



Designation: D8322 – 20

Standard Test Method for Determination of Elements in Residual Fuels and Crude Oils by Microwave Plasma Atomic Emission Spectroscopy (MP-AES)¹

This standard is issued under the fixed designation D8322; 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.

1. Scope

1.1 This test method covers the determination of metals and other elements in residual fuel and crude oil by microwave plasma atomic emission spectroscopy (MP-AES). The specific elements within the scope of this method are V, Ni, Ca, Na, Al, Si, Zn, P, and S for residual fuel oil and Fe, V, Ni, Ca, Na, K, and S for crude oils.

1.2 Method working range:
 high expected concentration limit = highest ILS sample mean
 low expected concentration limit = lowest ILS sample mean if:

(1) lowest ILS sample mean – $R_{\text{lowest ILS sample mean}} > 0$;
 otherwise it is determined by solving for X using the following equation:

(2) $X - R_x = \text{coarsest resolution, determined by } 0.5 \cdot \sigma_r \text{ lowest ILS sample mean}$

Crude Oil:	
Element	Method Working Range (expected mg/kg)
Iron	0.70 to 161.02
Vanadium	2.88 to 417.50
Nickel	0.36 to 107.66
Calcium	5.41 to 96.78
Sodium	1.18 to 97.13
Potassium	7.01 to 63.83
Sulfur	1059 to 35194

Residual Fuel Oil:	
Element	Method Working Range (expected mg/kg)
Vanadium	3.88 to 370.09
Nickel	1.47 to 96.68
Calcium	4.41 to 102.01
Sodium	2.80 to 112.67
Aluminum	4.13 to 154.12
Silicon	5.99 to 237.56
Zinc	2.75 to 102.46
Sulfur	1314 to 30134

1.3 This test method uses soluble metals in organic solvents for calibration and does not purport to quantitatively determine insoluble particulates. Analytical results are particle size

dependent, and particles larger than a few micrometers may cause results to appear low

1.4 Elements present at mass fractions above the upper limit of the calibration curves can be determined with additional appropriate dilutions. Elements shall be measured at the wavelengths presented in [Table 1](#).

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

1.6 *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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

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

2. Referenced Documents

- 2.1 *ASTM Standards*:²
- [D1298 Test Method for Density, Relative Density, or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method](#)
 - [D1548 Test Method for Vanadium in Heavy Fuel Oil¹ \(Withdrawn 1997\)³](#)
 - [D4052 Test Method for Density, Relative Density, and API Gravity of Liquids by Digital Density Meter](#)
 - [D4175 Terminology Relating to Petroleum Products, Liquid Fuels, and Lubricants](#)
 - [D5708 Test Methods for Determination of Nickel, Vanadium, and Iron in Crude Oils and Residual Fuels by](#)

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 The last approved version of this historical standard is referenced on www.astm.org.

TABLE 1 Element Wavelengths

NOTE 1—These wavelengths shall be used for this method. The precision for this method is based on these wavelengths.

Element	Wavelength, nm	Standards Used in Each Curve (mg/kg)
Iron	259.940	Solvent blank, 0.1, 1.0, 10, 25
Vanadium	311.070	Solvent Blank, 0.1, 1.0, 10, 25, 50
Nickel	341.476	Solvent Blank, 0.1, 1.0, 10, 25, 50
Calcium	396.847	Solvent Blank, 0.1, 1.0, 10
Calcium	616.217	Solvent Blank, 10, 25, 50, 70
Sodium	588.995	Solvent Blank, 0.1, 1.0, 10
Aluminum	396.152	Solvent Blank, 0.1, 1.0, 10, 25, 50
Silicon	288.158	Solvent Blank, 0.1, 1.0, 10, 25
Zinc	213.857	Solvent Blank, 0.1, 1.0, 10
Potassium	766.491	Solvent Blank, 0.1, 1.0, 10, 25, 50, 70
Sulfur	181.972	Solvent Blank, 40, 200, 500, 1000, 2000
Yttrium (IS)	371.029	

