



Designation: D7260 – 06

# Standard Practice for Optimization, Calibration, and Validation of Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) for Elemental Analysis of Petroleum Products and Lubricants<sup>1</sup>

This standard is issued under the fixed designation D7260; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 This practice covers information on the calibration and operational guidance for the multi-element measurements using inductively coupled plasma-atomic emission spectrometry (ICP-AES).

1.2 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

## 2. Referenced Documents

### 2.1 ASTM Standards:<sup>2</sup>

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

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

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

### 2.2 ICP-AES Related Standards:

C1111 Test Method for Determining Elements in Waste Streams by Inductively Coupled Plasma-Atomic Emission Spectroscopy

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

D1976 Test Method for Elements in Water by Inductively-Coupled Argon Plasma Atomic Emission Spectroscopy

D4951 Test Method for Determination of Additive Elements

in Lubricating Oils by Inductively Coupled Plasma Atomic Emission Spectrometry

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 Determination of Additive Elements, Wear Metals, and Contaminants in Used Lubricating Oils and Determination of Selected Elements in Base Oils by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)

D5600 Test Method for Trace Metals in Petroleum Coke 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

D6130 Test Method for Determination of Silicon and Other Elements in Engine Coolant by Inductively Coupled Plasma-Atomic Emission Spectroscopy

D6349 Test Method for Determination of Major and Minor Elements in Coal, Coke, and Solid Residues from Combustion of Coal and Coke by Inductively Coupled Plasma—Atomic Emission Spectrometry

D6357 Test Methods for Determination of Trace Elements in Coal, Coke, and Combustion Residues from Coal Utilization Processes by Inductively Coupled Plasma Atomic Emission Spectrometry, Inductively Coupled Plasma Mass Spectrometry, and Graphite Furnace Atomic Abs

D7040 Test Method for Determination of Low Levels of Phosphorus in ILSAC GF 4 and Similar Grade Engine Oils by Inductively Coupled Plasma Atomic Emission Spectrometry

D7111 Test Method for Determination of Trace Elements in Middle Distillate Fuels by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)

E1479 Practice for Describing and Specifying Inductively-Coupled Plasma Atomic Emission Spectrometers

### 2.3 Other Standards:

<sup>1</sup> This practice is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.03 on Elemental Analysis.

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<sup>2</sup> 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.

IP 437 Determination of Additive Elements in Unused Lubricating Oils and Additive Packages by Inductively Coupled Plasma-Atomic Emission Spectrometry  
 ISO/TC 17/SC 1 N 883 Guidelines for the Preparation of Standard Methods of Analysis Using Inductively Coupled Plasma-Atomic Emission Spectrometry and for Use of ICP Spectrometry for the Determination of Chemical Composition (1991)

### 3. Summary of Practice

3.1 An Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) instrument is one that is used to determine elemental composition of various liquid matrices. Details of the instrument components are given in Practice E1479. This practice summarizes the protocols to be followed during calibration and verification of the instrument performance.

### 4. Significance and Use

4.1 Accurate elemental analysis of petroleum products and lubricants is necessary for the determination of chemical properties, which are used to establish compliance with commercial and regulatory specifications.

4.2 Inductively Coupled Plasma-Atomic Emission Spectrometry is one of the more widely used analytical techniques in the oil industry for multi-element analysis as evident from at least twelve standard test methods (for example, Test Methods C1111, D1976, D4951, D5184, D5185, D5600, D5708, D6130, D6349, D6357, D7040, and D7111) published for the analysis of fossil fuels and related materials. These have been briefly summarized by Nadkarni.<sup>3</sup>

4.3 The advantages of using an ICP-AES analysis include high sensitivity for many elements of interest in the oil industry, relative freedom from interferences, linear calibration over a wide dynamic concentration range, single or multi-element capability, and ability to calibrate the instrument based on elemental standards irrespective of their elemental chemical forms, within limits described below such as solubility and volatility assuming direct liquid aspiration. Thus, the technique has become a method of choice in most of the oil industry laboratories for metal analyses of petroleum products and lubricants.

### 5. Apparatus

5.1 *Spectrometer*—An inductively coupled plasma emission spectrometer with a spectral bandpass of 0.05 nm or less is required. The spectrometer may be of the simultaneous multi-elemental or sequential scanning type. The spectrometer may be of the air path, inert gas path, or vacuum type, with spectral lines selected appropriately for use with specific instrument. Either an analog or digital readout system may be used.

