Designation: D7691 – 16

Standard Test Method for Multielement Analysis of Crude Oils Using Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)[1]

This standard is issued under the fixed designation D7691; 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 several elements (including iron, nickel, sulfur, and vanadium) occurring in crude oils.

1.2 For analysis of any element using wavelengths below 190 nm, a vacuum or inert gas optical path is required.

1.3 Analysis for elements such as arsenic, selenium, or sulfur in whole crude oil may be difficult by this test method due to the presence of their volatile compounds of these elements in crude oil; but this test method should work for resid samples.

1.4 Because of the particulates present in crude oil samples, if they do not dissolve in the organic solvents used or if they do not get aspirated in the nebulizer, low elemental values may result, particularly for iron and sodium. This can also occur if the elements are associated with water which can drop out of the solution when diluted with solvent.

1.4.1 An alternative in such cases is using Test Method D5708, Procedure B, which involves wet decomposition of the oil sample and measurement by ICP-AES for nickel, vanadium, and iron, or Test Method D5863, Procedure A, which also uses wet acid decomposition and determines vanadium, nickel, iron, and sodium using atomic absorption spectrometry.

1.4.2 From ASTM Interlaboratory Crosscheck Programs (ILCP) on crude oils data available so far, it is not clear that organic solvent dilution techniques would necessarily give lower results than those obtained using acid decomposition techniques.[2]

1.4.3 It is also possible that, particularly in the case of silicon, low results may be obtained irrespective of whether organic dilution or acid decomposition is utilized. Silicones are present as oil field additives and can be lost in ashing. Silicates should be retained but unless hydrofluoric acid or alkali fusion is used for sample dissolution, they may not be accounted for.

1.5 This test method uses oil-soluble metals for calibration and does not purport to quantitatively determine insoluble particulates. Analytical results are particle size dependent and low results may be obtained for particles larger than a few micrometers.

1.6 The precision in Section 18 defines the concentration ranges covered in the interlaboratory study. However, lower and particularly higher concentrations can be determined by this test method. The low concentration limits are dependent on the sensitivity of the ICP instrument and the dilution factor used. The high concentration limits are determined by the product of the maximum concentration defined by the calibration curve and the sample dilution factor.

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

1.8 As a generality based on this interlaboratory study (see 18.1), the trace elements identifiable in crude oils can be divided into three categories:

1.8.1 Element levels that are too low for valid detection by ICP-AES and hence, cannot be determined: aluminum, barium, lead, magnesium, manganese, and silicon.

1.8.2 Elements that are just at the detection levels of the ICP-AES method and hence, cannot be determined with a great deal of confidence: boron, calcium, chromium, copper, molybdenum, phosphorus, potassium, sodium, and zinc. Perhaps the determination of these elements can be considered as semi-quantitative.

1.8.3 Elements that are at higher levels of concentration and can be determined with good precision: iron, nickel, sulfur, and vanadium.

1.9 The detection limits for elements not determined by this test method follow. This information should serve as an indication as to what elements are not present above the detection limits typically obtainable by ICP-AES instruments.

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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] Nadkarni, R. A., Hwang, J. D., and Young, L., "Multielement Analysis of Crude Oils Using Inductively Coupled Plasma Atomic Emission Spectrometry," *J. ASTM International,* Vol 8, No. 10, 2011, pp. 103837.

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

Element	mg/kg
Aluminum	1
Barium	0.2
Boron	1
Calcium	0.1
Chromium	0.1
Copper	0.1
Lead	1.4
Magnesium	1
Manganese	0.1
Molybdenum	0.2
Phosphorous	1
Potassium	0.5
Silicon	4
Zinc	0.5

1.10 This test method determines all possible elements simultaneously and is a simpler alternative to Test Methods D5184, D5708, or D5863.