Inductively Coupled Plasma (ICP) Atomic Emission Spectrometry

D6021 Test Method for Measurement of Total Hydrogen Sulfide in Residual Fuels by Multiple Headspace Extraction and Sulfur Specific Detection

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, Liquid Fuels, and Lubricants

D6792 Practice for Quality Management Systems in Petroleum Products, Liquid Fuels, and Lubricants Testing Laboratories

D7372 Guide for Analysis and Interpretation of Proficiency Test Program Results

2.2 ISO Standard.⁴

ISO 8573-1 Compressed air – Part 1: Contaminants and purity classes

3. Terminology

3.1 Definitions:

3.1.1 *calibration*, *n*—process by which the relationship between signal intensity and elemental mass fraction is determined for a specific element analysis. **D4175**

3.1.2 *emission spectroscopy*, *n*—measurement of energy spectrum emitted by or from an object under some form of energetic stimulation; for example, light, electrical discharge, and so forth. **D4175**

3.2 Definitions of Terms Specific to This Standard:

3.2.1 *calibration curve*, *n*—plot of signal intensity versus elemental mass fraction using data obtained by making measurements with standards.

3.2.2 *check standards*, *n*—a second source QC sample prepared in o-xylene (wt/wt), such that the mass fraction is the

median of the linear calibration range and 10 % of the highest mass fraction standard (see Practice **D6792** for guidance in this area).

3.2.3 *continuing calibration blank (CCB)*, *n*—a blank calibration standard that does not contain any elements of interest, analyzed immediately following each CCV; this solution is the sample blank.

3.2.4 *continuing calibration verification (CCV)*, *n*—a mid-range calibration standard analyzed after every ten sample analyses to verify that the instrument calibration has not drifted.

3.2.5 *diluted stock standard (DSS)*, *n*—a material prepared by gravimetric dilution of stock standard (OSS) to facilitate preparation of working standards.

3.2.6 *high solids nebulizer*, *n*—a device that generates an aerosol by flowing a liquid over a surface that contains an orifice from which gas flows at a high velocity.

3.2.7 *internal standard (IS)*, *n*—a high purity compound not present in the sample which is added to each solution, calibration blank, working standards, and samples and used to calculate quantitatively the compound of interest.

3.2.8 *microwave plasma (MP)*, *n*—a high temperature microwave plasma created by coupling the magnetic field of the microwave energy into the plasma.

3.2.9 *organometallic stock standard (OSS)*, *n*—a material which is well characterized for the elements of interest, with assigned mass fraction values traceable to the SI.

3.2.10 *profiling*, *n*—a technique that determines the wavelength at which the signal intensity is measured for a particular analyte is a maximum.

3.2.11 *quality control (QC) sample*, *n*—for use in quality assurance programs to determine and monitor the precision and stability of a measurement system, a stable and homogeneous material having physical or chemical properties, or both, similar to those of typical samples tested by the analytical measurement system; the material is properly stored to ensure sample integrity and is available in sufficient quantity for repeated, long term testing.

3.2.12 *residual fuel oil*, *n*—the heavier oils that remain after the distillate fuel oils and lighter hydrocarbons are distilled away in the refinery process (viscosity at 40 °C between 5.5 mm²/s and 24.0 mm²/s, inclusive). **D6021**

3.2.13 *working standard (WS)*, *n*—a material prepared from dilution of the DSS organometallic solution containing the elements of interest for the purpose of quantitative calibration.

4. Summary of Test Method

4.1 *Test Method*—For determination of elements in residual fuels and crude oils, a homogenized sample is diluted in a suitable organic solvent and introduced through the nebulizer and spray chamber into the microwave plasma atomic emission spectrometer. Quantification of elements is achieved by comparing measurements of emission intensity at the appropriate wavelength for each element to measurements of emission intensity made under the same conditions on organic standard reference solutions in the same organic solvent.

⁴ Available from International Organization for Standardization (ISO), ISO Central Secretariat, BIBC II, Chemin de Blandonnet 8, CP 401, 1214 Vernier, Geneva, Switzerland, <http://www.iso.org>.

