



Designation: ~~D7111 – 15a~~ D7111 – 16

# Standard Test Method for Determination of Trace Elements in Middle Distillate Fuels by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)<sup>1</sup>

This standard is issued under the fixed designation D7111; 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 reappraisal. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reappraisal.

## 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.

<sup>1</sup> 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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**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

\*A Summary of Changes section appears at the end of this 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:<sup>2</sup>

**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<sup>3</sup>

## 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.

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** regarding the optimum operation of any ICP-AES system.

## 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

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

<sup>3</sup> Available online at <http://quicksearch.dla.mil> or <http://assistdocs.com>

**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

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  $\mu\text{m}$  or 1.0  $\mu\text{m}$  pore size.

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

7.7 *Pipette*, 1000  $\mu\text{L}$ .

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.<sup>4</sup> 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.

<sup>4</sup> *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.

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  $\mu\text{m}$  or 1.0  $\mu\text{m}$  (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.

## 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~~ ~~mg/kg~~ ~~Tare/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~~ ~~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  $\mu$ L 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  $\mu$ L 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~~) (~~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 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.

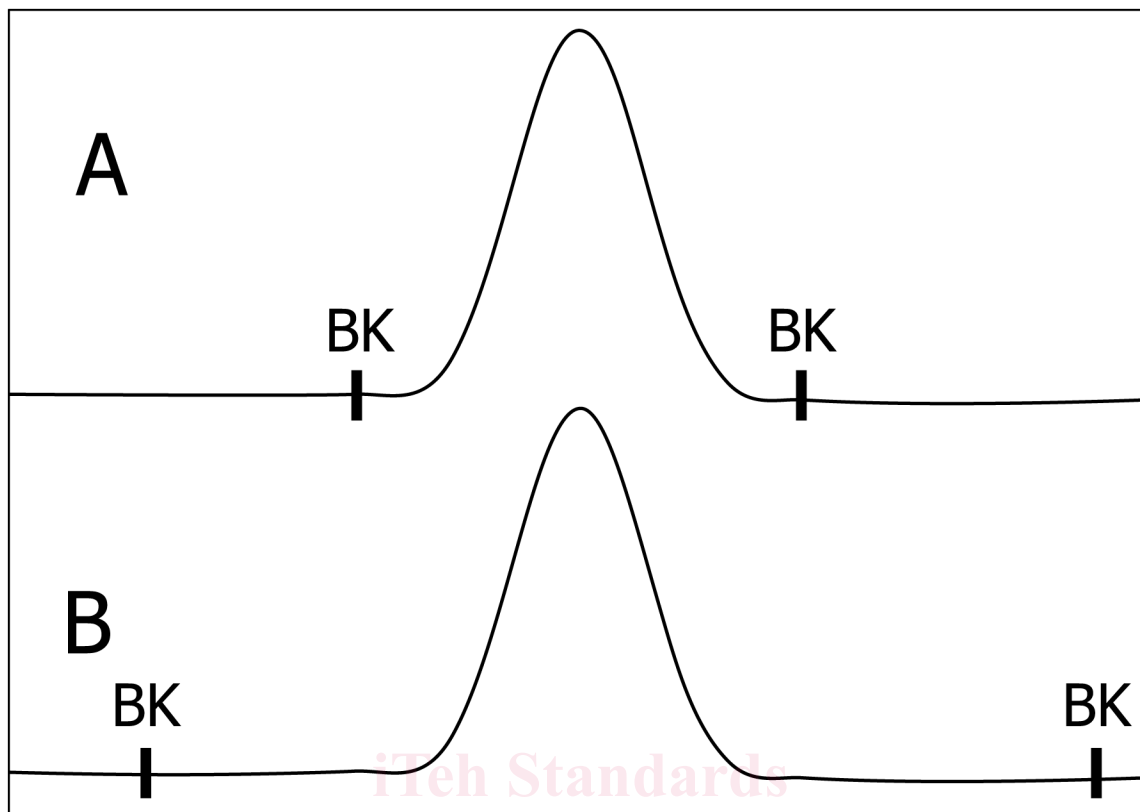


FIG. 1 Correct (A) and Incorrect (B) Selection of Background

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  $\mu\text{L}$  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.