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

1.12 *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:*[3]

C1109 Practice for Analysis of Aqueous Leachates from Nuclear Waste Materials Using Inductively Coupled Plasma-Atomic Emission Spectroscopy

D1552 Test Method for Sulfur in Petroleum Products by High Temperature Combustion and IR Detection

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products

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

D5184 Test Methods for Determination of Aluminum and Silicon in Fuel Oils by Ashing, Fusion, Inductively Coupled Plasma Atomic Emission Spectrometry, and Atomic Absorption Spectrometry

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

D5708 Test Methods for Determination of Nickel, Vanadium, and Iron in Crude Oils and Residual Fuels by Inductively Coupled Plasma (ICP) Atomic Emission Spectrometry

D5854 Practice for Mixing and Handling of Liquid Samples of Petroleum and Petroleum Products

D5863 Test Methods for Determination of Nickel, Vanadium, Iron, and Sodium in Crude Oils and Residual Fuels by Flame Atomic Absorption Spectrometry

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

E135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials

3. Terminology

3.1 For the definition of *emission spectroscopy*, refer to Terminology E135.

3.2 *Definitions of Terms Specific to This Standard:*

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

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

3.2.3 *calibration, n*—process by which the relationship between signal intensity and elemental concentration is determined for a specific element analysis.

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

3.2.5 *detection limit, n*—concentration of an analyte that results in a signal intensity that is some multiple (typically two) times the standard deviation of the background intensity at the measurement wavelength.

3.2.6 *inductively-coupled plasma (ICP), n*—high-temperature discharge generated by flowing an ionizable gas through a magnetic field induced by a load coil that surrounds the tubes carrying the gas.

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

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

3.2.9 *radio frequency (RF), n*—range of frequencies between the audio and infrared ranges (3 GHz to 300 GHz).

4. Summary of Test Method

4.1 This test method usually requires several minutes per sample. A weighed portion of a thoroughly homogenized crude oil is diluted tenfold by weight with mixed xylenes, kerosene, or other suitable solvent. Standards are prepared in the same manner. A mandatory internal standard is added to the solutions to compensate for variations in test specimen introduction efficiency. The solutions are introduced to the ICP instrument by a peristaltic pump. By comparing emission intensities of

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[3] 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.

TABLE 1 Elements Determined and Suggested Wavelengths[A]

Element	Wavelength, nm
Aluminum	308.215, 396.153, 309.271, 237.01
Barium	233.53, 455.403, 493.410
Boron	249.773, 182.59, 249.68
Calcium	315.887, 317.933, 364.44, 422.67
Chromium	205.552, 267.716, 298.92, 283.563
Copper	324.754, 219.226
Iron	259.94, 238.204, 271.44, 259.837
Lead	220.353, 224.688, 283.306
Magnesium	279.079, 279.553, 285.21, 293.65
Manganese	257.61, 293.31, 293.93, 294.92
Molybdenum	202.03, 281.616, 204.598, 203.844
Nickel	231.604, 227.02, 221.648, 341.476
Phosphorus	177.51, 178.289, 214.914, 253.40
Potassium	766.491, 769.896
Sodium	588.995, 330.29, 589.3, 589.592
Silicon	288.159, 251.611, 212.412, 282.851
Sulfur	180.731, 182.04, 182.62
Vanadium	292.403, 309.31, 310.23, 311.07
Zinc	202.551, 206.209, 213.856, 334.58, 481.05, 202.48

[A] These wavelengths are only suggested and do not represent all possible choices. Not all of these elements were determined in this interlaboratory study.

elements in the test specimen with emission intensities measured with the standards, the concentrations of elements in the test specimen are calculable.

5. Significance and Use

5.1 Most often determined trace elements in crude oils are nickel and vanadium, which are usually the most abundant; however, as many as 45 elements in crude oils have been reported. Knowledge of trace elements in crude oil is important because they can have an adverse effect on petroleum refining and product quality. These effects can include catalyst poisoning in the refinery and excessive atmospheric emission in combustion of fuels. Trace element concentrations are also useful in correlating production from different wells and horizons in a field. Elements such as iron, arsenic, and lead are catalyst poisons. Vanadium compounds can cause refractory damage in furnaces, and sodium compounds have been found to cause superficial fusion on fire brick. Some organometallic compounds are volatile which can lead to the contamination of distillate fractions, and a reduction in their stability or malfunctions of equipment when they are combusted.

5.2 The value of crude oil can be determined, in part, by the concentrations of nickel, vanadium, and iron.

5.3 Inductively coupled plasma-atomic emission spectrometry (ICP-AES) is a widely used technique in the oil industry. Its advantages over traditional atomic absorption spectrometry (AAS) include greater sensitivity, freedom from molecular interferences, wide dynamic range, and multi-element capability. See Practice D7260.