5. Significance and Use

5.1 This test method covers the determination of V, Ni, Ca, Na, Al, Si, Zn, P, and S for residual fuels and Fe, V, Ni, Ca, Na, K, and S for crude oils. This test method complements and extends the capabilities of Test Methods **D1548** and **D5708**, which only apply to the determination of Ni, V, and Fe in crude oils and residual fuels.

5.2 The metals and other elements tested for in this method may occur naturally or may be added as a result of production (that is, catalyst fines).

6. Interferences

6.1 *Spectral*—Check all spectral interferences expected from the elements listed in **Table 1** using manufacturer's operating guide to develop and apply correction factors to compensate for the interferences. To apply interference corrections, all mass fractions must be within the linear response range of each element listed in **Table 1**.

6.2 Spectral interferences can usually be avoided by using the specified wavelengths in **Table 1**.

6.3 *Particulates*—Particulates can clog the nebulizer thereby causing low results. Nebulizer and sample introduction requirements are defined in Section 7. Use of nebulizers or sample introduction devices, or both, that do not meet these requirements shall not be used.

7. Apparatus

7.1 *Balance*, top loading or analytical, with automatic tare, that measures to at least 0.0001 g and with sufficient capacity to weigh prepared solutions.

7.2 *Microwave Plasma Atomic Emission Spectrometer*⁵ (MP-AES)—A sequential, emission based multi-element analytical technique that uses a microwave-induced plasma for sample excitation. The operating software provides programmed sequential sample operation and quantitative data processing. A torch and microwave generator are used to form a sustained plasma that can be used for making measurements at the specified wavelengths.

7.2.1 *Sample Introduction*—The sample introduction system shall be composed of solvent-resistant tubing, a double-pass cyclonic chamber, and an inert high solids nebulizer. The nebulizer must provide a homogeneous aerosol, comprised of small droplets with a narrow distribution of droplet sizes, to increase nebulization efficiency and improve sensitivity.

7.2.2 *Gas Control System*—All gas flows shall be controlled by automated flow system. The purge control system facilitates nitrogen purging of the monochromator for optimal sulfur determination.

⁵ The sole source of supply of the Microwave Plasma Atomic Emission equipment, OneNeb Series 2 and instrumentation, known to the committee at this time is Agilent Technologies, Inc., 5301 Stevens Creek Blvd., Santa Clara, CA 95051. Agilent Technologies also has authorized sales and service organizations in selected geographical areas. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,¹ which you may attend.

7.2.3 *Instrument Control Software for Background Correction*—Spectrum correction software which allows for manual or automated background correction. Software optimizes nebulizer flow at each wavelength. Introduction conditions and settings are presented in **Table 2**. Instrument operating conditions for elemental determination in residual fuel and crude oil samples are presented in **Table 3**.

7.3 *Peristaltic Pump*—Using a peristaltic pump is required for a constant flow of solution. The pump rate recommended is 5 rpm to 10 rpm.

NOTE 1—The precision was determined using 5 rpm.

7.4 *Peristaltic Pump Tubing (Viton)*—The pump tubing must be able to withstand at least 6 h exposure to the dilution solvent. Use Viton tubing for testing hydrocarbon solvents. Inspect the peristaltic pump tubing daily and replace deteriorating tubing.

7.5 *Test Specimen Solution Containers*, of appropriate size, glass or Teflon vials or bottles, with screw caps.

7.6 *Filters*, 0.45 μm, 0.8 μm, or 1.0 μm (nylon, TFE-fluorocarbon, cellulose acetate/cellulose nitrate, or other compatible material).

7.7 *Dispensing Vessel*, provides a consistent means for dispensing of solutions more easily for gravimetric measurements.

7.8 *Internal Standard Peristaltic Tee Assembly*—Any tee-type fitting composed of solvent resistant material used to facilitate the simultaneous addition of the internal standard and sample directly into the nebulizer.

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.⁶

8.2 *Organometallic Reference Materials in Organic Matrix*—An appropriate SI-traceable certified reference material may be available for V, Ni, Na, and S from NIST or another

⁶ *ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials*, 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.

