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Standard Guide for
Calibration Requirements for Elemental Analysis of Petroleum Products and Lubricants[1]

1. Scope*

1.1 This guide covers different ways by which the test methods used for elemental analysis of petroleum product and lubricant samples are calibrated before the sample analysis.

1.2 Uniform practice for test method calibration is beneficial in standardizing the procedures, and obtaining consistent results across different laboratories.

1.3 This guide includes only the basic steps for generally encountered instrument types. Anything out of the ordinary may require special procedures. See individual test methods for instructions to handle such situations.

1.4 This guide is not a substitute for a thorough understanding of the actual test method to be used, caveats it contains, and additional instrument preparation that may be required.

1.5 The user should not expand the scope of the test methods to materials or concentrations outside the scope of the test methods being used.

1.6 This guide should also be applicable to sample preparation of non-petroleum based bio-fuels for elemental analysis. Work is underway on these aspects in Subcommittee D02.03. As more information becomes available, it will be added to this standard.

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

1.8 *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:*[2]

D129 Test Method for Sulfur in Petroleum Products (General High Pressure Decomposition Device Method)

D445 Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and Calculation of Dynamic Viscosity)

D482 Test Method for Ash from Petroleum Products

D808 Test Method for Chlorine in New and Used Petroleum Products (High Pressure Decomposition Device Method)

D874 Test Method for Sulfated Ash from Lubricating Oils and Additives

D892 Test Method for Foaming Characteristics of Lubricating Oils

D1018 Test Method for Hydrogen In Petroleum Fractions

D1091 Test Methods for Phosphorus in Lubricating Oils and Additives

D1266 Test Method for Sulfur in Petroleum Products (Lamp Method)

D1318 Test Method for Sodium in Residual Fuel Oil (Flame Photometric Method)

D1548 Test Method for Vanadium in Heavy Fuel Oil[1] (Withdrawn 1997)[3]

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

D1839 Test Method for Amyl Nitrate in Diesel Fuels

D2622 Test Method for Sulfur in Petroleum Products by Wavelength Dispersive X-ray Fluorescence Spectrometry

D2784 Test Method for Sulfur in Liquefied Petroleum Gases (Oxy-Hydrogen Burner or Lamp)

D3120 Test Method for Trace Quantities of Sulfur in Light Liquid Petroleum Hydrocarbons by Oxidative Microcoulometry

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

D7039 Test Method for Sulfur in Gasoline, Diesel Fuel, Jet Fuel, Kerosine, Biodiesel, Biodiesel Blends, and Gasoline-Ethanol Blends by Monochromatic Wavelength Dispersive X-ray Fluorescence Spectrometry

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

D7041 Test Method for Determination of Total Sulfur in Light Hydrocarbons, Motor Fuels, and Oils by Online Gas Chromatography with Flame Photometric Detection

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

D7171 Test Method for Hydrogen Content of Middle Distillate Petroleum Products by Low-Resolution Pulsed Nuclear Magnetic Resonance Spectroscopy

D7212 Test Method for Low Sulfur in Automotive Fuels by Energy-Dispersive X-ray Fluorescence Spectrometry Using a Low-Background Proportional Counter

D7220 Test Method for Sulfur in Automotive, Heating, and Jet Fuels by Monochromatic Energy Dispersive X-ray Fluorescence Spectrometry

D7260 Practice for Optimization, Calibration, and Validation of Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) for Elemental Analysis of Petroleum Products and Lubricants

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

D7318 Test Method for Existent Inorganic Sulfate in Ethanol by Potentiometric Titration

D7319 Test Method for Determination of Existent and Potential Sulfate and Inorganic Chloride in Fuel Ethanol and Butanol by Direct Injection Suppressed Ion Chromatography

D7328 Test Method for Determination of Existent and Potential Inorganic Sulfate and Total Inorganic Chloride in Fuel Ethanol by Ion Chromatography Using Aqueous Sample Injection

D7343 Practice for Optimization, Sample Handling, Calibration, and Validation of X-ray Fluorescence Spectrometry Methods for Elemental Analysis of Petroleum Products and Lubricants

D7455 Practice for Sample Preparation of Petroleum and Lubricant Products for Elemental Analysis

D7622 Test Method for Total Mercury in Crude Oil Using Combustion and Direct Cold Vapor Atomic Absorption Method with Zeeman Background Correction

D7623 Test Method for Total Mercury in Crude Oil Using Combustion-Gold Amalgamation and Cold Vapor Atomic Absorption Method

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

D7740 Practice for Optimization, Calibration, and Validation of Atomic Absorption Spectrometry for Metal Analysis of Petroleum Products and Lubricants

D7751 Test Method for Determination of Additive Elements in Lubricating Oils by EDXRF Analysis

D7757 Test Method for Silicon in Gasoline and Related Products by Monochromatic Wavelength Dispersive X-ray Fluorescence Spectrometry