6. Interferences

6.1 *Spectral*—There are no known spectral interferences between elements covered by this test method when using the spectral lines listed in Table 1. However, if spectral interferences exist because of other interfering elements or selection of other spectral lines, correct for the interference using the technique described in Test Method D5185.

TABLE 2 Suggested Internal Standards

Element	Concentration, mg/kg	Wavelength,[A] Nm
Cadmium	10	226.502; 228.802; 214.438
Cobalt	10	228.616; 238.892; 237.662
Lanthanum	10	379.48; 379.08
Scandium	10	255.237; 361.384; 357.253
Yttrium	10	371.030; 324.228; 360.073

[A] These wavelengths are only suggested and do not represent all possible choices.

6.2 Check all spectral interferences expected from the elements listed in Table 1. Follow the manufacturer's operating guide to develop and apply correction factors to compensate for the interferences. To apply interference corrections, all concentrations shall be within the previously established linear response range of each element listed in Table 1. (**Warning—** Correct profiling is important to reveal spectral interferences from high concentrations of some elements on the spectral lines used for determining trace metals.)

6.2.1 Spectral interferences can usually be avoided by judicious choice of analytical wavelengths. When spectral interferences cannot be avoided, the necessary corrections should be made using the computer software supplied by the instrument manufacturer or the empirical method described below. Details of the empirical method are given in Test Method C1109 and by Boumans.[4] This empirical correction method cannot be used with scanning spectrometer systems when both the analytical and interfering lines cannot be located precisely and reproducibly. With any instrument, the analyst shall always be alert to the possible presence of unexpected elements producing interfering spectral lines.

6.2.2 The empirical method of spectral interference correction uses interference correction factors. These factors are determined by analyzing the single-element, high purity solutions under conditions matching as closely as possible those used for test specimen analysis. Unless plasma conditions can be accurately reproduced from day to day, or for longer periods, interference correction factors found to affect the results significantly shall be redetermined each time specimens are analyzed.

6.2.3 Interference correction factors can be negative if off-peak background correction is employed for element, *i*. A negative *Kia* correction factor can result when an interfering line is encountered at the background correction wavelength rather than at the peak wavelength.

6.3 *Viscosity Effects*—Differences in the viscosities of test specimen solutions and standard solutions can cause differences in the uptake rates. These differences can adversely affect the accuracy of the analysis. The effects can be reduced by using a peristaltic pump to deliver solutions to the nebulizer or by the use of internal standardization, or both. When severe viscosity effects are encountered, dilute the test specimen and standard twentyfold rather than tenfold while maintaining the same concentration of the internal standard. See Table 2.

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[4] Boumans, P. W. J. M., "Corrections for Spectral Interferences in Optical Emission Spectrometry with Special Reference to the RF Inductively Coupled Plasma," *Spectrochimica Acta*, Vol 31B, 1976, pp. 147-152.

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

7. Apparatus

7.1 *Balance*—Top loading or analytical, with automatic tare, capable of weighing to 0.001 or 0.0001 g, with sufficient capacity to weigh prepared solutions.

7.2 *Inductively-Coupled Plasma Atomic Emission Spectrometer*—Either a sequential or simultaneous spectrometer is suitable, if equipped with a quartz ICP torch and RF generator to form and sustain the plasma. Suggested wavelengths for the determination of the elements in crude oils are given in Table 1. For the analysis of sulfur, the spectrometer shall be capable of operating in the wavelength region of 180 nm.

7.3 *Nebulizer*—A Babington-type[5,6] high-solids nebulizer is strongly recommended. This type of nebulizer reduces the possibility of clogging and minimizes aerosol particle effects.

7.4 *Peristaltic Pump*—A peristaltic pump is strongly recommended to provide a constant flow of solution. The pumping speed shall be in the range 0.5 mL/min to 3 mL/min. The pump tubing shall be able to withstand at least 6 h exposure to the dilution solvent. Viton tubing is typically used with hydrocarbon solvents, and polyvinyl chloride tubing is typically used with methyl isobutyl ketone.

7.5 *Solvent Dispenser, (Optional)*—A solvent dispenser calibrated to deliver the required weight of dilution solvent for a tenfold dilution of test specimen is very useful.