5.2 An ICP-AES instrument system is typically comprised of several assemblies including a radio-frequency (RF) generator, an impedance matching network (where required), an induction coil, a plasma torch, a plasma igniter system, a sample introduction system, a light gathering optic, an entrance

slit and dispersing element to separate and measure the intensity of the wavelengths of light emitted from the plasma, one or more devices for converting the emitted light into an electrical current or voltage, one or more analog preamplifiers, one or more analog-to-digital converter(s), and a dedicated computer with printer. Solid state CCD or CID detectors if used may not require extra analog-to-digital components. Recently modern camera-type instruments have been supplanting the photomultiplier tube type detectors. Cameras may not have high resolution, but they offer greater wavelength choice.

5.2.1 Plasma can be monitored either axially versus radially. Potential for improved sensitivity as much as tenfold is often realized with axial monitoring. However, the increased interference from molecular background may compromise these gains depending on the wavelength monitored and matrix used (especially for organics versus aqueous).

5.2.2 *Echelle Spectrometers*—More recently echelle gratings are being increasingly used in several commercial plasma spectrometers. A prism is used as an order-sorter to improve sensitivity. To measure widely separated lines with useful efficiency, echelle instruments have to be operated in many different orders. This involves complex wavelength scanning programs for computer controlled echelle monochromators. While the resolution of a grating monochromator is relatively constant across its working range, practical resolution of an echelle monochromator can vary considerably with wavelength. Inherently higher theoretical resolving power of the echelle when used in high order, relative to the diffraction grating used in the first order, allows a relatively compact echelle instrument to achieve high resolving power. The detection limits obtained with echelle plasma spectrometers are comparable to those achieved by grating spectrometers.

#### 5.3 Spectrometer Environment:

5.3.1 Temperature fluctuations affect the instrument stability. Some manufacturers provide systems for maintaining a constant internal temperature within the optical compartment and sample introduction area that assumes changes in the outside temperature are not being controlled within the necessary specified range and rate of change to insure stability. Other manufacturers design their spectrometers to be stable over a specified temperature range without attempting to control the spectrometer's internal temperature.

5.3.2 Since temperature and humidity changes may also affect the sample introduction system, detectors, and electronic readout as well as the spectrometer alignment, some manufacturers specify that care be used in selecting a location for the spectrometer that experiences minimal variation in temperature and relative humidity. The user needs to provide a controlled environment as specified by the manufacturer. This is a very important factor in optimum performance of an ICP-AES system.

5.3.3 The generator output power and the plasma gas flow determine the plasma temperature and thus significantly influence the emission signal and the background. Thus, the power applied and gas flow adjustments may be used to control the signal to background ratio and, matrix, and some spectral interferences.

#### 5.4 Optical Path:

<sup>3</sup> Nadkarni, R. A., "Use of ICP-AES for Metal Analysis in the Oil Industry," *ICP Information Newsletter*, Vol 30(10), 2005, pp. 1059–1061.

5.4.1 Since oxygen exhibits increasing absorbance with decreasing wavelengths below 200 nm, the performance of an air path instrument degrades below that wavelength and is generally not useful below approximately 190 nm.

5.4.2 Purging the optical path with nitrogen or argon, or another gas with low absorption in this ultraviolet region may extend the spectral region to wavelengths below 167 nm. Use of these purge gases is in general less expensive to maintain than the vacuum path systems. Sealed optics filled with an inert gas is also available for such work.

#### 5.5 *Wavelength Selection:*

5.5.1 When selecting the fixed position wavelengths to be utilized in a Paschen-Runge polychromator for particular applications, close collaboration between user and instrument manufacturer is critical. Camera instruments do not have this problem.

5.5.2 If possible, use the peak and background wavelengths suggested in the methods. When there is a choice such as with the sequential instruments, choose the wavelength that will yield signals of 100 to 1000× the detection limit sought. Also, ensure that the chosen wavelength will not be interfered with from unexpected elements. See Section 6.

5.5.3 Often ion lines may be chosen for use over atom lines to avoid interelement interference and sensitivity of detection. This choice will be dependent on the analyte of interest and the sample matrix being analyzed.