E77 Test Method for Inspection and Verification of Thermometers

E319 Practice for the Evaluation of Single-Pan Mechanical Balances

E898 Test Method of Testing Top-Loading, Direct-Reading Laboratory Scales and Balances

2.2 *NIST Standard:*[4]

NIST Special Publication 260-136 Definitions of Terms and Modes Used at NIST for Value-Assignment of Reference Materials for Chemical Measurements

2.3 *ISO Standard:*[5]

ISO Guide 30 Terms and definitions used in connection with reference materials

3. Terminology

3.1 *Definitions:*

3.1.1 *calibration standard, n*—material with a certified value for a relevant property, issued by or traceable to a national organization such as NIST, and whose properties are known with sufficient accuracy to permit its use to evaluate the same property of another sample. **D6792**

3.1.2 *certified reference material, CRM, n*—reference material one or more of whose property values are certified by a technically valid procedure, accompanied by a traceable certificate or other documentation which is issued by a certifying body. **ISO Guide 30**

3.1.3 *check standard, n*—material having an assigned (known) value (reference value) used to determine the accuracy of the measurement system or instrument. This standard is not used to calibrate the measurement instrument or system. **D7171**

3.1.4 *reference material, RM, n*—material with accepted reference value(s), accompanied by an uncertainty at a stated level of confidence for desired properties, which may be used for calibration or quality control purposes in the laboratory.

3.1.4.1 *Discussion*—Sometimes these may be prepared "in-house" provided the reference values are established using standard primary procedures with known precision uncertainties. See below for further discussion. **D6792**

3.1.5 *traceability, n*—property of the result of a measurement or the value of a standard whereby it can be related to stated references, usually national or international standards, through an unbroken chain of comparisons all having stated uncertainties. **D6792**

4. Summary of Guide

4.1 This guide covers procedures used for calibrating instruments or methods for the analysis of petroleum products or

lubricant samples for elemental analysis measurements. The means of calibration may vary from none to elaborate dependent on the test method and the measurement technique used. Test method requirements will take precedence over this guide where applicable.

4.2 This guide may also be applicable to non-petroleum based biofuels. Work is underway to validate this.

5. Significance and Use

5.1 Crude oil, petroleum, petroleum products, additives, biofuels, and lubricants are routinely analyzed for their elemental content such as chlorine, nitrogen, hydrogen, phosphorus, sulfur, and various metals using a variety of analytical techniques. Some of these methods require little to no method calibration; some others require only simple one step calibration; while others require elaborate calibration routine before the product is analyzed for its elemental content.

5.2 Fairly often it can be shown that the round robin results by a co-operator are all biased with respect to those from other laboratories. Presumably, the failure to follow good laboratory practices and instructions in the test methods can be a causal factor of such errors. A further consequence is an unnecessarily large reproducibility estimate or the data being dropped from the study as an outlier.

5.2.1 Another cause of such discrepancies could be different or inadequate calibration practice used in the laboratory. Most test methods spell out the calibration requirements but often do not quote the frequency required letting the laboratories use good laboratory practices for this task. Thus, uniform practice for instrument calibration would be beneficial in standardizing the test procedures and obtaining consistent results across the laboratories.

5.3 Committee D02 has already issued standard practices for uniform sample preparation (D7455), standard operating procedures for ICP-AES (D7260) and XRF (D7343) as well as standard quality assurance protocol (D6792). This guide should be considered as a continuing effort on behalf of this subcommittee to achieve standardized practices in all parts of an analytical sequence.

6. Basic Considerations

6.1 All apparatus and instruments used in a laboratory require some kind of calibration or verification before an instrument is used for producing reliable data. A perfect analysis needs a perfect calibration as a first step and perfect quality control as perhaps the last step in the sequence of analytical events. Often this cycle is depicted as:

Calibration → Sample Analysis → QC Analysis → Calibration → →

6.1.1 Some test methods may additionally require a step of verification of calibration using a check standard.

6.2 The overall program of calibration of equipment should be designed and operated so as to ensure that the measurements made in the testing laboratories are traceable (where the concept is applicable) to national standards of measurement, and where available, to international standards of measurement specified by such bodies.

6.2.1 Where the concept of traceability to national or international standards of measurement is not applicable, the testing laboratory should provide satisfactory evidence of correlation or accuracy of test results (for example, by participating in a suitable program of interlaboratory comparison), or by primary and interference-free classical chemistry techniques such as gravimetry or titrimetry.

6.3 Different test methods require different calibration intervals. Thus, a decision about appropriate calibration frequency shall be made on a case by case basis. However, it goes without saying that the calibration practices are a must for all analytical testing and shall be thoroughly documented both regarding the plan and the factual evidence that it is being followed. There is a tendency among many laboratories to do the bare minimum calibrations similar to their approach towards quality control requirements. This is not the way to achieve superior performance. Moreover, if an instrument is found to be out-of-calibration, and the situation cannot be immediately addressed, then the instrument shall be taken out of operation and tagged as such until the situation is corrected. Under no circumstances can data from that instrument be reported to the customers.

