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Standard Practice for Optimization, Calibration, and Validation of Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) for Elemental Analysis of Petroleum Products and Lubricants[1]

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

1.3 *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]

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 Management Systems in Petroleum Products, Liquid Fuels, 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 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 Multielement Determination of Used and Unused Lubricating Oils and 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

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[1] This practice 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.

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

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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 Absorption Spectro

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)

D7303 Test Method for Determination of Metals in Lubricating Greases by Inductively Coupled Plasma Atomic Emission Spectrometry

D7691 Test Method for Multielement Analysis of Crude Oils Using Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)

D7876 Practice for Practice for Sample Decomposition Using Microwave Heating (With or Without Prior Ashing) for Atomic Spectroscopic Elemental Determination in Petroleum Products and Lubricants

D8056 Guide for Elemental Analysis of Crude Oil

D8110 Test Method for Elemental Analysis of Distillate Products by Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

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

2.3 *Other Standards:*

IP 437 Determination of Additive Elements in Unused Lubricating Oils and Additive Packages by Inductively Coupled Plasma-Atomic Emission Spectrometry[3]

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)[4]

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.

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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, D7111, D7303, and D7691) published for the analysis of fossil fuels and related materials. These have been briefly summarized by Nadkarni (**1**).[5]

4.2.1 Determination of mercury and trace metals in crude oils using atomic spectroscopic methods is discussed in Guide D8056.

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.

4.4 In addition to the ICP-AES standards listed in 2.2, a new ICP-MS standard, Test Method D8110, has been issued for analysis of distillate products for multi-element determination of Al, Ca, Cu, Fe, Pb, Mg, and K.

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

[3] Available from Energy Institute, 61 New Cavendish St., London, W1G 7AR, U.K., http://www.energyinst.org.

[4] Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, http://www.ansi.org.

[5] The boldface numbers in parentheses refer to a list of references at the end of this standard.

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.

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5.4 *Optical Path:*

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 classifies 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 to become aware of possible overlaps, especially when analyzing samples of unknown composition (Refs **2-7**). 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 *Interelement 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 (**6**). 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.

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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, photo-multiplier 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.

6.3.1 The torch aperture constriction is as much a problem with carbon soot for organics as it is for salt deposits in aqueous solutions that generally have the higher dissolved (as opposed to suspended) solids content. Also, for organics the matrix effects are exacerbated relative to aqueous matrix. The inherent diversity in organic matrix solution characteristics commonly impact transport more significantly due to volatility, polarity, surface tension, and so forth, as well as viscosity. Without a doubt, analyte volatility will most significantly impact transport effects and accuracy of the analysis.

6.3.2 Suspended analyte and other wear particles in the used oil also cause problem in getting accurate analysis. It is critical to keep the sample solution homogenized to get good results. Often the used oil samples are mixed using ultrasonic bath or a vortex mixer before actual ICP-AES measurements; however, the time lag between such homogenization and ICP-AES measurement should be kept to a minimum so that the particles do not settle out during the waiting period. Thus, for such samples autosampler may not be useful.

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6.3.3 To minimize nebulizer transport effects caused by high viscosity oils or viscosity improvers and additives in the oil, and to reduce potential spectral interferences, dilute the samples and standards as appropriate to minimize transport effects (minimum tenfold dilution). Both calibration standards and sample solutions should not contain more than ~~10 mass %~~ 10 % by mass oil. The calibration standards should be prepared with analyte-free oil added to the solution matrix such that all solutions contain the same mass % oil. Also, when diluting samples to greater dilution factors, consistent oil to solvent ratio should be maintained. See 7.2 about the dilution solvents.

6.3.4 Use of internal standard(s) could also be used in place of dilution or standard additions. With samples containing acids, the biggest variation can actually be observed at low acid concentrations. A common solution to this problem is to ensure that all samples and standards contain the same acid concentration (for example, 2 % nitric acid).

6.3.5 *Viscosity Index Improver Effect*—Viscosity index improvers that may be present in multi-grade lubricating oils, can bias the measurements (**8**). However, these biases can be reduced to negligible proportion by using the above specified solvent-to-sample dilution or an internal standard, or both. Following internal standards have been successfully used in the laboratories: Ag, Be, Cd, Co (most common), La, Mn, Pb, Sc, and Y. Often a viscosity index improver is included in the diluting solution to help reduce the effect on multi-grade oils.

6.3.6 The use of an internal standard assumes the sample to contain essentially no quantity of this internal standard element (see 8.8.4). This can be monitored by several means beyond analysis of the sample beforehand to ascertain the un-doped internal standard concentration. This may include the monitoring of multiple internal standard elements or comparison of the expected magnitude of correction imposed by the internal standard relative to a known or blank solution analyzed as a sample. Also, the internal standard must be analyte-free as well as free of concomitant species that may impose a spectral interference on the analyte lines applied.