5.6 *Peristaltic Pump*—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. These effects can be minimized by using a peristaltic pump (or an internal standard). If a peristaltic pump is used, inspect the pump tubing and replace it, if necessary, before starting each day. Verify the solution uptake rate daily and adjust to the desired rate. Compatibility of the solution with the peristaltic pump tubing must also be confirmed to prevent premature pump failure. A variety of polymeric material options are available for pump tubing to address this concern by simple empirical testing with the given solvent/sample matrix used. Generally speaking, the selected tubing soaked overnight in the solvent/sample matrix should not soften, crack, or embrittle the tubing.

5.7 Depending on the nebulizer design, starving solvent flow (that is, flow below natural free aspiration rates) can have an effect on aerosol generation. Consistent flow can help achieve enhanced analyte sensitivity.

5.8 *Torch*—Inspect the torches before use for cracks and discarded or repaired as appropriate. Clean torches that are free of carbon buildup should be used. The load coil should be replaced or cleaned if oxidation or leaking of coolant is observed. The glass also can devitrify especially at the aerosol tip with oxygen injection.

5.9 *Safety*—The ICP-AES instrument is not normally considered as a hazardous instrument. However, appropriate precautions should be taken regarding the fumes, heat, and UV/visible light radiation as well as appropriate RF shielding. The equipment should always be used according to the manufacturer's operating instructions. No attempt should be made to bypass the interlocks. Adequate cooling times must be allowed before handling any hot components. Any safety covers must be in position.

5.9.1 Fumes from the plasma and any ozone generated by the UV radiation must be removed by means of a suitable heat and acid resistant (acids can be formed from halogens or sulfate and nitrates in the solution) chimney fitted with an exhaust fan of sufficient capacity.

5.9.2 A UV/visible light absorbing viewing window (with RF shielding) must always be in place to protect the eyes and skin of the operator from radiation.

5.9.3 Often the organic samples and solvents used in organic ICP-AES analysis are toxic and hazardous. All appropriate precautions must be taken in handling such materials to protect the operators. Consult MSDS and other safety information before handling these chemicals.

## 6. Interferences

6.1 Several types of interference effects may contribute to inaccuracies in the elemental determination using ICP-AES. Principally these interferences can be classified as spectral, physical, and chemical.

### 6.2 *Spectral Interferences:*

NOTE 1—An empirical method for correcting spectral interferences is detailed in Test Method D5185.

6.2.1 Spectral interferences can be categorized as (1) unresolved overlap of a spectral line from another element, (2) unresolved overlap of molecular band spectra, (3) background contribution from continuous or recombination phenomena, and (4) background contribution from stray light from line emission of high concentration of elements. With echelle spectrometers it may be possible to look at two or more lines to identify interference.

6.2.2 *Interelement Interferences*—This interference can be compensated for by computer correction of the raw data, which requires measurement of the interfering element at the wavelength of interest. Various analytical systems may exhibit somewhat different levels of interferences. Therefore, the interference effects must be evaluated for each individual system. Perhaps a 2 % maximum correction may be acceptable.

6.2.2.1 Potential spectral overlaps from concomitant elements may be estimated by measuring the signal arising from a high-purity single-element reference solution of the concomitant element. It is useful to consult tables of spectral



lines<sup>4,5,6,7,8,9</sup> to become aware of possible overlaps, especially when analyzing samples of unknown composition. The overlaps may appear at the measured wavelength peak or at one of the two background points selected, thus prompting correction on only one side of the peak if the interferant is suspected present. If the overlap is severe (for example, 50 %), alternate line selection may be indicated to minimize spectral interferences. Judicious selection of background correction points may also prevent potential interferences affecting analyte quantification from interfering concomitant elements. It is recommended that multiple high purity solutions be used to confirm consistency of the suspected spectral source of a potential interference. Some analyte elements may be difficult to remove in manufacturing a high purity solution for the suspected interfering element, especially for organometallic standard solutions.

6.2.2.2 Potential interferences should be considered in the line selection process for polychromators. With sequential instruments, it may be desirable to select an alternate line to avoid spectral overlaps even though the sensitivity of the alternate line may be lower. This issue should be carefully considered for selection of fixed wavelength options for applicable polychromator when purchased.