6.4 The performance of apparatus and equipment used in the laboratory but not calibrated in that laboratory (that is, pre-calibrated, vendor supplied) should be verified by using a documented, technically valid procedure at periodic intervals.

6.5 *Calibration Standards*—Calibration standards appropriate for the method and characterized with the accuracy demanded by the analysis to be performed, shall be utilized during analysis. Quantitative calibration standards should be prepared from constituents of known purity. Use should be made of primary calibration standards or certified reference materials specified or allowed in the test method. A wide variety of such standards are available from commercial sources, NIST, etc. Many laboratories have capabilities of preparing reliable in-house standards. Calibration standards identical to the samples being analyzed would be ideal, but failing that, at least some type of standards shall be used to validate the analytical sequence. In physical measurements this is usually achievable, but it is often difficult or sometimes almost impossible in chemical measurements. Even the effects of small deviations from matrix match and analyte concentration level may need to be considered and evaluated on the basis of theoretical or experimental evidence, or both. Sometimes the use of standard additions technique to calibrate the measurement system is a possibility. But because an artificially added analyte may not necessarily respond in the same manner as a naturally occurring analyte, this approach may not be always valid, particularly in molecular speciation work.

NOTE 1—See Practice D4307 for recommendations in preparing liquid blends for use as analytical standards.

6.5.1 If a laboratory wants to prepare in-house calibration standards, the appropriate values for reference materials should be produced following the certification protocol used by NIST or other standards issuing bodies, and should be traceable to national or international standard reference materials, if required or appropriate.

6.5.1.1 NIST uses seven models for value assignment of reference materials for chemical measurements: NIST certified values are derived from certification at NIST using a single primary method with confirmation by other method(s) or using two independent critically-evaluated methods, or using one method at NIST and different methods by outside collaborating laboratories; NIST reference values are derived from last of the two models mentioned, as well as values based on measurements by two or more laboratories using different methods in collaboration with NIST, or based on a method specific protocol, or NIST measurements using a single method or measurement by an outside collaborating laboratory using a single method, or based on selected data from interlaboratory studies. The last four means are used also for assigning NIST information values. See NIST Special Publication 260-136 for further details on this subject.

6.5.2 In addition to the oil-soluble organometallic compounds used for the calibration of instruments such as AAS, ICP-AES, or XRF, single-element or multi-element calibration standards may also be prepared from materials similar to the samples being analyzed, provided the calibration standards to be used have previously been characterized by independent, primary (for example, gravimetric or volumetric) analytical techniques to establish the elemental concentration at mass percent levels.

6.5.3 *Reference Materials (RM)*—These can be classified as primary or secondary.

6.5.3.1 The primary RMs are well-characterized, stable, homogenous materials produced in quantity, and with one or more physical or chemical property experimentally determined, within the stated measurement uncertainties. These are certified by a recognized standardization laboratory using the most accurate and reliable measurement techniques.

6.5.3.2 The secondary RMs are working standards or QC standards and may have undergone less rigorous evaluation for day-to-day use in the laboratory.

6.5.3.3 The two most important considerations when preparing reference materials are its homogeneity and stability. Considerable time and money would be wasted if analytical certification measurements were done on reference materials, which were later found to be inhomogeneous with respect to properties of interest. Hence, several randomly selected representative aliquots should be analyzed first to ensure homogeneity.

6.5.3.4 Similarly, if a reference material is found to be unstable over the period of its use, it would be of little benefit to standardization community. However, it is not very practical to check the stability over an inordinately extended period of time before issuing the reference material for general use. Hence, testing the stability of the material continues as part of ongoing quality control of reference materials.

6.5.3.5 Whether stock or working standards, they need to be stored in clean containers and out of direct sunlight and preferably in amber glass bottles to safeguard against physical degradation and in contamination-free environment. One way of checking for degradation is to measure the response of an aliquot of the standard by the same instrument under identical instrumental conditions over a period of time and monitor it for

TABLE 1 Precautions to be taken for Storage and Use of Reference Materials

a. Store only in the original containers in the dark and do not subject it to variations in temperature and humidity.
b. Do not heat the material in the original container for any reason, unless so dictated by the nature of the material.
c. Shake the material well before removing any material from the original container, unless the method specifically prohibits shaking the sample.
d. Never place any equipment such as glass rods, metal spatulas, etc. in the original container.
e. When preparing calibration standards, remove the necessary amount into a secondary container.
f. Any material removed from the original container should never be poured back into it.
g. When two-thirds of the material has been used up, prepare additional material using standardized protocols and methods.
h. The long term stability of some of the calibration standard materials may be unknown. If any changes in appearance or other characteristics are observed suggesting material instability, discard the material and obtain a new batch of the material.

changes, if any. A list of suggested precautions to be taken in storage of reference materials is given in Table 1.

