Designation: D7111 − 16

Standard Test Method for Determination of Trace Elements in Middle Distillate Fuels by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)[1]

1. Scope*

1.1 This test method covers the determination of selected elements in middle distillate fuels by inductively coupled plasma atomic emission spectrometry (ICP-AES). The specific elements are listed in Table 1. The concentration range of this test method is approximately 0.1 mg/kg to 2.0 mg/kg. The test method may be used for concentrations outside of this range; however, the precision statements may not be applicable. Middle distillate fuels covered in this test method have all distillation fractions contained within the boiling range of 150 °C to 390 °C. This includes, but is not limited to, diesel fuels and aviation turbine fuels.

1.2 This test method is not intended to analyze insoluble particulates. However, very small particulate matter (smaller than a micrometre) will be carried into the plasma and be included in the quantitative analysis.

1.3 This test method may give a result that is higher than the true value if an analyte is present in the sample in a form which is sufficiently volatile. For example, hexamethyldisiloxane will generate a biased high result for silicon.

1.4 The values stated in SI units are to be regarded as standard.

1.5 *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.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D2880 Specification for Gas Turbine Fuel Oils
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
D4306 Practice for Aviation Fuel Sample Containers for Tests Affected by Trace Contamination
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
D6792 Practice for Quality System in Petroleum Products and Lubricants Testing Laboratories
D7260 Practice for Optimization, Calibration, and Validation of Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) for Elemental Analysis of Petroleum Products and Lubricants

2.2 *Military Standard:*

MIL-DTL-16884 Fuel, Naval Distillate[3]

3. Terminology

3.1 *Definitions:*

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

3.1.2 *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.

3.1.3 *calibration standard, n*—a standard having an accepted value (reference value) for use in calibrating a measurement instrument or system.

3.1.4 *detection limit, n*—a stated limiting value that designates the lowest concentration that can be determined with confidence and that is specific to the analytical procedure used.

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[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] 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] Available online at http://quicksearch.dla.mil or http://assistdocs.com

***A Summary of Changes section appears at the end of this standard**

TABLE 1 Elements and Recommended Wavelengths

Element	Wavelengths, nm
Aluminum	308.215, 396.153
Barium	455.403, 493.408
Calcium	393.366
Chromium	267.716, 283.563
Cobalt	228.615, 236.375, 238.892
Copper	324.752
Iron	259.939
Lithium	670.784
Lead	220.353, 224.688, 283.306
Magnesium	279.553
Manganese	257.610
Molybdenum	202.030, 204.597, 281.616
Nickel	221.648, 341.476
Phosphorus	177.495, 178.287, 185.944, 214.914, 213.618
Palladium	340.458, 342.124
Platinum	214.423
Potassium	766.490
Sodium	588.995
Silicon	251.611
Silver	328.068
Strontium	407.771
Tin	283.999, 189.991
Titanium	334.940
Vanadium	310.230
Zinc	213.857

3.1.5 *emission spectroscopy, n*—measurement of the energy spectrum emitted by or from an object under some form of energetic stimulation; for example, light or electrical discharge.

3.1.6 *inductively coupled plasma, n*—a high temperature discharge generated by passing an ionizable gas through a magnetic field induced by a radio frequency coil surrounding the tubes that carry the gas.

3.1.7 *radio frequency, n*—the range of frequencies between 3 kHz and 300 GHz.

3.1.8 *standard, n*—a physical or chemical reference used as a basis for comparison or calibration.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *detection limit, n*—the lowest concentration value for an element that can be determined by ICP analysis and that is calculated by multiplying three times the standard deviation of ten repetitive element analyses of the blank solution.

3.2.2 *internal standard, n*—a 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.

4. Summary of Test Method

4.1 Calibration standards are prepared by mixing organometallic standard materials in kerosine. An internal standard material is added to the calibration standards and fuel samples. The calibration standards and the fuel samples are aspirated into the ICP-AES instrument. The concentrations of the elements in the fuel are calculated by comparing emission intensity ratios of the fuel and calibration standards to the internal standard.

4.2 Consult Practice D7260 regrading the optimum operation of any ICP-AES system.

TABLE 2 Internal Standards, Recommended Wavelengths, and Approximate Use Concentrations

Internal Standard	Wavelength, nm	Concentration, mg/kg
Scandium	361.383	1-2
Yttrium	371.029	1-5

5. Significance and Use

5.1 Trace elemental analysis is used to indicate the level of contamination of middle distillate fuels. Trace metals in turbine fuels can cause corrosion and deposition on turbine components at elevated temperatures. Some diesel fuels have specification limit requirements for trace metals to guard against engine deposits. Trace level copper in middle distillate aviation turbine fuel can significantly accelerate thermal instability of the fuel, leading to oxidation and production of detrimental insoluble deposits in the engine.