TABLE 2 Sample Introduction Conditions for Elemental Determination in Residual Fuel and Crude Oil Samples

Instrument Parameter	Operating Condition
Nebulizer	Inert High Solids nebulizer (such as the OneNeb Series 2)
Spray Chamber	Cyclonic double-pass
Sample Tubing	Viton Orange/Green. Internal standard if teeing is Viton orange/green (0.38 mm ID)
Waste Tubing	Blue/blue Viton 1.65 mm ID

TABLE 3 Instrument Operating Conditions for Elemental Determination in Residual Fuel and Crude Oil Samples

Instrument Conditions	MP-AES
Pump Rate	5 rpm
Read Time	3 s – 10 s
Number of Replicates	3
Sample Uptake Delay	Approximately 60 s (depends on lab set-up)
Stabilization Delay	Approximately 30 s (depends on lab set-up)
Background Correction	Auto
Air Injection Required	Yes

national metrology institute. Commercial reference material producers may also be able to provide SI traceable reference materials.

8.3 *Blank Mineral Oil*—U.S.P. white oil or equivalent. Material should be free of elements being measured.

8.4 *Nitrogen*—High purity compressed gas cylinder or from a nitrogen generator. Working pressure is 450 kPa to 600 kPa (65 psi to 87 psi).

8.4.1 *Plasma Support Gas*—99.5 % purity nitrogen containing <0.5 % oxygen and <4 ppm water vapor, supply at 0 L/min to 25 L/min.

8.4.2 *Monochromator Purge Gas*—99.95 % purity nitrogen containing <0.5 % oxygen and <4 ppm water vapor, supply at 0 L/min to 10 L/min.

8.5 *Air*—Air supply used for nitrogen generator supply, as follows:

8.5.1 *Plasma Support Nitrogen Generator*—ISO 8573-1:2010 CLASS 1.4.3, supply at 115 L/min.

8.5.2 *Plasma Support Nitrogen Generator*—ISO 8573-1:2010 CLASS 1.4.3, supply at 0 L/min to 25 L/min.

8.6 *Argon*—99.999 % purity, supply at 0 L/min to 1.5 L/min.

8.7 *Viton Tubing*—Orange/green (0.38 mm ID), Blue/blue Viton 1.65 mm ID.

8.8 *Organic Solvents*—o-xylene free of elements of interest. The solvent is considered acceptable for use under the condition where the solvent elemental (elements of interest) intensity response is equal to or less than 25 % compared to the intensity response of the lowest calibration point.

8.9 *Organometallic Internal Standards in Organic Matrix*—Commercially available Internal standard solutions containing oil soluble Yttrium (Y) at known certified concentrations with expanded uncertainty not exceeding 10 % relative uncertainty of the certified mass fraction.

9. Sampling

9.1 General Requirements:

9.1.1 Prior to weighing, homogenize the sample in the original container by stirring the sample or shake the sample container. Vortex mixers can help in making the samples uniform and homogenous. If the sample does not readily flow at room temperature, heat the sample in an oven, hot block, or dry bath at 60 °C. The estimated time required to sufficiently heat each sample varies and is dependent on sample density and sample volume; the sample should flow when removed from heating device.

9.2 Sample Handling During Analysis:

9.2.1 When analyzing samples using the MP-AES, the sample temperature must be within the range of 20 °C to 25 °C.

9.2.2 After analysis, if the sample is to be retained, reseal the container before storing.

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

NOTE 2—It is unlikely that solids are visible in the actual crude oil sample, especially if it is thick. Once diluted it is fluid enough that the particles are either visibly suspended in o-xylene or settle to bottom.

10. Preparation of Apparatus

10.1 *Instrument*—The optics need to be purged for 30 min with the plasma turned on prior to acquiring test data. A stable laboratory temperature between 20 °C and 25 °C shall be maintained during the entire warm-up and testing process. For best sulfur sensitivity, the optics need to be purged for at least 3 h. This only needs to be done once if leaving the purge continuously running. If the instrument loses power or is shut down for more than 1 h, the 3 h optics purge shall be repeated before attempting sulfur testing.