7.6 *Specimen Solution Containers*—Of appropriate size, glass or plastic vials or bottles, with screw caps.

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

7.8 *Vortexer, (Optional)*—Vortexing the sample is an alternative to ultrasonic homogenization.

7.9 *High Speed Homogenizer, (Optional).*

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.[7] 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 *Internal Standard*—Oil-soluble cadmium, cobalt, lanthanum, scandium, or yttrium (or other suitable metal) is required for internal standardization.

8.3 *Organometallic Standards*—Multi-element standards, containing 0.0500 mass % of each element, can be prepared from the individual concentrates. Refer to Practice D4307 for a procedure for preparation of multi-component liquid blends. When preparing multi-element standards, be certain that proper mixing is achieved. An ultrasonic bath is recommended. Standard multi-element concentrates, containing 0.0500 mass % of each element, are also satisfactory. (**Warning—**Some commercially available organometallic standards are prepared from metal sulfonates and therefore contain sulfur. For sulfur determinations, a separate sulfur standard would be required.)

8.3.1 More than one multi-element standard can be necessary to cover all elements, and the user of this test method can select the combination of elements and their concentrations in the multi-element standards. It can be advantageous to select concentrations that are typical of crude oils. However, it is imperative that the concentrations are selected such that the emission intensities measured with the working standards can be measured precisely (that is, the emission intensities are significantly greater than background) and that these standards represent the linear region of the calibration curve. Frequently, the instrument manufacturer publishes guidelines for determining linear range.

8.4 *Sulfur Standard*—To use a metal sulfonate as a sulfur standard, analyze the sulfonate by Test Method D1552. Alternatively, prepare a sulfur standard by diluting NIST SRM 1622c[8] in white oil. If sulfur is to be determined, the internal standard compound should not contain sulfur. Use metal napthenate or similar compounds rather than metal sulfonates. Non-sulfonate oil based sulfur standards are available commercially and can be used.

8.5 *Dilution Solvent*—A solvent that is free of analytes and is capable of completely dissolving all standards and samples. Mixed xylenes, kerosine, toluene, and ortho-xylene were successfully used as dilution solvents in the interlaboratory study on precision.

8.6 *Base Oil or White Oil.*

9. Sampling

9.1 It is critical that a representative sample be obtained for analysis from the bulk material. Maintaining compositional integrity of these samples from the time of collection until their analysis requires care and effort. Sampling procedure also should not introduce any contaminants into the sample or otherwise alter the sample composition so that the subsequent test results are affected.

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[5] Babington, R. A., *Popular Science*, May 1973, pp. 102.

[6] Fry, R. C., and Denton, M. B., *Analytical Chemistry*, Vol 49, 1977.

[7] *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] Available from National Institute of Standards and Technology (NIST), 100 Bureau Dr., Stop 1070, Gaithersburg, MD 20899-1070, http://www.nist.gov.

9.2 See Practices D4057 and D4177 for manual and automatic sampling of petroleum and petroleum products, respectively. In sampling of crude oils, the material may contain a heavy component, such as free water, which tends to separate from the main component. Guide D5854 provides a guide for selecting suitable containers for crude oil samples for various analyses.

10. Preparation of Apparatus

10.1 *Instrument*—Design differences between instruments, ICP excitation sources, and different selected analytical wavelengths for individual spectrometers make it impractical to detail the operating conditions. Consult the manufacturer's instructions for operating the instrument with organic solvents. Set up the instrument for use with the particular dilution solvent chosen.

10.2 *Peristaltic Pump*—Before using the 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 *ICP Excitation Source*—Initiate the plasma source at least 30 min before performing analysis. During this warm up period, nebulize dilution solvent. Inspect the torch for carbon buildup during the warm up period. If carbon buildup occurs, replace the torch immediately and consult the manufacturer's operating guide to take proper steps to remedy the situation.

NOTE 1—Some manufacturers recommend even longer warm-up periods to minimize changes in the slopes of calibration curves.

NOTE 2—Carbon that accumulates on the tip of the torch injector tube can be removed by using nebulizer gas that consists of approximately 1 % oxygen in argon.

NOTE 3—Generally, the carbon buildup can be minimized by increasing the intermediate argon flow rate or lowering the torch, or both, relative to the load coil.