5.2 Gas turbine fuel oil Specification D2880 provides recommended upper limits for five trace metals (calcium, lead, sodium, potassium, and vanadium). Military specification MIL-DTL-16884 for naval distillate fuel sets requirements for maximum concentrations of the same five metals. Both specifications designate Test Method D3605, an atomic absorption/flame emission method, for the quantitative analysis of four of the metals. Test Method D3605 does not cover potassium. This test method provides an alternative to Test Method D3605, covers potassium and a number of additional elements.

5.3 There are several sources of multi-element contamination of naval distillate fuel. Sea water is pumped into the diesel fuel tanks (as ballast) to trim ships. Also, some of the oilers (fuel supply ships) have dirty tanks. Corrosion products come from unlined tanks, piping, pumps, and heat exchangers.

6. Interferences

6.1 Elemental wavelengths listed in Tables 1 and 2 have been found to be free of spectral interferences with all other elements listed in Tables 1 and 2 in the concentration range of this test method.

6.2 If a spectral interference does exist, then selecting an analytical wavelength other than those listed in Table 1 or Table 2 may be used as long as the new wavelength possesses appropriate sensitivity for the scope of the method.

6.3 Alternatively, the ICP spectrometer manufacturer's software may be used to provide corrections to interferences that cannot be avoided by wavelength selection and background correction.

6.4 An empirical method for correcting for spectral interferences is detailed in Test Method D5185, Section 6.1 (*Spectral*).

7. Apparatus

7.1 *Inductively-Coupled Plasma Atomic Emission Spectrometer*—Any commercial sequential or simultaneous ICP-AES instrument capable of measuring emission intensities of the elements of interest (and listed in Table 1). A vacuum or inert gas optical path is required for analysis of any element at wavelengths below 190 nm.

7.2 *Nebulizer*—For samples without particulates, a concentric nebulizer is recommended to provide higher sensitivity for low concentrations and for low sensitivity elements. For unknown samples, a Babington-type high solids nebulizer is recommended to reduce the possibility of clogging from particulate.

7.3 *Spray Chamber,* suitable for organic materials.

7.4 *Peristaltic Pump*—A peristaltic pump is required to provide a constant flow of liquid to the ICP. Viton pump tubing is recommended for use with fuels and kerosine.

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

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

7.7 *Pipette,* 1000 µL.

7.8 *Volumetric Flasks,* 25 mL and 50 mL, glass.

7.9 *Glass or High Density Polyethylene (HDPE) Bottles,* 125 mL, round.

7.10 *Analytical Balance,* measuring to 0.0001 g.

8. Reagents and Materials

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.[4] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

8.2 *Organometallic Standards,* single element and multielement organometallic standards, nominal 100 mg/kg of each element of interest.

8.3 *Internal Standard,* fuel soluble yttrium, cobalt, scandium or other single element organometallic standard, not a component of the fuel test specimen or calibration standard, nominal 5000 mg/kg.

8.4 *Kerosine,* with analyte concentrations below the detection limits of the instrument. The kerosine can be screened for the presence of analytes as detailed in 12.1 by performing a wavelength scan for analyte wavelengths.

8.5 *Argon Gas,* 99.995 % minimum purity. (**Warning—**Argon may be a compressed gas under high pressure.)

8.6 *Nitrogen Gas,* 99.999 % minimum purity. (**Warning—**Nitrogen may be a compressed gas under high pressure.)

8.7 *Nitric Acid,* 10 % aqueous solution. (**Warning—**Nitric acid may cause severe burns.)

8.8 *Quality Control (QC) Samples,* preferably are portions of one or more fuel or kerosine materials 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 Section 18. If a suitable QC fuel is not available, obtain a stable QC concentrate, and dilute it with kerosine on the day of the QC check to the trace level required as described in 12.3. Use HDPE plastic bottles to contain concentrated organometallic solutions and for sodium analysis.

9. Hazards

9.1 Gases under high pressure and corrosive acid are used in this method. Wear appropriate personal protective equipment when working with nitric acid. Use only apparatus rated for handling the high gas pressures that occur in this test method.

10. Sampling and Test Specimens

10.1 Samples shall be taken in accordance with procedures described in Practice D4057. Suitable sample containers for aviation fuels are described in Practice D4306. Use HDPE plastic containers for sodium analysis.

10.2 Samples shall be thoroughly mixed in their containers immediately prior to testing.

10.3 If particulate matter is observed in the sample, filter it through a 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 kerosine blank material used for the analysis of these samples.