6.5.3.6 Shaking the bottle containing the standard is recommended before an aliquot is taken out of the bottle to ensure the uniformity of the blends. If stirring is necessary, a PTFE-coated (polytetrafluoroethylene) magnetic stirrer is advisable. If the test method specifically prohibits shaking then this instruction may not apply.

6.5.4 Materials available from ASTM Proficiency Testing Programs may be used provided the data does show normal Gaussian distribution of results and normal frequency distribution. The consensus value is most likely the value closest to the true value of this material; however, the uncertainty attached to this mean value is dependent on the precision and the total number of the participating laboratories. The expanded uncertainty of the consensus value is inversely proportional to the square root of the number of laboratories (L) used to establish the consensus value. Regardless of the variance of the results, for a large enough number of laboratories (L), the uncertainty of the consensus value will, for some value of L, be suitable for calibration purposes. It has been observed that in some cases the variance on the mean value of such proficiency testing program is large (that is, larger than reproducibility of the test method used), making such materials not very useful for calibration work. They are, however, suited for use as quality control materials.

6.5.5 *Analysis of CRMs*—Since the CRMs will be potentially used for calibration and quality control of a large number of instruments and measurements, the values assigned to them need to be "accurate" values, that is, they should be within the overall uncertainty of "true" values. Hence, the methods used in certifying the values shall have a valid and well-described theoretical foundation, shall have negligible systematic errors and a high level of precision, and shall give "true" values with high reliability. These primary methods require skilled and

experienced personnel, are time consuming and comparatively expensive to perform, and perhaps uneconomical for routine field use. Three types of such methods may be used for certifying the CRMs.

6.5.5.1 Measurement by a method of known and demonstrated accuracy performed by two or more analysts independently. Frequently an accurately characterized backup method is used to provide assurance of correctness of data.

6.5.5.2 Measurement by two or more independent and reliable methods whose estimated inaccuracies are small, relative to required accuracy for certification. The basic principles of two techniques shall be entirely different, for example, copper determination by electrogravimetry and titrimetry is acceptable, but not by AAS and ICP-AES, since both latter methods are based on atomic spectroscopy. The likelihood of two independent methods being biased by the same amount in the same direction is small. When the results by two methods agree, there is a good possibility that the results are accurate; three methods would almost guarantee it.

6.5.5.3 Measurement via a worldwide network of laboratories, using both methods of proven accuracy and using existing certified reference materials as controls. It has to be recognized, however, that the mean value of results from a large number of laboratories may not necessarily represent an accurate value when the repeatability and reproducibility are large (that is, greater than those quoted in the test method used).

6.6 Sometimes because of necessity, some values for reference materials are quoted based on only one technique that does not qualify it as a referee method for that analysis. Such values are usually labeled as "for information only." These can be upgraded later to certified values when subsequently additional techniques or laboratories produce reliable confirmatory data.

6.7 *Calibration Frequency*—The calibration schedules will vary with the instrument type, some needing calibration before each set of analysis (for example, AAS), others requiring calibration at less frequent periods (for example XRF). An important aspect of calibration is the decision on calibration intervals, that is, the maximum period between successive recalibrations. Two basic and opposing considerations are involved: the risk of being out of tolerance at any time of use, and the cost in time and effort. The former should be the major concern because of the dilemma of what to do with the data obtained during the interval between the last known in and the first known out of calibration. However, an overly conservative approach could be prohibitively expensive. A realistic schedule should reduce the risk of the former without undue cost and disruption to work schedules. The factors that need to be considered in a realistic schedule include:

6.7.1 Accuracy requirement for the measured data.

6.7.2 Level of risk involved.

6.7.3 Experience of the laboratory in use of the equipment or methodology.

6.7.4 Experience of the measurement community.

6.7.5 Manufacturer's recommendations.

6.7.6 External requirements for acceptability of data.

6.7.7 Cost of calibration and quality control.

6.8 An initial choice of calibration intervals may be made on the basis of previous knowledge or intuition. Based on the experience gained during its use, the intervals could be expanded if the methodology is always within tolerance at each recalibration, or it should be decreased if significant out-of-tolerance is observed. Control charts may be used to monitor the change of measured value of a stable test item correlated with the need to recalibrate. Many laboratories use a posted schedule of calibration which is followed by the analysts. This is fine, so long as intelligent judgment is used in adhering to this schedule. If the quality control sample or routine sample data produced by an instrument appears to be of doubtful quality, the first thing to check is the quality control and calibration of the instrument, irrespective of what the calibration schedule is.

6.8.1 There are some tests (for example, ICP-AES) where calibration is an integral part of the analysis and ASTM test methods explicitly state the needed frequency. In all such cases, this requirement shall be met.