10.4 *Wavelength Profiling*—Perform any wavelength profiling that may be called for in the normal operation of the instrument.

10.5 *Operating Parameters*—Assign the appropriate operating parameters to the instrument task file so that the desired elements can be determined. Parameters to be included are element, wavelength, background correction points (optional), interelement correction factors (optional), integration time, and internal standard correction (optional). Multiple integrations are required for each measurement, and the integration time is typically 10 s.

11. Calibration

11.1 The linear range shall be established once for the particular instrument being used. This is accomplished by running intermediate standards between the blank and the working standard and by running standards containing higher concentrations than the working standard. Analyses of test specimen solutions shall be performed within the linear range of response.

11.1.1 The linear range will also be determined by the instrument parameters (power, gas flow rates, nebulizer type, nebulizer flow rates, etc.). It is likely that this would need to be established more than once for each instrument. Correlation coefficient should be better than 0.995.

11.2 *Working Standard*—At the beginning of the analysis of each batch of specimens, perform a two-point calibration consisting of the blank and working standard. Use the check standard to determine if each element is in calibration. When the results obtained with the check standard are within 5 % of the expected concentrations for all elements, proceed with test specimen analyses. Otherwise, make any adjustments to the instrument that are necessary and repeat the calibration. Repeat this procedure with the check standard every five samples.

11.3 *Working Standard with Internal Standard*—Calibrate the instrument as described in 11.2. Calculate an intensity ratio for each element by the following equation:

$$I(Re) = (I(e) - I(Be))/I(is) \tag{1}$$

$I(Re)$ = intensity ratio for element, e,
$I(e)$ = intensity for element, e,
$I(Be)$ = intensity of the blank for element, e, and
$I(is)$ = intensity of internal standard element.

11.3.1 Calculate the calibration factors from the intensity ratios. In most modern ICPAES instruments the computer software provided by the instrument's manufacturer will do these calculations.

11.4 *Internal Standardization:*

11.4.1 The internal standard procedure requires that every test specimen solution have the same concentration (or a known concentration) of an internal standard element that is not present in the original specimen. Specimen to specimen changes in the emission intensity of the internal standard element can be used to correct for variations in the test specimen introduction efficiency, which is dependent on the physical properties of the test specimen.

11.4.2 The internal standard is usually combined with the dilution solvent. Internal standard compensation is typically handled in one of two different ways, summarized below

11.4.2.1 Calibration curves are based on the measured intensity of each analyte divided by the measured intensity of the internal standard per unit internal standard element concentration. The concentrations for each analyte in the test specimen solution are read directly from these calibration curves.

11.4.2.2 For each analyte and the internal standard element, calibration curves are based on measured intensities. Uncorrected concentrations for each analyte in the test specimen solution are read from these calibration curves. Corrected analyte concentrations are calculated by multiplying the uncorrected concentrations by a factor equal to the actual internal standard concentration divided by the uncorrected internal standard concentration determined by analysis.

11.4.3 *Internal Standard Solution*—Weigh 2 g to 4 g of 0.500 mass % cadmium, cobalt, scandium, or yttrium (or any other suitable metal) organometallic concentrate into a 1 L volumetric flask and dilute to 1 L with the dilution solvent. Prepare fresh, at least weekly, and transfer this solution into a dispensing vessel. The stability of this solution shall be monitored. The concentration of the internal standard element is not required to be 1a specific concentration; however, the concentration of the internal standard element in the test specimen solution should be at least 100 times its detection limit. A concentration in the range of 10 mg/kg to 20 mg/kg is typical. This would require one part of oil sample to be diluted tenfold with the internal standard solution.

NOTE 4—This test method specifies that the internal standard is combined with the dilution solvent because this technique is common and efficient when preparing many samples. However, the internal standard can be added separately from the dilution solvent as long as the internal standard concentration is constant or accurately known.

12. Sample Handling

12.1 *Homogenization*—It is extremely important to homogenize the crude oil in the sample container in order to obtain a representative test specimen. Failure to follow this homogenization procedure can invalidate the results because non-representative aliquots could be obtained and this could lead to erroneous results.

12.2 Place the sample container in an oven at a temperature of 50 °C to 60 °C. Keep the container in the oven until the sample comes to temperature. These three ways of mixing the sample after heating are permissible.