10.2 *Peristaltic Pump*—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 *Nitrogen Purge*—Ensure that the gas lines are adequately purged with nitrogen before attempting to ignite the plasma following the manufacturer's recommended procedure.

10.4 *MP Excitation Source*—Light the plasma source according to manufacturer's instructions at least 30 min before performing analysis. Purge sampling system and nebulizer during the warm up period using dilution solvent. Inspect the torch for carbon buildup during the warm up period. If carbon buildup occurs, replace the torch immediately and consult the MP-AES Easy Fit Torch manufacturer's maintenance guide for corrective action instructions.

10.5 *Wavelength Calibration*—Prepare the instrument for analysis by performing a wavelength calibration, dark current scan and torch alignment scan in accordance with manufacturer's instructions when the method is first run on the MP-AES. Subsequent wavelength calibration, torch alignment and dark current is typically only necessary once a month or following instrument maintenance.

10.6 *Operating Parameters*—Assign the appropriate operating parameters as shown in Table 4, so that the desired elements can be determined. Parameters to be included are element, wavelength, background correction points.

11. Calibration

11.1 The linear range must be established once for the particular instrument being used. This is accomplished by running a blank and standards. To prepare a blank, dilute the mineral oil ten-fold by mass with o-xylene. Prepare serial

TABLE 4 Analyte Nebulizer Flow Rate

Element	Wavelength, nm	Viewing Position ^A	Nebulizer Flow (L/min)	Air Injection Flow Rate	Background Correction
Iron	259.940	0	0.5	Medium	Auto
Vanadium	311.070	0	0.5	High	Auto
Nickel	341.476	0	0.5	High	Auto
Calcium	396.847	0	0.5	High	Auto
Calcium	616.217	0	0.5	High	Auto
Sodium	588.995	0	0.5	High	Auto
Aluminum	396.152	0	0.5	High	Auto
Silicon	288.158	0	0.5	Medium	Auto
Zinc	213.857	0	0.5	Medium	Auto
Potassium	766.491	0	0.5	High	Auto
Sulfur	181.972	0	0.5	Low	Auto
Yttrium (IS)	371.029	0	0.5	Medium	Auto

^AViewing position of "0" is the center of the central channel of the plasma.

dilutions of working standards (WS) for V, Ni, Ca, Na, Al, Si, Zn, P, S, Fe, and K at final mass fractions of 0.1 mg/kg, 1.0 mg/kg, 10.0 mg/kg, 25.0 mg/kg, 50.0 mg/kg, 70.0 mg/kg. For Sulfur: prepare serial dilutions of standard solutions (WS) at final mass fractions of 40.0 mg/kg, 200.0 mg/kg, 500.0 mg/kg, 1000.0 mg/kg, 2000.0 mg/kg. See [Table 1](#) for suggested calibration standards

11.1.1 Spectral background correction shall be used. When mass fractions are low, background changes, which can result from variability in the compositions of test specimen solutions, can affect the accuracy of the analysis. Background correction minimizes errors due to variable background intensities.

11.2 Standard solutions for residual fuels and crude oils are prepared by adding an adequate amount of a corresponding standard of the element to be analyzed to a viscosity-matched mineral oil (or 75 cts oil) and diluted with o-xylene to give a total oil concentration of 10 % (wt/wt) in each solution. See [Table 5](#) for example.

11.2.1 The sample-to-calibration standards viscosity must be consistent. Sufficient mineral oil is added to calibration standard when making dilutions so that the weight of the total oil content (that is, mineral oil) is constant in each diluted standard. This ensures that the sample and standards have similar physical properties in order to remove any sample introduction effects which may affect the results.