11. Preparation of Apparatus

11.1 *Spectrometer*—Prepare the ICP spectrometer according to the manufacturer's instructions and parameter settings for organic materials and the elements of interest. At least three integrations should be made for all samples (standards, blank, fuels) run. Table 1 provides recommended element wavelengths for fuels; however, other wavelengths may be used due to possible instrument variations or spectral interferences. The optical path can be purged with argon or another high purity gas (for example, nitrogen) recommended by the manufacturer. Before igniting the plasma, inspect the quartz torch to make sure that it is clean. If carbon build-up is observed, replace the torch and make the manufacturer's recommended adjustments for this problem. Warm up the instrument while purging the optics for the time period recommended by the ICP manufacturer. If necessary, replace the peristaltic pump tubing and adjust the solution uptake to the desired rate. Ignite the torch, then begin aspirating kerosine through the nebulizer and into the spray chamber. Continue plasma warm-up/stabilization for the duration specified by the ICP manufacturer.

11.2 *Glassware, Plasticware*—Acid clean glassware and plasticware with 10 % nitric acid (trace metal analysis grade) followed by several distilled water rinses. Do not use glassware and plasticware that has previously contained solutions with high concentrations of the element(s) of interest.

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[4] *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 *Annual 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.

12. Preparation of Standards and Test Specimens

12.1 *Purity of Kerosine*—Sources of satisfactory high purity kerosine are commercially available. For ICP instruments which provide a visual profile of emission peaks, a check may be made of the kerosine purity by aspirating the kerosine and viewing the spectral regions where the element emissions of interest are to be found. The absence of emission peaks in these regions is evidence that the purity is satisfactory.

12.2 *Internal Standard Stock Solution:*

12.2.1 The analyst's selection of the single element internal standard may be influenced by the capabilities (wavelength availability, sensitivity) of the ICP instrument available. The single element chosen for the internal standard should not be a component of the fuel test specimen or calibration standard. Organometallic yttrium has performed well as an internal standard for this test method and is recommended. Table 2 lists internal standards, their recommended wavelengths, and their approximate use concentrations for this test method.

12.2.2 Prepare a stock solution of the internal standard by weight from a 5000 mg/kg single element organometallic standard material and kerosine. Prepare a concentration that is approximately 50 times the concentration required in the fuel test specimen and working standard. Prepare a minimum of 50 grams of internal standard stock solution. Prepare fresh internal standard stock solution weekly.

12.2.3 The following is an example for preparing a nominal 50 mg/kg yttrium internal standard stock solution: Tare on an analytical balance a clean glass or HDPE plastic container (for example, 125 mL bottle, use HDPE for sodium analysis) sized for the following procedure. Weigh a nominal 0.5 g (to the nearest 0.001 g) of the 5000 mg/kg yttrium organometallic internal standard into the container. Add kerosine to bring the solution mass to a nominal 50.0 g. Determine the solution mass to the nearest 0.001 g. Seal the container and mix well. The internal standard stock solution concentration is determined in the same manner as described for the calibration standard in 16.1.

12.3 *Working Standard:*

12.3.1 Preparation of a nominal 2.0 mg/kg elemental working standard is described in this test method as an example. Higher or lower working standard concentrations may be prepared depending on the sensitivity of the ICP spectrometer (for example, radial or axial viewing, detector type, age of ICP) and the elements of interest in the fuel sample. Determine the suitability of the working standard concentration after calibration by analyzing a kerosine sample prepared with a known concentration (for example, 1.0 mg/kg) of the elements of interest. Measured values within 5 % of the prepared concentration are acceptable. Commercially available organometallic standards with certified element concentrations are suitable for this test method.

12.3.2 *Calibration Standard Solution* (nominal 2.0 mg⁄kg)—Tare on an analytical balance a clean glass or HDPE plastic container (for example, 125 mL bottle, use HDPE for sodium analysis) sized for the following procedure: Weigh a nominal 1.0 g (to the nearest 0.0001 g) of the nominal 100 mg⁄kg organometallic standard (for all elements of interest) into the container. Add kerosine to bring the solution mass to a nominal 50.0 g. Determine the solution mass to the nearest 0.0001 g. Seal the container and mix the solution well. Calculate the element concentrations as shown in 16.1. Use these values for establishing the calibration lines (see Section 14). The calibration standard solution is to be prepared daily when samples are to be analyzed.