6.9 *Calibration versus Verification*—Although often the two words verification and calibration are synonymously used, they indeed have different connotations. Verification pertains to checking that the instrument or a system is in a condition fit to use, while calibration involves standardization as in a measuring instrument by determining the deviation from a reference standard so as to ascertain the proper correction factors. For example, in the D5800 Noack evaporation loss test method, the instrument is verified with a CEC check standard that it gives the correct value. In Test Method D892 (foam test method), the air diffusers are verified for their maximum pore diameter and permeability against specifications before proceeding with the test. In the ash test (Test Method D482) and sash test (Test Method D874), no specific verification or calibration is done other than appropriate thermometers for monitoring the temperature in the oven or furnace, and balance calibration. On the other hand in D4951 and D5185 ICP-AES methods for metals, the instrument is calibrated over several concentration ranges to check that the linearity is acceptable and other additional checks are also required.

6.9.1 Many ASTM test methods either do not specify the calibration steps or do not give the frequency of calibration. In such cases, the incidence and the frequency is determined from prior laboratory experience, or industry practice, or both.

6.9.2 ASTM Standard Practice for Quality System in Petroleum Products and Lubricants Testing Laboratories D6792-07 states that "Procedures shall be established to ensure that measuring and testing equipment is calibrated, maintained properly, and is in statistical control. Items to consider when creating these procedures include:

6.9.2.1 Records of Calibration and Maintenance.

6.9.2.2 Calibration and Maintenance Schedule.

6.9.2.3 Traceability to National or International Standards.

6.9.2.4 Requirements of the Test Method or Procedure.

6.9.2.5 Customer Requirements.

6.9.2.6 Corrective Actions.

6.10 *Calibration Documentation*—All calibration records should be documented either in the instrument computer software or in manually prepared laboratory notebooks. This

TABLE 2 Classification of Analytical Instrumentation Used in Laboratories

Class I	Class II	Class III
Glassware	Colorimeter	AAS
Centrifuge	Pressure Gauges	ICP-AES
Cold Baths	Hach Turbidimeter	XRF
Hot Baths	Titrators	Thermometers (E77)
Freezers	Glassware, if critical in the final results	Balances (E319, E898)
Mixers		ICP-MS
Stirrers		GF-AAS
Shakers		
Ovens		
Hot Plates		
Furnaces		
Refrigerators		
Sonic Baths		
Non-Critical Thermometers		
Syringe Pumps		

should include information such as date of last and next calibrations, the person who performed the calibration, method or procedure used for calibration, the material used for calibration, the values obtained during calibration, and the nature and traceability (if applicable) of the calibration standards. Records may be maintained electronically.

6.10.1 For instruments that require calibration, calibration and maintenance records may be combined. See Table 2.

6.11 *Types of Calibrations*—The laboratory apparatus and analytical instruments used in elemental analysis can be (arguably) divided into three categories as Class I, II, and III based on the extent of calibration needed in each case from minimal or no calibration to extensive.

6.11.1 *Class I*—Apparatus include miscellaneous, unsophisticated equipment which may need no calibration or minimal verification such as motor speed or temperature maintained. Perhaps stirrers or some types of thermometers will fall in this category. Generally, these apparatus do not produce actual analytical data.

6.11.2 *Class II*—Apparatus includes equipment that should be maintained, and/or possibly calibrated on a routine basis and may have minimal verification requirements. This might include balances, temperature controllers, gas flow meters, etc, unless the data from these instruments is the final result of the analysis. The data from Class II instruments usually is not sent to the customers.

6.11.3 *Class III*—Instruments include sophisticated instrumentation/equipment that should require scheduled full verification, or calibration, or both, as given in the standard ASTM protocols before the instrument is used for the sample analysis. These may be done either by the analysts or outside contractors or Original Equipment Manufacturers (OEM). For all of these instruments there are ASTM standard test methods available which should be followed in operation. The data produced from these instruments could be provided to the customers. Some of the specifics of calibration routines for Classes I, II, and III follow:

6.12 The three most commonly used accessories in most analytical testing are temperature measuring devices, time measuring devices, and balances.

6.12.1 *Temperature Measuring Devices*—These include liquid-in-glass thermometers and electronic digital thermometers and thermocouple probes. With the increasing concern about mercury toxicity, thermometers are being replaced in the laboratories as well as in ASTM test methods with electronic devices. These calibrated thermometers should have tags affixed to them indicating the date of current and next calibration, correction factor, if any, and the name of the person calibrating them.

6.12.1.1 The critical TMDs are purchased from vendors with a certificate verifying that they are calibrated using ASTM standard methods and are traceable to NIST standards. One certified set of thermometers should be used exclusively for verification of other TMDs. Annually, the certified set of thermometers is verified using the NIST traceable standards. Over and above the annual recalibration of TMDs, some ASTM test methods specifically require additional calibration of thermometers as a part of the analytical procedure. Individual ASTM test methods should be consulted for details of required recalibrations. However, many ASTM test methods do not specify the frequency of calibration.