11.3 Establish the calibration curve by analyzing the working standards (WS). The acceptable calibration correlation coefficient is 0.995 or greater. If the correlation coefficient is less than 0.995 the user shall investigate to determine the

source of error or contamination and make corrections before proceeding with testing

11.4 Analyze the Quality Control (QC), Continuing Calibration Blank (CCB), and Continuing Calibration Verification (CCV) standards and unknown samples in the same manner as the calibration standards (that is, same integration time, plasma conditions, and so forth). Calculate mass fractions by multiplying the mass fraction determined for the test specimen solution by the dilution factor. Mass fraction calculations can be performed using the MP-AES instrument software. If any result is not within the expected mass fraction, take corrective action, repeat the calibration, and reanalyze the specimen solutions back to the previous acceptable QC standard analysis.

11.4.1 *Continuing Calibration Blank (CCB), and Continuing Calibration Verification (CCV)*—To ensure accuracy during the course of each analytical run, the CCB and CCV shall be analyzed at a frequency of every ten samples during an analytical run and recorded for each wavelength. The CCB and CCV standard shall also be analyzed at the beginning of the run, and again after the last analytical sample. The CCV precision shall meet the precision defined in the precision and bias section of this standard following quality control measure defined in [Section 14](#).

11.4.2 Analyze a continuing calibration blank (CCB) immediately following each CCV.

11.5 When the measured intensities for the check standards or unknown samples test specimen solution exceed the corresponding intensities for the working standard, either ensure that the calibration curve is linear to the mass fraction of the element in the test specimen solution or dilute the test specimen solution with the blank solution and reanalyze.

12. Internal Standard

12.1 Internal standard (IS) is used to analyze the test specimen solutions and the instrument software will calculate an intensity ratio for each of the elements found in the test specimen solutions. From these intensity ratios, mass fractions of the elements can be calculated.

12.2 *Internal Standard (IS)*—The mass fraction of the internal standard shall be at least 100 times its detection limit. A mass fraction in the range of 5 mg/kg to 20 mg/kg is typical (20 mg/kg is recommended). The internal standard may be added to the sample solution by using a tee assembly for

TABLE 5 Example Table on How to Make Calibration Standards (with a 900 ppm multi-element standard)

A	B	C	D	E	F
Calibration Standards (made from 885 mg/kg OSS)	Estimate of Wt of 885 mg/kg Measured	Estimate of Wt of Mineral Oil (g)	Estimate of COMBINED TOTAL "Oil" Wt (g), Column D = B + C	Estimate of Final Wt	Estimate of Final Mass Fraction (mg/kg), Column F = (885 mg/kg * B)/E
Solvent Blank	0	5	5.000	50.0	0
0.1 ppm	0.0055	4.9945	5.000	50.0	0.10
1.0 ppm	0.0555	4.9445	5.000	50.0	1.00
10.0 ppm	0.5555	4.4445	5.000	50.0	10.00
25.0 ppm	1.3887	3.6112	5.000	50.0	25.00
50.0 ppm	2.7775	2.2225	5.000	50.0	50.00
70.0 ppm	3.8885	1.1115	5.000	50.0	69.99

continuous addition or by gravimetric addition during sample preparation. An example of continuous addition is shown below in Fig. 1.

13. Preparation of Test Specimens, Standards, and Quality Control (QC) Samples

13.1 *Blank*—Prepare a blank by diluting the mineral oil ten-fold using o-xylene solvent. The elemental content of the dilution solvent is critical and must not contain the element of interest. The prepared blank shall be tested on the designated instrument described in this standard. The dilution solvent test shall be performed by testing the blank and the lowest calibration point standard under the same instrumentation conditions. The solvent blank shall be the lowest calibration point (refer to Table 1).

13.2 *Working Standard*—Prepare working standards by first diluting multi-element standards (OSS) to establish a diluted stock standard (DSS). Use the multi-element stock standard (DSS) and adjusting the weight of the blank for each calibration level to obtain appropriate calibration mass fractions. Weigh a quantity of diluted stock standard or commercial multi-element stock standard to the precision of the balance used (see 7.1) into an appropriately sized container and o-xylene. Refer to Section 16 for calculations. Weigh a quantity of the multi-element standard to the precision of the

balance used (see 7.1) into an appropriately sized container and add appropriate weight of viscosity-matched blank oil so 10 % of standard is either multi-element standard and xylene.