12.3.3 *Working Standard*—The working standard is prepared with the calibration standard solution and the internal standard stock solution as follows: To a 50 mL volumetric flask, pipette 1000 µL of the internal standard stock solution. Fill the volumetric flask to the volume mark with the calibration standard solution prepared in 12.3.2. Seal the volumetric flask and mix well. Working standards are to be prepared daily when samples are to be analyzed.

12.3.3.1 Use of the yttrium internal standard stock solution described in 12.2.3 will provide a nominal 1.0 mg/kg internal standard in the working standard.

12.4 *Check Standard*—Prepare an instrument check standard in the same manner as the working standard (see 12.3) at element concentrations that are anticipated for the fuel samples to be analyzed. It is advisable to prepare the check standard from an alternative source of certified organometallic standard.

12.5 *Test Specimens*—To a 50 mL volumetric flask, add 1000 µL of the internal standard stock solution. Fill the flask to the mark with the fuel to be analyzed. This provides a fuel test specimen with an internal standard at the same concentration as provided in the working standard. If insufficient fuel sample is available, the flask volume and added internal standard stock solution volume may be proportionally reduced. Since the same amount of internal standard stock solution has been added to the working standard and the fuel test specimens, no dilution factor correction is needed.

13. Wavelength Selection and Background Correction

13.1 Recommended wavelengths for each element to be determined and for internal standards are given in Table 1 and Table 2, respectively. To accommodate different ICP instruments and their performances, other wavelengths not shown in these tables may be used. Select wavelengths with best intensity, peak shape, and lack of interferences. Since analyses are for trace levels of elements, background correction is required. Thus, for all elements possible, the baseline for the emission peak should be set with points as close to both sides of the peak without measuring the element wavelength intensity (see Fig. 1). After these baselines are set, a check standard is used to test the system response and calibration as described in the next section.

13.2 Appropriate selection of wavelengths for background corrections is extremely critical for the determination of sodium since the predominate sodium emission line (588.995 nm) resides near a significant argon emission interference. During method development it is recommended, if possible, that the spectra of samples and standards be compared at the sodium emission wavelength to ensure that signal integration occurs accurately.

NOTE 1—Some emission wavelengths occur on a highly structured background (for example, sodium emission at 588.995 nm); hence a single

