RF load coil, (*5*) diluting the sample, and (*6*) making other adjustments described in the instrument manual. Replace or clean the load coil if oxidation is observed.

X3.15 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 of 0.05 mL⁄min to 0.1 mL⁄min. Inspect the peristaltic pump tubing daily, and replace deteriorating tubing. Daily replacement is recommended.

X3.16 After initially igniting the plasma, allow the instrument to warm up to a minimum of 30 min. Some instrument manufacturers recommend even longer warm-up periods to minimize changes in the slopes of calibration curves. During this warm-up period, nebulize dilution solvent.

X3.17 Dilute the samples and calibration standards as much as possible to minimize nebulizer transport effects caused by high viscosity samples, and to reduce potential spectral interferences.

X3.18 Always use a blank sample with all solvents and other reagents added to the standards and the samples to check for contamination. When blank values are significant, correct for the blank or select alternate reagents that give insignificant blank values.

X3.19 Use a blank and appropriate check standard after every fifth sample, or if at least 30 min have elapsed from the time of last analysis. Recalibrate if the intensity of the standard changes by more than 10 % relative to the previous check. The blank solution must contain all the reagents and be the same volume as used in the processing of the samples. Carry the blank solution through the complete analytical procedure.

X3.20 Standardize the instrument each time the plasma is ignited. Carry out calibration prior to each group of samples to be analyzed and after any change in instrumental conditions, as variation occurs in the instrument behavior.

X3.21 A single check standard should be analyzed from time to time during a series of samples to check whether the calibration has changed. A check after every fifth sample or if at least 30 min have elapsed from the time of the last analysis is recommended. Recalibrate if the net intensity of the standard changes by more than 5 % relative to previous check.

X3.22 Low level working calibration standards should be prepared fresh on the day of analysis from higher concentration (for example, 500 mg⁄kg or 1000 mg/kg) stock solution.

X3.23 By experiment, determine the frequency of standards preparation. Then, prepare fresh, as needed.

X3.24 When preparing multi-element standards, ensure that the various reagents are mutually soluble in the solvent employed, and do not form insoluble compounds by reacting with each other. Stability of commercial standards is only applicable to the standard as provided. Once the standard is diluted with a solvent, the stability is no longer assured by the manufacturer.

X3.25 Standard addition technique may be employed for samples known to have elemental or other interferences.

X3.26 For best results, use a bracketing technique for calibration. This involves measuring emission intensity readings for the calibration solutions before and after each of the sample solutions.

X3.27 Verify the linearity of the concentrations/emission response for each analyte following the instrument manufacturer's instructions. Perform all determinations within this concentration range. Prepare the standard solutions with concentrations at the top of the linear range. Match the matrix of the standard solutions to sample solutions as closely as possible. Keep all emission intensities within the linear and calibration ranges. Dilute the sample solutions gravimetrically, if necessary, with analyte free solvents.

X3.28 Before use, check the accuracy of element concentrations of commercially-obtained calibration standards, by comparing against suitable primary standards, using alternative sources or analyzing by independent analytical methods.

X3.29 Periodically, as needed determine the linearity of the calibration curves. Perform quantitative analyses with linear curves only.

X3.30 The instrument shall be calibrated using a minimum of three calibration standards and a calibration blank. The calibration coefficient shall be equal or greater than 0.995.

X3.31 Use the atomic masses specified in the test method for measurement, because they have been established by experiment and experience to be the optimum masses, and free from spectral interference.

X3.32 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 sample and skimmer cones and from the buildup of sample material in the plasma torch and sample introduction system. To minimize memory effects, allow sufficient solvent rinse time (not less than 60 s) between the determinations. Memory effects are present if a steady instead of an abrupt decrease in signal is observed from taking multiple measurements. 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. Refer to the interference section of the standard for further instructions.

X3.33 Differences in the viscosities of test specimen solutions and calibration standard solutions can cause differences in the uptake rates of if self-aspiration is used. These differences can adversely affect the accuracy of the analysis. These 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. Use of a peristaltic pump is strongly recommended to provide a constant flow of the solution.

X3.34 Particulates can plug the nebulizer thereby causing low results. Also, the sample introduction system can limit the transport of particulates, and the plasma can incompletely atomize the particulates, thereby causing low results. Use of a concentric or alternatively a Babington type high-solids nebulizer helps to minimize this effect.

X3.35 A mass flow controller to regulate the nebulizer gas may be used as recommended by the instrument manufacturer.

X3.36 Spectral interferences are far more serious than those encountered in AAS or ICP-AES test methods. See the Interferences section of the test method for properly detecting and minimizing such interferences. Check for all spectral interferences expected from the elements present in the sample. Follow the manufacturer's operating guide to develop and apply correction factors to compensate for interferences. Avoid spectral interferences where possible by judicious choice of atomic mass to be used or by comparing the results of two different atomic masses for the same element.

X3.37 With any instrument, the analyst must always be alert to the possible presence of unexpected elements producing interfering mass peaks.

X3.38 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. Internal standards should have similar analytical behavior to the elements being determined.

X3.39 In choosing an internal standard consider the purity of (freedom from analyte), sensitivity/isotope abundance, interferences (polyatomic and isobaric), quadruple mass bias, ionization energies (i.e., internal standard vs. analyte), soluble/compatible with sample matrix and coexistent species, and so forth.

X3.40 If using the internal standard method, it is necessary to spike with the same amount of internal standard stock solution as added to the samples.

X3.41 High levels of dissolved solids in the sample may contribute deposits of material on the cones reducing the effective diameter and shape of the orifice and, therefore, ion transmission. Dissolved solid levels not exceeding 0.2 % (w/v) are recommended to reduce such effects.

X3.42 Hydrocarbon compounds are decomposed in argon plasma resulting into ionized carbon, un-ionized carbon and carbon dioxide. Much of the un-ionized carbon deposits on the sample cone and can very rapidly occlude the sample cone orifice. The plugging of the sample cone causes significant signal drift and more importantly will cause the instrument to shut down or cause 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 sample cone. Refer to instrument manufacturer's recommendations for details on specific oxygen flow rates and introduction techniques.

X3.43 Establish and implement a quality control protocol that can aid in achieving the required data quality. It is strongly recommended that a quality control sample be analyzed for every 5 or 10 samples used in analysis. A control chart should be plotted using the results and appropriate actions should be taken when the chart indicates out-of-statistical control behavior. See Practice D6792 for guidance in this area.

X3.44 Report results using the number of significant figures specified in the test method standard.