12.2.1 Insert the shaft of a high speed homogenizer into the sample container so that the head of the shaft is immersed to approximately 5 mm from the bottom of the sample container. Mix the sample for about 5 min.

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

12.2.3 *Vortex Homogenization*—As an alternative to ultrasonic homogenization, vortex mix the crude oil in the sample container, if possible.

13. Preparation of Test Specimen and Standards

13.1 *Internal Standard*—Add internal standard solution to the working standard, check standard, and test specimen before diluting with the dilution solvent. Ensure that the standard or test specimen concentration is 10 mass %. Alternatively, the internal standard can be present in the dilution solvent.

13.2 *Blank*—Prepare a blank by diluting the base oil or white oil tenfold by mass with the dilution solvent.

13.3 *Working Standard, 10 µg/g*—Weigh a quantity of the 0.0500 mass % multielement standard to the precision of the balance used (see 7.1) into an appropriately sized container, add four times the weight of the multi-element standard of base oil and dilute with 45 times the weight of the multi-element standard of dilution solvent. Working standards containing higher or lower concentrations can be prepared depending on the concentrations of elements in the crude oils. In addition, solutions containing single elements can also be prepared. However, ensure that the tenfold dilution is maintained for all solutions.

13.4 *Check Standards*—Prepare instrument check standards in the same manner as the working standards such that the concentrations of elements in the check standards are similar to the concentrations of elements in the test specimen solutions. It is advisable to prepare the check standard from alternative sources of certified organometallic standards.

NOTE 5—Organometallic standards are not as stable as aqueous standards when diluted to working standard strength. They should be prepared fresh before use.

13.5 *Test Specimen*—Weigh a portion of the well-homogenized sample into a suitable container. Record the mass to three significant figures. Add dilution solvent until the test specimen concentration is 10 mass %.

14. Procedure

14.1 *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.). Between test specimens, nebulize dilution solvent. In many instruments switching valves are in use and will reduce the needed rinse time. A rinsing time of 60 s for peristaltic pump samples may be necessary but different rinse times are possible as long as baseline intensities are achieved. 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.

14.2 When the concentration of any analyte exceeds the linear range of the calibration curve, prepare another test specimen by mixing the sample with base oil or white oil before adding diluent. Then analyze.

14.3 *Quality Control with Check Standard*—Analyze the check standard after every fifth sample, and if any result is not within 5 % of the expected concentration, recalibrate the instrument and reanalyze the test specimens solutions back to the previous acceptable check standard analysis.

NOTE 6—To verify the accuracy and precision of the instrument calibration, certified standards such as NIST SRM 2721, 2722, or RM 8505 should be regularly analyzed.[8]

14.4 *Analysis with Internal Standardization*—Analyze the test specimen solutions and calculate an intensity ratio for each of the elements found in the test specimen solutions using Eq 1 given in 11.3. From these intensity ratios, concentrations of the elements can be calculated.

15. Calculations

15.1 Calculate the concentrations, based on sample, using Eq 2. Generally, the ICP instrument software performs this calculation automatically.

$$C = S\frac{(W_1 + W_2 + W_3)}{W_1} \tag{2}$$

C = analyte concentration in the sample mass %,
S = analyte concentration in the test specimen, mass %,
W_1 = sample mass, g,
W_2 = diluent mass, g, and
W_3 = base oil mass (if any), g.

16. Quality Control

16.1 Confirm the performance of the instrument and the test procedure by analyzing a control (QC) sample. See Guide D6792 for guidance.

TABLE 3 Precision of Results

NOTE 1—X is the mean of two results.

Element	Range, mg/kg	Repeatability	Reproducibility
Iron	1 to 40	$0.1885\ X^{0.9145}$	$0.5649\ X^{0.9145}$
Nickel	1 to 100	$0.1764\ X^{1.0168}$	$1.1389\ X^{0.7085}$
Sulfur	400 to 50 000	$0.01971\ X^{1.1606}$	$0.06360\ X^{1.1606}$
Vanadium	1 to 1000	$0.0392\ (X + 0.7485)^{0.8668}$	$0.8628\ (X + 0.7485)^{0.8668}$

16.1.1 When QA/QC protocols are already established in the testing facility, these may be used to confirm the reliability of the test result.