6.12.1.2 The thermometers which are not used in analytical testing are considered non-critical and generally are not calibrated. ASTM 120C and 121C certified liquid-in-glass thermometers used in kinematic viscosity (Test Method D445) baths are typically controlled at working temperatures of 40 and 100°C and are verified as described in Test Method D445. This service is conducted by an outside contractor. An ice point calibration can be done as an interim step between full calibrations. This procedure is described in Test Method D445, Annex A2.

6.12.1.3 In addition to general use of thermometers, the following specific test methods require monitoring using calibrated TMDs: Test Method D482 (ash), Test Method D874 (sulfated ash), D1548 (vanadium in fuel oil), and D1552 (sulfur by high temperature combustion).

6.12.2 *Timers*—Both stopwatches and electronic time measuring devices, if necessary, can be calibrated using the time signals as broadcast by NIST and received by calling the NIST phone number in Boulder, Co. The procedure is given in Test Method D445, Annex A3. The verification data should be recorded. Any timer not meeting the verification standard should be discarded. No other maintenance is expected on these timers.

TABLE 3 Suggested Calibration Frequency for Generic Laboratory Equipment

Instrument	Calibration Frequency	Possible Calibrator[A]
Pipettes	Annual	In-house
Balances	Annual	Vendor
Volumetric Ware	Only Class A materials Used	
Thermometers	Annual	In-house or Vendor
Stop-Watches	Annual	In-house
Flowmeters	Annual	In-house or Vendor
AAS	At the Time of Analysis	In-house
ICP-AES	At the Time of Analysis	In-house
XRF	Annual	In-house or Manufacturer

[A] Other sources for calibration services are acceptable.

6.12.3 *Balances*—The procedure for calibration of laboratory electronic mass balances is described in E319 and E898. Balances are usually calibrated once a year using NIST traceable standard weights. A record of such calibrations should be maintained.

6.12.4 A suggested calibration frequency for generic equipment used in elemental analysis is given in Table 3. In-house calibrations should follow reliable procedures and protocols recommended by NIST or other recognized standards writing bodies.

7. Calibration in Empirical Test Methods

7.1 In this guide, empirical methods are defined as the methods for which no special calibration of instrumentation is necessary or if needed is minimal. Examples of such analysis include Test Methods D129 (Sulfur by Bomb Method), D482 (Ash), D808 (Chlorine by Bomb Method), D874 (Sulfated Ash), D1018 (Hydrogen), D1091 (Phosphorus), D1266 (Sulfur by Lamp Method), D2784, A (Sulfur), D3228 (Kjeldahl Nitrogen), D4047 (Phosphorus), and D5384 (Chlorine). In most of these cases either gravimetric or titrimetric finish are required. Thus, only calibrations involved will be for analytical balance, temperature probe for ashing steps, and standardization of titrants, where required.

8. Calibration in Photometric Test Methods

8.1 A number of test methods use flame emission or colorimetric measurements for quantitation of analytes, usually after reacting the matrix with a chromogenic reagent. Such instruments need to be calibrated using appropriate standards developed by reacting the pure metal analyte with the chromogenic reagent. The calibration curve of analyte concentration versus the photo-signal (absorbance or transmittance) should follow Beer-Lambert Law. The sample analysis should be carried out only in the linear range of the plot. If necessary, solutions with higher concentrations of metals should be diluted to bring them into the linear range of calibration.

8.2 Generally, between three and eight standards are used for developing the calibration curve. The absorbance or transmittance of standard solutions is corrected by subtracting the signal from the blank solution. If a chemical procedure is used to develop the color, the same reagents and steps need also to be included in developing the blank color.

8.3 The test methods using such photometric methods appear in Table 4.

9. Calibration in Electrometric Test Methods

9.1 A number of elemental analysis test methods are based on final measurements using electrometric techniques such as use of microcoulometry, thermal conductivity, chemiluminescence, UV-fluorescence, etc. Most of these test methods are used for the determination of non-metals such as halogens, oxygen, sulfur, carbon-hydrogen-nitrogen, as well as anions such as sulfate and chloride.

9.2 Three to six calibration standards are usually used to construct a response curve for the analysis. Specific requirements are given in each ASTM Standard Test Methods listed below. Mostly these calibrants are pure compounds. Some examples of such compounds are given here, although other appropriate compounds may be used for calibration if they are shown to produce equivalent results as the following:

Nitrogen:	Carbazol, Pyridine, Acridine
Sulfur:	Di-Butyl Sulfide, Dibenzothiophene, Thionaphthene, Dimethyl Sulfide
Chlorine:	Chlorobenzene, Sodium Chloride
Oxygen:	Anhydrous Methanol, NIST SRM 1837
Sulfate:	Anhydrous Sodium Sulfate
C-H-N:	Acetanilide, Atropine, etc.

9.3 A calibration curve with at least three standards is recommended, covering the range of analyte concentrations expected in the samples being analyzed. Calibration curves with one or two standards can be used if it can be shown that the calibration curve is linear over the concentration range being measured and the standards meet the performance criteria given in the test method. Larger series of standards can also be used if it can be shown that the calibration curve is linear over the concentration range being measured and the standards meet the performance criteria of the test method.