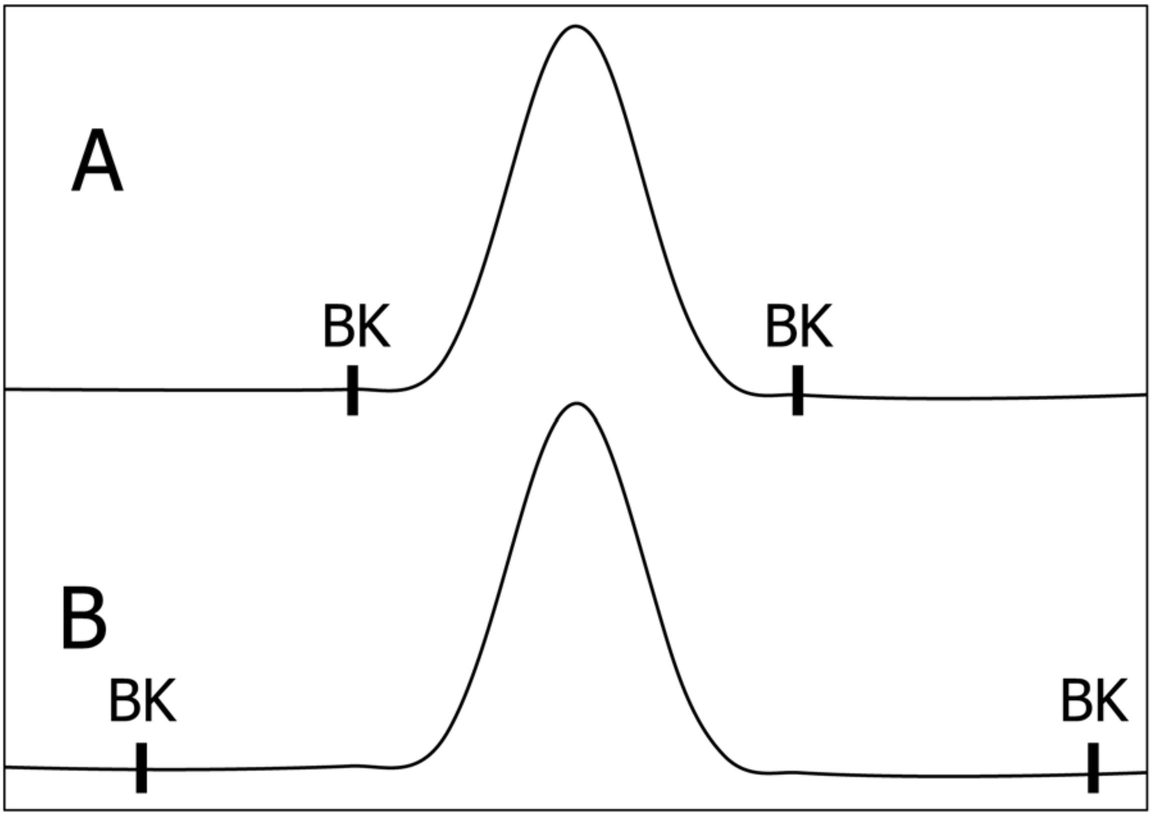

FIG. 1 Correct (A) and Incorrect (B) Selection of Background

off-peak background measurement may provide inaccurate results. For emission wavelengths on a structured background, background correction is recommended at both lower and higher wavelengths from the emission wavelength. In addition, some low-resolution, photomultiplier tube-based instruments may require a comprised selection of background points, which could also provide inaccurate results.

14. Calibration

14.1 A two-point calibration, consisting of the kerosine blank and the working standard, of the instrument is conducted within the linear range of the spectrometer. Calibration shall be performed each time a new batch of fuel samples is to be analyzed.

14.2 Analyze the check standard to determine if all elements are in calibration. Each element must be within 5 % of its prepared concentration in order to proceed to testing of fuel samples. If not, make necessary instrument adjustments and recalibrate until all elements are within 5 % of check standard values.

14.3 Aspirate kerosine between standard (and fuel 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 kerosine purge to ensure that it has been removed.

14.4 Most ICP spectrometers have software that automatically performs the calculations to establish the calibration curve when using an internal standard. Element emission intensities are ratioed to the internal standard emission intensities. Subsequent references to emission intensities in this section and Section 15 pertain to baseline corrected peak areas. The calibration curve is a plot of the intensity ratio for an element *e* in the working standard (R_{ws}) versus the concentration of element *e* in the calibration standard (C_{cs}), and

$$R_{ws} = (I_{ws} - I_b)/I_{ints} \quad (1)$$

where:

I_{ws} = emission intensity for element *e* in the working standard,

I_b = emission intensity for element *e* in the kerosine blank, and

I_{ints} = emission intensity of the internal standard in the working standard solution.

15. Analysis

15.1 Determine the ICP detection limits for all elements of interest as follows: Prepare a kerosine blank with an internal standard by pipetting 1000 µL of the internal standard stock solution into a 50 mL volumetric flask, and fill to the volume marker with kerosine. Seal the flask, and mix well. Perform ten consecutive analyses of this solution for all elements of interest under the same conditions/parameters that the two-point calibration standards were run. With the ICP instrument software, determine the standard deviation of the ten results for each element of interest. The detection limit of each element is its standard deviation multiplied by three. Detection limits should be determined daily after calibration.

15.2 Conduct fuel sample analyses under the same conditions/parameters that the two-point calibration standards were run. Aspirate kerosine between fuel samples to clear the system of elements from the prior sample. The ICP instrument software generates concentration values for each element.

15.3 In a manner similar to that described in 14.4 for the calibration, the analysis of the fuel sample generates an intensity ratio as follows:

$$R_f = I_f / I_{intf} \tag{2}$$

where:

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

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

$$C_f = (R_f \times C_{cs})/R_{ws} \tag{3}$$

where:

C_f = concentration (mg/kg) of element *e* in the fuel,
C_{cs} = concentration (mg/kg) of element *e* in the calibration standard,
R_f = intensity ratio of element *e* in the fuel, and
R_{ws} = intensity ratio of element *e* in the working standard.

15.3.1 Eq 3 applies if the density of the working standards and the test specimen are similar. If the density of the test specimen is dissimilar (greater than 6 %) to that of the working standards, the accuracy of the result calculated by Eq 3 will be impacted. The effect of the density difference can be corrected for by multiplying the result of Eq 3 (C_f) by the density of the working standard divided by the density of the test specimen. Alternatively, the working standards can be prepared using a diluent of similar density to that of the test specimen.

NOTE 2—The procedure described in 15.3 only works if the internal standard fully compensates for sample transport and nebulization differences between the sample and the standard. This may not be the case for larger density differences. However, the middle distillate fuels covered in this test method have all distillation fractions contained within the boiling range of 150 °C to 390 °C and the differences in density typically should not be significant enough to cause sample transport and nebulization differences.

15.4 Analyze the check standard after every fifth fuel test specimen. If any result is not within 5 % of the prepared concentration, recalibrate the instrument and reanalyze the previously analyzed fuel test specimens back to the previously acceptable check standard analysis.