16.1.2 When there is no QA/QC protocol established in the testing facility, Appendix X1 can be used as the QA/QC protocol.

16.2 Users of this test method are advised that in contractual agreements, one or more of the contracting parties can and may make Appendix X1 a mandatory practice.

17. Report

17.1 Report mg/kg to two to three significant figures for the elements determined by this test method. State that these analyses were done by Test Method D7691.

18. Precision and Bias[9]

18.1 *Precision*—The precision of this test method was determined by statistical analysis of interlaboratory results. In this study, dilution solvents were limited to xylene or kerosine. All laboratories used Babington-type nebulizers, peristaltic pumps, and background correction, and internal standards. Eleven laboratories analyzed 18 specimens in duplicate. The samples included 12 diverse crude oils, three NIST SRMs, and three ASTM ILCP crude oil samples.

18.1.1 *Repeatability*—The difference between two test 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.

18.1.2 *Reproducibility*—The difference between two single and independent results, obtained by different operators working in different laboratories on identical test materials, 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.

18.1.3 Precisions for some typical concentrations of these elements calculated from the precisions given in Table 3 are given in Table 4.

18.2 *Bias*—Bias was evaluated by analyzing quantitative dilutions of NIST SRM 2721 and 2722 and RM 8505.[8] The means of the reported values for sulfur and vanadium do not differ from the corresponding expected values by more than the repeatability of the method, when no significant interferences from other elements exist (see 6.1).

19. Keywords

19.1 crude oil; inductively coupled plasma-atomic emission spectrometry; iron; nickel; sulfur; vanadium

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[9] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1716.

TABLE 4 Calculated Precisions for Some Concentrations of Elements

NOTE 1—r = Repeatability. R = Reproducibility.

Element	1 mg/kg		10 mg/kg		50 mg/kg		100 mg/kg	
	r	R	r	R	r	R	r	R
Iron	0.19	0.57	1.11	3.35	...	...	...	...
Nickel	...	...	1.83	5.8	9.4	18.2	19.1	29.8
Sulfur	...	...	...	...	...	...	...	...
Vanadium	...	...	...	...	1.14	23.5	2.14	47.0

APPENDIXES

(Nonmandatory Information)

X1. GENERIC QUALITY CONTROL STATEMENT FOR D02 TEST METHODS

X1.1 Confirm the performance of the instrument or the test procedure by analyzing a quality control (QC) sample that is, if possible, representative of the samples typically analyzed.

X1.2 Prior to monitoring the measurement process, the user of the method needs to determine the average value and control limits of the QC sample (see Practice D6299 and MNL 7[10]).

X1.3 Record the QC results and analyze by control charts or other statistically equivalent techniques to ascertain the statistical control status of the total test process (see Practice D6299, Guide D6792, and MNL 7). Any out-of-control data should trigger investigation for root cause(s). The results of this investigation may, but not necessarily, result in instrument recalibration.

X1.4 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 should be analyzed each testing day with routine samples. The QC frequency should be increased if a large number of samples is 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 periodically checked against the ASTM method precision to ensure data quality.

X1.5 It is recommended that, if possible, the type of QC sample that is regularly tested be representative of the sample routinely analyzed. An ample supply of QC sample material should be available for the intended period of use, and shall be homogeneous and stable under the anticipated storage conditions.

X1.6 Refer to relevant documents (see Practice D6299, Guide D6792, and MNL7) for further guidance on QC and control charting techniques.

X2. HELPFUL HINTS FOR THE OPERATION OF TEST METHOD D7691

X2.1 It is extremely important to homogenize the crude oil in the sample container to obtain a representative specimen. Otherwise, it can lead to erroneous results.

X2.2 Check the temperature and humidity controls of the laboratory containing the ICPAES instruments, and verify adequacy for performing accurate and precise analyses. Ensure that stable environmental conditions exist throughout the period of use.

X2.3 If feasible, check the accuracy of elemental concentrations of commercially obtained calibration standards before use, either by comparing against suitable primary standards or by an independent analytical method.

X2.4 Verify the absence of analytes in all solvents and reagents used by performing a wavelength scan. The net intensity should be zero. In any case, the intensity counts from the blank, or individual solvents and reagents, be well below the intensity counts associated with the reporting limit. As a general rule, the blank counts, if not zero, should be ten times lower than the counts obtained for a standard at the reporting limit.