6.2.2.3 There is also the possibility of spectral overlap from an element that is not being determined. With simultaneous instruments, it may be necessary to install additional hardware to correct for concomitant elements or to allow determination of a given element at two or more wavelengths. Sequential instruments permit measurement of other lines of interfering elements to allow correction of their contributions at the analytical wavelength.

6.2.3 *Inter-element Interferences*—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 in Test Method **D5185**. Further details of the empirical method are given in the Test Method **C1109** and by Boumans.<sup>8</sup> This empirical 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 must always be alert to the possible presence of unexpected elements producing interfering spectral lines.

6.2.3.1 The empirical method of spectral interference correction uses interference correction factors that are determined

by analyzing single-element high-purity solutions under conditions matching as closely as possible those used for test specimen solution analysis. Unless plasma conditions can be accurately reproduced from day to day, and sample matrix to sample matrix, or for longer periods, interference correction factors found to significantly affect the results must be determined each time specimens are analyzed. One way to accurately do this is to daily monitor the ratio of Mg I to Mg II lines, or copper to magnesium ratio.

6.2.4 *Molecular Band Interferences*—These arise from overlap of molecular band spectra at the wavelength of interest, and can be eliminated by careful selection of wavelength.

6.2.5 *High Background Interferences*—These can be compensated for by background correction adjacent to the analyte line. Signal to background ratios should be of the order of at least 3 to 5 factor.

6.2.5.1 Wavelength should be selected with best intensity, peak shape, and lack of interferences. When analysis is being done for elements at trace levels, background correction is required. Thus, for all elements possible, the baseline for the emission peak should be set with points as close to both sides of the peak without measuring the element wavelength intensity (see Figure 1 of Test Method **D7111**). After these baselines are set, a check standard should be used to test the system response and calibration.

6.2.5.2 Appropriate selection of wavelengths for background corrections is extremely critical for the determination of some elements. For example, since the predominate sodium emission line (588.995 nm) resides near a significant argon emission interference, it is recommended, if possible, compare the spectra of the sample and the standards at the sodium emission wavelength to ensure that the signal integration occurs accurately.

6.2.5.3 When emission wavelengths occur on a highly structured background (as in the example of sodium line above), a single off-peak background measurement may not provide accurate results. For such emission wavelengths on a structured background, background correction is recommended at both lower and higher wavelengths from the emission wavelengths. Additionally, some low resolution, photomultiplier tube-based instruments may require a comprised selection of background points, and this could also provide inaccurate results.

6.3 *Physical Interferences*—These are generally considered effects associated with the sample nebulization and transport processes. Such properties as change in viscosity and surface tension can cause significant inaccuracies, especially in samples that may contain high dissolved solids or acid concentrations (such as in aqueous ICP-AES analysis), or both. Use of a high-solid Babington type nebulizer (although optional in most methods) is highly recommended for avoiding plugging, particularly when analyzing used oils (which would contain particulates). The use of a peristaltic pump may also lessen these interferences. If these types of interferences are operative, they may be reduced by dilution (for example, tenfold) of these samples or utilization of standard addition techniques, or both. However, dilution or standard addition will not compensate for volatilization of some species.

<sup>4</sup> Winge, R. K., Peterson, V. J., and Fassel, V. A., "Inductively Coupled Plasma-Atomic Emission Spectrometry: Prominent Lines," *Applied Spectroscopy*, Vol 33(3), 1979, pp. 206–219.

<sup>5</sup> Winge, R. K., Fassel, V. A., Peterson, V. J., and Floyd, M. A., "Inductively Coupled Plasma-Atomic Emission Spectrometry: An Atlas of Spectral Information," Elsevier, New York, 1985.

<sup>6</sup> Nygaard, D. D. and Leighty, D. A., "Inductively Coupled Plasma Emission Lines in the Vacuum Ultraviolet," *Applied Spectroscopy*, Vol 39(6), 1985, pp. 968–976.

<sup>7</sup> Wohlers, C. C., "Spectral Tables for Inductively Coupled Plasma Atomic Emission Spectrometry," *ICP Information Newsletter*, Vol 10(8), 1985, pp. 593–688.

<sup>8</sup> 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.

<sup>9</sup> Varma, A., "CRC Handbook of Inductively Coupled Plasma Atomic Emission Spectrometry," CRC Press, Boca Raton, FL, 1991.