16. Calculation

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

$$C_{cs} = (M_{100}/M_{cs})\, C_{100} \tag{4}$$

where:

C_{cs} = the concentration (mg/kg) of element *e* in the calibration standard solution,
C_{100} = the concentration (mg/kg) of element *e* in the nominal 100 mg/kg organometallic standard,
M_{100} = the mass (g) of the nominal 100 mg/kg organometallic standard, and
M_{cs} = the mass (g) of the prepared solution of the nominal 100 mg/kg organometallic standard and kerosine.

17. Report

17.1 Report element concentrations in mg/kg to two decimal places. If a concentration is determined to be below the detection limit (BDL) of the instrument, it should be identified as such (BDL) along with the determined detection limit for the element.

18. Quality Control

18.1 Confirm the performance of the instrument or the test procedure by analyzing a quality control (QC) sample (see 8.8).

18.1.1 If a suitable QC fuel sample is not available, prepare QC samples daily from the QC concentrate at different concentrations in the working range in the same manner described in 12.3.

18.1.2 When QC/quality assurance (QA) protocols are already established in the testing facility, these may be used when they confirm the reliability of the test result.

18.1.3 When there is no QC/QA protocol established in the testing facility, Appendix X2 can be used as the QC/QA system.

19. Precision and Bias

19.1 *Precision*—The precision of this test method was determined by the statistical examination of two interlaboratory studies.[5] The first interlaboratory study involved eight laboratories and twelve fuel samples analyzed in duplicate (six diesel, three aviation jet, and three kerosine fuels spiked with organometallics at varied levels within the range of the method). The second interlaboratory study (a rerun of sodium only, using HDPE sample bottles) involved six laboratories and twelve fuel samples analyzed in duplicate (six diesel, three aviation jet, and three kerosine fuels spiked with organometallics at varied levels within the range of the test method). The precision determined is as follows:

19.1.1 *Repeatability*—The difference between successive results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the values in Table 3 only in one case in twenty.

19.1.2 *Reproducibility*—The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would in the long run, exceed the values in Table 4 only in one case in twenty. Calculated reproducibility (and repeatability) values for a 1.0 mg/kg result are shown in Table 5.

19.2 *Bias*—Since there are no accepted reference materials for determining bias for this test method, no statement on bias is being made.

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[5] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1569.

TABLE 3 Repeatability

Element	Range,[A] mg/kg	Repeatability,[B] mg/kg
Aluminum	0.13 – 1.77	0.09692 $X^{0.5202}$
Barium	0.11 – 1.92	0.05896 $X^{0.7520}$
Calcium	0.10 – 1.77	0.0887 $X^{0.7391}$
Chromium	0.11 – 1.73	0.05839 $X^{1.0350}$
Cobalt[C]	0.15 – 1.60	0.2007 $(X + 0.0001)^{0.4577}$
Copper	0.11 – 1.85	0.03470 $(X + 0.6579)$
Iron	0.11 – 1.71	0.05312 $X^{0.9114}$
Lithium	0.10 – 1.83	0.06941 $(X – 0.02484)$
Lead	0.08 – 1.73	0.1166 $X^{0.6934}$
Magnesium	0.10 – 1.76	0.04820 $X^{0.6570}$
Manganese	0.10 – 1.75	0.04522 $X^{0.9759}$
Molybdenum	0.11 – 1.74	0.08204 $X^{0.9591}$
Nickel	0.10 – 1.72	0.05274 $(X + 0.3444)$
Phosphorus[C]	0.20 – 1.80	0.1396 $X^{0.522}$
Potassium	0.19 – 1.80	0.1191 $X^{0.3661}$
Palladium[C]	0.12 – 1.88	0.1530 $X^{0.9144}$
Platinum[C]	0.49 – 1.52	0.2288 $X^{0.7489}$
Sodium	0.21 – 2.03	0.02916 $(X + 1.8414)$
Silicon	0.17 – 1.95	0.07106 $X^{0.3976}$
Silver	0.08 – 2.02	0.07236 $X^{0.5626}$
Strontium[C]	0.08 – 1.78	0.1557 $(X + 0.0125)^{0.6319}$
Tin[C]	0.38 – 1.43	0.1099 $(X + 0.0241)^{0.2606}$
Titanium	0.11 – 1.73	0.04993 $X^{0.6002}$
Vanadium	0.10 – 1.72	0.06637 $X^{0.5841}$
Zinc	0.09 – 1.65	0.05507 $X^{0.7402}$

[A] Range of sample means in interlaboratory study.