6.4 *Chemical Interferences:*

6.4.1 Chemical interferences are caused by molecular compound formation, ionization effects, and thermochemical effects associated with sample vaporization and atomization in the plasma. Normally these effects are not pronounced and can be

minimized by careful selection of operating conditions such as incident power, plasma observation position, and so forth, by matrix matching, and by standard addition procedures. These types of interferences can be highly dependent on matrix type and the specific analyte.

6.4.2 Selective volatilization can occur when the analyte is present in the sample in a relatively volatile form and can vaporize during the nebulization process. Whereas the transport efficiency of droplets produced from a standard pneumatic nebulizer is typically around 1 % or 2 %, for vapor it can be much higher giving rise to enhanced results that can vary depending on the relative concentrations of various chemical species present in the sample (for example, volatile sulfur species such as H_2S, lead alkyls, and some silicon compounds).

6.5 Salt buildup at the tip of the nebulizer can occur from high dissolved solids (for example, in solutions prepared by alkali fusion with subsequent dilution with acids). This salt buildup affects aerosol flow rate that can cause instrumental drift. To control this problem, in cases of aqueous analysis argon should be wetted prior to nebulization, using a tip washer, or by diluting the sample.

6.6 *Carbon Buildup*—Inspect the torch for carbon build-up during the warm up period. If it occurs, replace the torch immediately and consult the manufacturer's operating guide to take proper steps to remedy the situation.

6.6.1 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. However, oxygen absorbs radiation and cools the plasma that affects most of the elements. Hence, it may not be a useful practice, except when high sensitivity for sodium is desired. Also, oxygen in the nebulizer or auxiliary gas streams may defeat the purpose of purged optical path or vacuum for lines below 190 nm.

6.6.2 The carbon buildup can also be cleaned off-line by baking the torch in a furnace at 500 °C for 1 h to 3 h depending on the amount of carbon buildup.

6.6.3 Generally, carbon buildup can be minimized by reducing the pump rate, adjusting the intermediate argon flow rate, using a chilled spray chamber, diluting the sample, adjusting the torch vertically relative to the load coil, torch aerosol tip internal diameter selection, or making other adjustments possible described in the instrument manufacturer's instruction manual. Consider also selection of diluent for organics (re-evaporation issue such as comparing solvents suggested below of toluene versus xylenes versus kerosine. This consideration will obviously be affected as well by volatility of sample matrix components that often may be safely evaporated prior to dilution, as long as the analyte is not volatile. Often, increasing the argon flow rate may be the only way to avoid carbon buildup; other means do not work as well.

6.7 Better control of the argon flow rate improves instrument performance. This control of the argon flow rate can be accomplished with the use of mass flow controllers.

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7. Reagents and Materials

7.1 *Base Oil,* or other solvents used for diluting the samples should be free of analyte of interest and have a viscosity at room temperature as close as possible to that of the samples to be analyzed.

7.1.1 Lubricating base oils can contain sulfur. For preparation of sulfur standards and blending of additive packages, white oil should be used.

7.2 *Dilution Solvents,* Mixed xylenes, O-xylene, and kerosine have been successfully used in the laboratories. Use reagent grade quality as a minimum. Select solvents and other reagents that do not contain analytically significant levels of the analyte. Wavelength scanning can indicate contaminated reagents. For ICP-AES instruments that provide a visual profile of emission peaks, a check may be made of the solvent purity by aspirating the solvent and viewing the spectral regions where the element emissions of interest are to be found. The absence of emission peaks in these regions is evidence that the solvent purity is satisfactory.

7.3 Chemical stabilizers are often added to elemental standard and blank solutions to keep the elements in a homogenous stable solution without precipitating out over long periods of storage.

7.4 Water, acids, alkalies, and other chemicals used in preparation of samples to convert them from organic to aqueous matrices should be of reagent quality at the minimum.

7.5 *Glassware, Plasticware*—These should be acid cleaned with 10 % nitric acid (trace metal analysis grade) followed by several distilled or deionized water rinses. Glassware or plasticware that has previously contained solutions with high concentration(s) of element(s) of interest must also be thoroughly cleaned to remove trace analyte residues. This can be confirmed by running analysis of blank matrix solutions stored overnight in the containers.

8. Calibration

8.1 After a warm-up time of at least 30 min, operate the instrument according to the manufacturer's instructions. Some manufacturers recommend even longer warm-up periods to minimize changes in the slopes of the calibration curves.

8.2 *Wavelength Profiling*—Perform any wavelength profiling that is specified in the normal operation of the instrument, if so equipped. Correct profiling is important to reveal spectral interferences from high concentration of additive elements on the spectral lines used for determining low levels of other elements present.