9.4 Since these test methods often measure the elements at very low level of concentration, the pure organic compounds used shall be dissolved in appropriate organic solvents and diluted to bring the concentration down in the working linear range (usually in mg/kg or µg/mg).Clean glassware shall be used for dilution and storage purposes. Preparation of working and calibration standards on a regular basis is recommended, depending upon the frequency of usage and age. Stock solutions and particularly the working standards may have a limited useful life. Stock, working, and calibration standards from commercial sources can be used if checked for accuracy and can meet the performance criteria given in the test methods.

9.5 The tests methods using electrometric finish appear in Table 5.

TABLE 4 Test Methods Using Photometric Methods

ASTM Test Method	Analyte	Matrix	Measurement Technique
D1091, A	Phosphorus	Lube Oils and Additives	Colorimetry
D1318	Sodium	Fuel Oils	Flame Photometry
D1548	Vanadium	Fuel Oils	Colorimetry
D1839	Amyl Nitrate	Diesel	Spectrophotometry
D2784, B	Sulfur	LPG	Titrimetry or Photometry
D3231	Phosphorus	Gasoline	Spectrophotometry
D3340	Lithium / Sodium	Greases	Flame Photometry
D3341	Lead	Gasoline	Complexometry
D3348	Lead	Gasoline	Colorimetry
D4045	Sulfur	Petroleum	Rateometric Colorimetry
D4046	Alkyl Nitrate	Diesel	Spectrophotometry
D7041	Sulfur	Diesel	Flame Photometry

TABLE 5 Test Methods Using Electrometric Finish

ASTM Test Method	Analyte	Matrix	Measurement Technique
D3120	Sulfur	Light Liquid Petroleum Hydrocarbons	Microcoulometry
D3230	Salts	Crude Oil	Electrometry
D3246	Sulfur	Petroleum Gas	Oxidative Microcoulometry
D4629	Nitrogen	Liquid Petroleum Hydrocarbons	Chemiluminescence
D4929	Organic Chloride	Crude Oil	Microcoulometry
D5291	Carbon-Hydrogen-Nitrogen	Petroleum Products	Infra-red or Thermal Conductivity
D5453	Sulfur	Petroleum Products	UV-Fluorescence
D5622	Oxygen	Oxyfuels	Infra-red
D5762	Nitrogen	Petroleum Products	Chemiluminescence
D6470	Salts	Crude Oil	Potentiometry
D6667	Sulfur	LPG	UV-Fluorescence
D6920	Sulfur	Gasoline and Diesel	Electrochemical
D7318	Sulfate	Gasoline-Ethanol Blends	Potentiometric Titration
D7319	Sulfate and Chloride	Gasoline-Ethanol Blends	Ion Chromatography
D7328	Sulfate and Chloride	Gasoline-Ethanol Blends	Ion Chromatography

10. Calibration in Atomic Absorption Spectrometry

10.1 A number of metals are determined by the popular technique AAS. In all cases the instrument needs to be calibrated before each set of analysis. Usually solutions of organometallic standards dissolved in solvents such as xylene, toluene, MIBK, kerosene, etc. are utilized. Such standards are widely available from commercial sources or NIST. The concentration of metals in the standards for actual calibration is usually kept between 1 mg/kg to 10 mg/kg, prepared by dilution from stock solutions. Although the purchased stock solutions of high metal concentrations can be preserved for long periods of time, the diluted working standards should not be kept for more than a day, since it is possible that there may be loss of analyte by adsorption on the container walls.

10.2 Similar to the photometric methods, a plot or correlation based on metal concentration versus absorbance is prepared and the metal concentration in the samples is calculated based on this factor. The analysis should be done only within the range of linear curve. If expected metal concentration is higher than the linear range, the sample should be diluted with appropriate solvent otherwise results biased low will result.

10.3 The calibration curve may be manually plotted using x-axis for concentration of metal in the working standards versus corrected absorbance on the y-axis. Many AAS instruments have the capability of automatically constructing the calibration curve internally by way of the instrument software and displayed by way of the instrument computer terminal, making actual manual plotting unnecessary. A curve with the best possible fit of the data within the available means should be used

10.4 Most modern AAS instruments can store up to three or four calibration standards in memory. In such cases, follow the manufacturer's instructions, ensuring that the unknown sample's absorbance is in the linear part of the calibration range used.

10.5 Generally stock solutions of standards contain 100 mg/kg to 1000 mg/kg metal concentration. For working standards these are diluted with appropriate organic solvents to a level of about 10 mg/kg or lower mg/kg level.

10.6 Generally three to six standards are used for establishing the calibration curve of metal concentration versus absorption signal. Often though it has been found that one standard in the linear range is sufficient. A blank needs to be subtracted from the standard solutions' absorbance for compensating any contribution from the metals contaminating the standard solutions. If any chemical step is involved in final standard preparation, it should also be included in the blank solution preparation.