13.3 *Check Standards*—If CRMs are not available, prepare a second source QC samples in same organic solvent (wt/wt), such that the concentration is the median of the linear calibration range and 10 % of the top standard. See Practice D6792 for guidance

13.4 *Residual Fuel and Crude Oil Specimen*—It is extremely important to homogenize the oil to be tested in the sample container in order to obtain a representative test specimen. Viscous samples may need to be heated to 60 °C. Samples must be allowed to cool to room temperature before analysis. If the sample contains undissolved material it shall be removed by filtration with filters defined in 7.8.

13.5 *Vortex Homogenization*—As an alternative to ultrasonic homogenization, vortex mix the oil to be tested in the sample container, if possible. For viscous oils, first heat the sample to 60 °C.

13.6 Residual fuel and crude oil vary in density and require solvent dilution to facilitate sample introduction. A guide for the determination of dilution ratio is provided in Table 6. This table is intended for use when the sample API gravity or density is known. It is not possible to provide a complete range

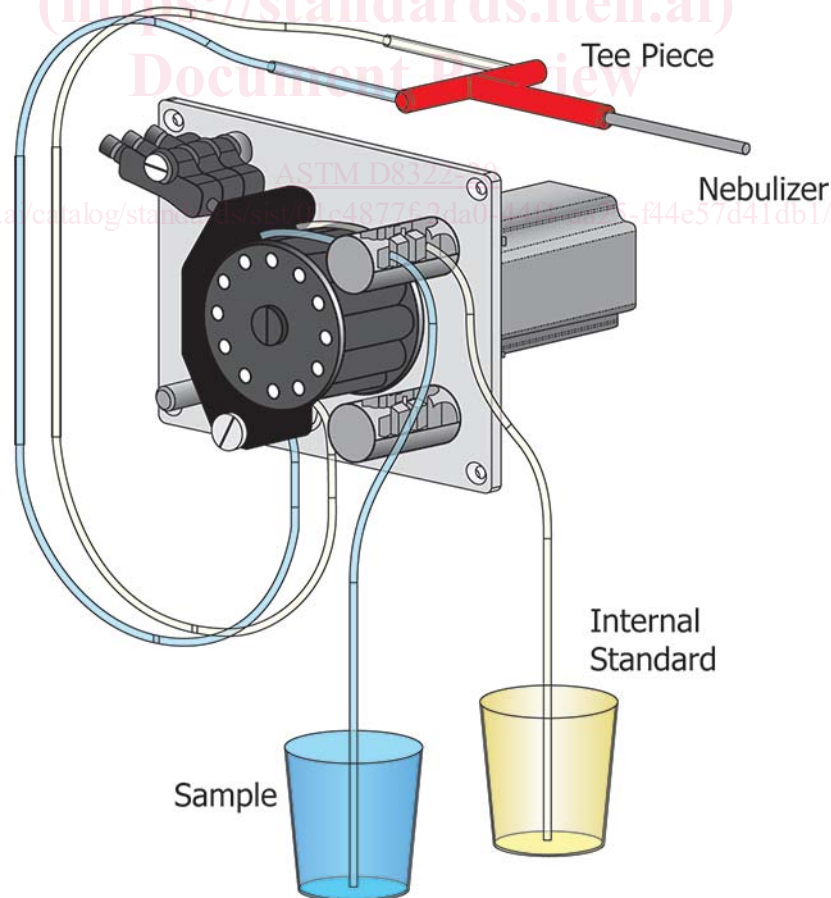


FIG. 1 Internal Standard Solution Tee Assembly

TABLE 6 Sample Dilution Guide

Crude oil classification according to the API degree:	Physical Description	Initial Mass Dilution Ratio
Light crude oil: API gravity higher than 31.1 °API (less than 870 kg/m ³)	Low-Viscosity	9:1 (Solvent:Sample)
Medium crude oil: API gravity from 31.1 °API to 22.3 °API (870 kg/m ³ to 920 kg/m ³)	Medium Viscosity	9:1 (Solvent:Sample)
Heavy crude oil: API gravity from 22.3 °API to 10 °API (920 kg/m ³ to 1000 kg/m ³)	Tar Like Viscosity	9:1 (Solvent:Sample)
Extra-heavy crude oil: API gravity below 10 °API (higher than 1000 kg/m ³)	Near Solid Form	19:1 (Solvent:Sample)

of dilution ratios spanning the entire API gravity range due to the nature and complexity of residual fuel and crude oil composition. The initial dilution ratio selection is simplified when the API gravity or density is known. Density determination may be obtained by a manual method D1298 or digital densitometer D4052.