X2.5 Establish the preparation frequency of calibration standards by experiment. Prepare fresh working and check standards before each set of measurements, or daily, as appropriate.

X2.6 Check the linearity of the calibration curve of each analyte every three months or more frequently.

X2.7 Inspect torches before use for cracks, and discard or repair as appropriate.

X2.8 Use clean torches that are free of carbon buildup.

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[10] ASTM MNL 7, "Manual on Presentation of Data Control Chart Analysis, 6th edition, section 3: Control Chart for Individuals", available from ASTM International Headquarters.

X2.9 Replace or clean the load coil if oxidation is observed.

X2.10 Allow the instrument to warm up for at least 30 min, or longer, as suggested by the manufacturer.

X2.11 Visually inspect the peristaltic pump tubing daily for cracks and flat spots, and replace it if it is defective. Verify the uptake rates daily.

X2.12 Run the blank and appropriate check standard after every fifth sample or if at least 30 min have elapsed from the time of the last analysis. Recalibrate if the net intensity of the standard changes by more than 5% relative to the previous check.

X2.13 Allow sufficient rinse time between measurements to avoid memory effects. Memory effects are present if a steady instead of an abrupt decrease in signal is observed from taking multiple measurements.

X2.14 Use the peak and background wavelengths suggested in the method, if possible. When there is a choice, such as with sequential instruments, choose the wavelengths that will yield signals of 100 to 1000 times the detection limit. Also, ensure that the chosen wavelengths will not be interfered with from unexpected elements.

X2.15 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 the interferences. Avoid spectral interferences where possible by judicious choice of wavelength or by comparing the results of two different wavelengths for the same element. See Section 6 for guidance.

X2.16 If sulfur is to be determined, do not use commercially available standards that contain sulfonates. Prepare separate standards with known concentration of sulfur.

X2.17 When preparing multi-element standards, ensure that elements will not react with one another resulting in insoluble compounds.

X2.18 When analyzing crude oils, use a high-solids Babington type nebulizer to avoid plugging problems caused by the presence of particulates in the samples. If not corrected, this can cause low results.

X2.19 Dilute the sample and standards as much as possible to minimize nebulizer transport effects caused by high viscosity oils and to reduce potential spectral interferences. Both standard and sample solutions should not contain more than 10 % oil by mass.

X2.20 Ensure that the standard solutions contain the same mass % oil as sample solutions. Maintain the correct amount of oil by adding analyte-free base oil. Maintain consistent oil to solvent ratio when diluting.

X2.21 The internal standard procedure described in this test method is mandatory to be used to eliminate nebulizer transport effects. Although it is not necessary to add the same exact concentration of internal standard element to all samples and standard solutions when the internal standard element is calibrated separately, it is a good practice to do so. If the internal standard is not calibrated separately, it is necessary to add the exact same concentration of internal standard to all samples and calibration standards. This approach is commonly used when the internal standard is pre-diluted in solvent.

X2.22 Check for carbon buildup on the torch while nebulizing the working standard. Make the necessary adjustments to eliminate buildup. These adjustments may consist of the following:

X2.22.1 Reducing the pump rate.

X2.22.2 Increasing the auxiliary gas flow.

X2.22.3 Using a chilled spray chamber.

X2.22.4 Diluting the sample.

X2.22.5 Making other adjustments described in the instrument manual.

X2.23 Differences in the viscosities of the test specimen solutions and standard solutions can cause differences in the uptake rates adversely affecting the accuracy of the analysis. Use a base oil that is free of analytes and has a viscosity at room temperature as close as possible to that of the sample to be analyzed. These effects can be minimized by using a peristaltic pump or an internal standard. Use of a peristaltic pump is strongly recommended to provide a constant flow of the solution. Although this test method allows the use of an internal standard as optional, it is strongly recommended that this option be used.

SUMMARY OF CHANGES

Subcommittee D02.03 has identified the location of selected changes to this standard since the last issue (D7691 – $11^{\varepsilon1}$) that may impact the use of this standard. (Approved June 1, 2016.)

(1) Added a new footnote to subsection 1.4.2.

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