[B] Where X is the mean concentration, mg/kg.

[C] Interim equations based on limited ILS. Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1778.

TABLE 4 Reproducibility

Element	Range,[A] mg/kg	Reproducibility,[B] mg/kg
Aluminum	0.13 – 1.77	0.3689 $X^{0.5202}$
Barium	0.11 – 1.92	0.2353 $X^{0.7520}$
Calcium	0.10 – 1.77	0.3097 $X^{0.7391}$
Chromium	0.11 – 1.73	0.2869$X^{1.0350}$
Cobalt[C]	0.15 – 1.60	0.8508 $(X + 0.0001)^{0.4577}$
Copper	0.11 – 1.85	0.2495 $(X – 0.09548)$
Iron	0.11 – 1.71	0.2717 $X^{0.9114}$
Lithium	0.10 – 1.83	0.09703 $(X + 0.4716)$
Lead	0.08 – 1.73	0.6039 $X^{0.6934}$
Magnesium	0.10 – 1.76	0.2200 $X^{0.6570}$
Manganese	0.10 – 1.75	0.2517 $X^{0.9759}$
Molybdenum	0.11 – 1.74	0.3725 $X^{0.9591}$
Nickel	0.10 – 1.72	0.2811 $(X – 0.01824)$
Phosphorus[C]	0.20 – 1.80	1.3089 $X^{0.522}$
Potassium	0.19 – 1.80	0.5212 $X^{0.3661}$
Palladium[C]	0.12 – 1.88	1.1924 $X^{0.9144}$
Platinum[C]	0.49 – 1.52	1.3488 $X^{0.7489}$
Sodium	0.21 – 2.03	0.2433 $(X + 1.8414)$
Silicon	0.17 – 1.95	0.2399 $X^{0.3976}$
Silver	0.08 – 2.02	0.3025 $X^{0.5626}$
Strontium[C]	0.08 – 1.78	0.7512 $(X + 0.0125)^{0.6319}$
Tin[C]	0.38 – 1.43	0.9926 $(X + 0.0241)^{0.5275}$
Titanium	0.11 – 1.73	0.2175 $X^{0.6002}$
Vanadium	0.10 – 1.72	0.3359 $X^{0.5841}$
Zinc	0.09 – 1.65	0.3593 $X^{0.7402}$

[A] Range of sample means in interlaboratory study.

[B] Where X is the mean concentration, mg/kg.

[C] Interim equations based on limited ILS. Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1778.

20. Keywords

20.1 aviation turbine fuel; diesel fuel; elemental analysis; fuel; ICP; inductively coupled plasma atomic emission spectrometry; internal standard; middle distillate fuels; trace elements

TABLE 5 Calculated Precision, mg/kg, at 1.0 mg/kg

Element	Repeatability, mg/kg	Reproducibility, mg/kg
Aluminum	0.097	0.369
Barium	0.059	0.235
Calcium	0.089	0.310
Chromium	0.058	0.287
Cobalt	0.201	0.851
Copper	0.035	0.226
Iron	0.053	0.272
Lithium	0.069	0.143
Lead	0.117	0.604
Magnesium	0.048	0.220
Manganese	0.045	0.252
Molybdenum	0.082	0.373
Nickel	0.071	0.276
Phosphorus	0.1369	1.309
Potassium	0.119	0.521
Palladium	0.153	1.192
Platinum	0.229	1.349
Sodium	0.083	0.691
Silicon	0.071	0.240
Silver	0.072	0.303
Strontium	0.157	0.757
Tin	0.111	1.005
Titanium	0.050	0.218
Vanadium	0.066	0.336
Zinc	0.055	0.359

APPENDIXES

(Nonmandatory Information)

X1. HELPFUL HINTS FOR OPERATION OF TEST METHOD D7111

X1.1 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.

X1.2 Work in a well-ventilated hood, and with adequate protection as prescribed in the appropriate safety practices.

X1.3 Check the temperature and humidity controls of the laboratory containing the ICP-AES instrument, and verify adequacy for performing accurate and precise analyses. Ensure that stable environmental conditions exist throughout the period of use.

X1.4 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 does not contaminate the analyses. Soak the glassware in warm dilute (5 % v/v) reagent grade 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. When possible, all plasticware should be replaced with FEP or PFA materials.

X1.5 Do not use glassware or plasticware that has previously contained solutions with high concentrations of the element(s) of interest.

X1.6 To minimize contamination during standard/sample preparation, prepare all aliquots in either PP or FEP/PFA pre-cleaned containers. The sample introduction system should be cleaned and maintained periodically based on sample volume and analyte concentration.

