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

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.

*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.

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.

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.

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 K_{ia} 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.