13.7 Weigh 1.00 g of sample and make up to 10.00 g with solvent using the same source solvent used to prepare calibration standards. The experimental weights obtained shall be recorded and used in the determination of final elemental concentrations. If elemental concentration exceeds the calibration range, the samples shall be diluted accordingly.

13.7.1 If internal standard is added to the dilution solvent the internal standard solution shall be added to every calibration standard, blank, QC, and sample.

14. Quality Control Monitoring

14.1 Confirm the method performance via regular testing of quality control (QC) sample(s) as defined in Practice D6299.

14.2 Record QC sample test results and confirm the statistical control status for the execution of the complete test method using control charts defined in Practice D6299.

14.3 Investigate any out-of-control result for root cause(s). The outcome from this investigation may, but not necessarily, result in instrument re-calibration.

14.4 The frequency of QC testing is dependent on the criticality of the property being measured, the demonstrated stability of the testing process, and business requirements. Generally, a QC sample should be 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 testing precision should be periodically checked against the ASTM International published method precision for consistency by Practice D6792.

14.5 The QC material (Practice D6299) that is regularly tested should be representative of the samples routinely analyzed. An ample supply of QC sample material should be available for the intended period of use, and must be homogeneous and stable under the anticipated storage conditions.

14.6 Participation in appropriate proficiency test programs is recommended for monitoring performance relative to industry requirements (Guide D7372).

15. Procedure

15.1 *Analysis*—Analyze the test specimen solutions in the same manner as the calibration standards (that is, same integration time, background correction points, plasma conditions, etc.). Analyze samples as soon as possible or up to 24 h after preparation. Allow sufficient rinse time (not less than 60 s) between measurements to avoid memory effects. Calculate elemental mass fractions by multiplying the determined mass fraction in the diluted test specimen solution by the dilution factor. Calculation of mass fraction can be performed manually or by computer when such a feature is available.

16. Calculations

16.1 Calculate elemental concentrations by multiplying the determined concentration in the diluted test specimen solution by the dilution factor. Calculation of concentrations can be performed manually or by computer when such a feature is available. Manual calculation of concentrations of each analyte in the sample are performed using the following equation:

$$\text{analyte concentration, mg/kg} = C \times F \quad (1)$$

where:

C = concentration of the analyte in the specimen solution, mg/kg, and
 F = dilution factor

17. Report

17.1 Report mg/kg to two decimal places for each element. Sulfur shall be rounded to the nearest whole number. The results were obtained according to Test Method D8322. Valid Test Result Range - due to testing variation, results within this range inclusively are considered valid for reporting and for applying the precision (R and r) functions:

high limit: highest ILS sample mean + $R_{\text{highest ILS sample mean}}$ (per D6300)
 low limit: lowest ILS sample mean - $R_{\text{lowest ILS sample mean}}$ (per D6300); if < 0, set to lowest non-rejected ILS result (per D02.94 recommendation).

18. Precision and Bias for Crude Oil⁷

18.1 *Precision*—The precision of this test method was determined by statistical analysis of interlaboratory study RR:D02-1485 results.

⁷ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1485. Contact ASTM Customer Service at service@astm.org.

TABLE 7 Crude Oil Valid Test Result Range

Element	Crude Oil	
	Valid Test Result Range (mg/kg)	
Iron	0.10 to 208.00	
Vanadium	0.24 to 528.86	
Nickel	0.11 to 143.09	
Calcium	0.38 to 130.11	
Sodium	0.14 to 127.20	
Potassium	1.65 to 93.93	
Sulfur	545 to 47,654	