X1.7 Select solvents and other reagents that do not contain significant levels of the analytes being determined.

X1.8 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. If using hand shaking, vigorously shake the sample container for about 30 s immediately prior to taking an aliquot for analysis. Ultrasonic homogenizers and vortex mixers can help in making the samples uniform in their content.

X1.9 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.

X1.10 Testing should be performed under normal laboratory conditions using an operator with good experience in ICP-AES technology.

X1.11 The instrument measurement capability is affected by instrument maintenance quality, laboratory environment/protocols, equipment age, and other factors.

X1.12 Inspect the torch for cracks. Discard defective torches. Use clean torches that do not have carbon deposits.

X1.13 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.

X1.14 Adjust the variations due to buildup of deposits on the nebulizer during the course of determinations by frequently nebulizing the check standard.

X1.15 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*) using 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.

X1.16 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.

X1.17 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.

X1.18 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.

X1.19 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.

X1.20 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 5 % 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.

X1.21 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.

X1.22 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.

X1.23 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.

X1.24 By experiment, determine the frequency of standards preparation. Then, prepare fresh, as needed.

X1.25 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.

X1.26 Standard addition technique may be employed for samples known to have elemental or other interferences.

X1.27 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.

X1.28 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.

X1.29 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.

X1.30 Periodically, as needed determine the linearity of the calibration curves. Perform quantitative analyses with linear curves only.

X1.31 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.

X1.32 Use the wavelengths specified in the test method for measurement, because they have been established by experiment and experience to be the optimum wavelengths, and free from spectral interference.

X1.33 Memory interferences result when higher levels of elements in a previous sample contribute to the signals measured in a subsequently analyzed sample. Memory effects can result 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 interferences section (Section 6) of this test method for further instructions.

X1.34 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.

X1.35 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.

X1.36 A mass flow controller to regulate the nebulizer gas may be used as recommended by the instrument manufacturer.

X1.37 At least three integrations of measurements should be made for all samples (standards, blank, fuels) run.

X1.38 See the interferences section of the test method for properly detecting and minimizing spectral 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. ICP spectrometer manufacturer's software may be used to provide corrections to interferences that cannot be avoided by wavelength selection and background correction. Avoid spectral interferences where possible by judicious choice of wavelengths to be used or by comparing the results of two different wavelengths for the same element.

X1.39 With any instrument, the analyst must always be alert to the possible presence of unexpected elements producing interfering spectral peaks.

X1.40 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.

X1.41 In choosing an internal standard, consider the purity of (freedom from analyte), sensitivity, interferences, ionization energies (that is, internal standard versus analyte), soluble/compatible with sample matrix and coexistent species, etc.

X1.42 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.

X1.43 High levels of dissolved solids in the sample may contribute deposits of material on the nebulizer reducing the effective diameter and shape of the orifice and, therefore, atom transmission. Dissolved solid levels not exceeding 0.2 % (w/v) are recommended to reduce such effects.

X1.44 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 five or ten 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.

X1.45 Report results using the number of significant figures specified in the test method standard.

X2. QUALITY CONTROL

X2.1 Confirm the performance of the instrument or the test procedure by analyzing a QC sample.

X2.2 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.[6]

X2.3 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, Practice D6792, and MNL 7.[6] Investigate any out-of-control data for root cause(s). The results of this investigation may, but not necessarily, result in instrument re-calibration.

X2.4 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.

X2.5 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

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[6] ASTM Manual MNL 7, *Manual on Presentation of Data Control Chart Analysis*, 6th ed., ASTM International.

should be available for the intended period of use, and must be homogenous and stable under the anticipated storage conditions. See Practice D6299, Practice D6792, and MNL 7,[6] or a combination thereof, for further guidance on QC and control charting techniques.

SUMMARY OF CHANGES

Subcommittee D02.03 has identified the location of selected changes to this standard since the last issue (D7111 – 15a) that may impact the use of this standard. (Approved Dec. 1, 2016.)

(1) Added new Appendix X1 incorporating helpful hints to the analyst using this test method.

Subcommittee D02.03 has identified the location of selected changes to this standard since the last issue (D7111 – 15) that may impact the use of this standard. (Approved July 1, 2015.)

(1) Revised subsection 15.3 by adding new subsection 15.3.1 and new Note 2.

Subcommittee D02.03 has identified the location of selected changes to this standard since the last issue (D7111 – 14) that may impact the use of this standard. (Approved April 1, 2015.)

(1) Updated reference to Military standard in 2.2; updated corresponding footnote.
(2) Updated reference to Military standard in 5.2.
(3) Updated Table 1.
(4) Revised 7.2.

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