8.3 Calibrate the instrument by aspirating the blank and standards. Allow at least 30 s aspiration beyond the point that the solution reaches the nebulizer to allow the instrument to equilibrate prior to signal integration. A total flush-out time of approximately 1.5 min to 2 min should be allowed between standards or following samples of comparably high or higher concentrations, during which diluent solvent is being aspirated. The computer establishes the slope, intercept, and correlation statistics for each element.

8.4 Often a two-point calibration is used. However, multiple calibration standards may be used for obtaining improved element to signal correlation or validate linearity of the concentration range intended for use for a given analyte.

8.5 To ensure the validity of calibration, check standards with known elemental concentration should be used after calibration but before actually analyzing the unknown samples. It is recommended that the calibration blank and standards be matrix matched if possible with the same solvent, base oil, and so forth.

8.6 To minimize physical interferences caused by changes in sample transport process (due to variations in sample viscosity and concentration), it may be necessary to use a peristaltic pump in conjunction with certain nebulizers. Internal standard(s) could also be used instead of or as well as peristaltic pump.

8.7 *Background Correction:*

8.7.1 Ion-electron recombination and stray radiation give rise to background continuum. Introduction of an aerosol into the plasma may affect the intensity of this background continuum. An additional recombination may also give rise to background continuum from dissolved major ions in the sample.

8.7.2 Background correction generally involves measuring the background emission at a wavelength near the analytical wavelength (free of line emission from concomitant elements), and subtracting that intensity from the total intensity measured at the analytical wavelength. Selection of these correction points should also be carefully considered so as not to fall on the concomitant emission lines of elements potentially present in the solutions being analyzed. Nor should any structured spectral peaks be used (as opposed to flat baseline) for this correction that might result from seemingly stable/consistent emission lines that may arise from matrix elements or argon.

8.7.3 In some cases, if the background continuum intensity varies with wavelength, it may be necessary to measure the background on both sides of the analytical wavelength and interpolate to estimate the continuum intensity to be subtracted.

8.8 *Internal Standardization:*

8.8.1 Several ICP-AES test methods (see 2.2) require the mandatory use of internal standard in analysis. This procedure requires that every test solution (sample and standard) have the same concentration (or a known concentration) of an internal standard element that is not present in the original sample. The internal standard is usually combined with the dilution solvent because this technique is common and efficient when preparing many samples. However, this assumes that the dilution solvent will be diluted with sample at a consistent ratio. For example, a tenfold dilution with an internal standard spiked solvent will render a differing final internal standard concentration solution than a one hundred-fold dilution of this sample if the same dilution solvent is used. Though mathematical corrections may be applied for the resulting disparate internal standard concentration in these solutions, analyte/internal standard free matrix additives are frequently used to prepare such greater (one hundred-fold) dilutions and thus address this concern. This practice also aids in maintaining a consistent solution matrix. Alternatively, the internal standard can be added separately from the dilution solvent as long as the internal standard concentration is constant or accurately known.

8.8.2 Internal standard compensation is typically handled in one of the two different ways. Note that blank (zero analyte concentration) calibration standard – internal standard concentrations must be addressed accordingly. This may be an issue on analysis accuracy if the internal standard contains traces of analyte contaminants (or spectral interference from the internal standard) that would be inherently subtracted with an alternate calculation (scaled)—given all standards, blanks, and samples have the same contaminant level.

8.8.2.1 Calibration curves are based on the measured intensity of each analyte divided (that is, scaled) by the measured intensity of the internal standard per unit internal standard element concentration. Concentration of each analyte in the test specimen solution is read directly from these calibration curves.

8.8.2.2 For each analyte and the internal standard element, calibration curves are based on measured (unsealed) intensities. Uncorrected concentration of each analyte in the test specimen solution is read from the calibration curves. These are multiplied by a factor equal to the actual internal standard concentration divided by the uncorrected internal standard concentration determined by analysis, to obtain corrected analyte concentrations.

8.8.2.3 Although normally the calibration curves would be linear, sometimes inclusion of a second order term can give a better fit, although in such cases it would require at least five standards for calibration.

8.8.3 The organometallic compound representing the internal standard should be dissolved in the dilution solvent. Solution stability must be monitored and prepared fresh (typically weekly) when the concentration of the internal standard element changes significantly. The concentration of the internal standard element shall be at least 100 times the detection limit. A concentration of 10 mg/kg to 20 mg/kg is typical. The internal standard must also remain stable and soluble in the sample solution, given the potential for precipitation due to the presence of unexpected concomitant species in the sample solution.

8.8.4 Ideally, the internal standard element should not be present in the sample being analyzed; its chosen spectral line should have the same excitation characteristics as the analyte line; the chosen internal standard line should occur in a similar region of

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