10.7 Calibration shall be carried out prior to each group of samples to be analyzed and after any change in instrumental conditions, as variation occurs in the instrument behavior. Readings also may vary over short periods of time from such causes as buildup of deposits on the burner slot or in the

TABLE 6 Test Methods Using AAS

ASTM Test Method	Analyte	Matrix
D3237	Lead	Gasoline
D3605	Trace Metals	Gas Turbine Fuels
D3831	Manganese	Gasoline
D4628	Additive Metals	Lube Oils and Additives
D5056	Trace Metals	Petroleum Coke
D5184, B	Aluminum and Silicon	Fuels Oils
D5863	Metals	Crude Oils and Residual Fuels
D6732	Copper	Jet Fuels
D7622	Mercury	Crude Oil
D7623	Mercury	Crude Oil

nebulizer. Thus, a single standard should be aspirated from time to time during a series of samples to check whether the calibration has changed. A check after every 5th sample is recommended. The visual appearance of the flame also serves as a useful check to detect changes of condition.

10.8 Although the AAS methods are depicted as single element analysis methods, they can be used for the determination of multiple elements in a single sample. In such cases the sequence of operations in analyzing several samples should also be considered. Aspiration of a sample to determine the absorbance is very quick. Changing wavelength setting and lamps takes longer. Thus, it is most economical to make measurements at a single wavelength on a series of samples and standards before changing conditions. In such cases use of multi-element calibration standards and multi-element hollow cathode lamps would be useful.

10.9 Some of the test methods available for petroleum products and lubricants analysis using AAS appear in Table 6.

10.9.1 Two of these methods listed for mercury determination in crude oil are based on cold vapor atomic absorption spectrometry.

10.10 Practice D7740 discusses the practice of optimization, calibration, and validation of atomic absorption spectrometric methods for the determination of metals in petroleum and lubricant products.

10.11 Although not strictly the AAS or ICP-AES type methods, D6595 and D6728 use rotating disc electrode atomic emission spectrometry methods for the determination of wear metals and contaminants in used lubricating oils, used hydraulic fluids, and gas turbine and diesel engine fuels. The calibration operation range of such instruments for each element is established through the analysis of organometallic standards at known concentrations in the instrument manufacturing factory. A calibration curve for each element is established and correction factors are set to produce a linear response. Analyses of the test specimen shall be performed within the linear range of the response. A minimum of a two point routine standardization should be performed if the instrument fails the validation check or at the start of each working shift. A minimum of three analyses should be made using the blank and working standard.

11. Calibration in ICP-AES Test Methods

11.1 Given the capability of ICP-AES for simultaneous multi-element capability, most laboratories use multi-element standards for instrument calibration. Although such standards can be prepared in-house from pure organometallic standards, it is much more practical and convenient to use pre-blended multi-element organic standards available from many commercial sources. Most are available dissolved in base oil or other organic solvents at levels from 20 to 1000 mg/kg individual element levels. Custom blended standards can also be obtained from these sources.

11.2 More than one multi-element standard may be necessary to cover all elements of interest. It is imperative that 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 these standards represent the linear region of the calibration curve. Frequently, the instrument manufacturer publishes guidelines for determining linear range.

11.3 Some commercially available organometallic standards are prepared from metal sulfonates, and therefore contain sulfur. Thus, for sulfur determination a separate sulfur calibration standard can be required. Metal sulfonates can be used as a sulfur standard if the sulfur content is known or determined by an appropriate test method such as D1552. Petroleum additives can also be used as organometallic standards if their use does not adversely affect the precision nor introduces significant bias.

11.4 Some of the ICP-AES methods (for example, D5184, D5600, and D7303) use aqueous solutions after decomposing the organic matrices converting them into dilute acidic aqueous solutions. In such cases aqueous metal standards shall be used. These are widely available from commercial sources usually in 100 to 1000 mg/kg concentrations. They also can be prepared in-house by dissolving inorganic metal salts in dilute acids.

11.5 The linear range of all ICP-AES curves shall be determined for the instrument being used. This is accomplished by running intermediate standards between the blank and the working standards and by running standards containing higher concentrations than the working standards. Analyses of test specimen solutions shall be performed within the linear range of the calibration curve. At the beginning of the analysis of each set of test specimen solutions, a two-point calibration using the blank and the working standard is performed. A check standard is used to determine if each element is in calibration. When the results obtained with a check standard are within 5 % relative of the expected concentration for all

TABLE 7 Test Methods using ICP-AES

ASTM Test Method	Analyte	Matrix
D4951	Additive Metals	Additives and Lubricants
D5184, A	Aluminum and Silicon	Fuel Oils
D5185	Additive Metals and Contaminants	Base Oils, Lube Oils, and Used Lube Oils
D5600	Trace Metals	Petroleum Coke
D5708	Nickel, Vanadium, and Iron	Crude Oils and Residual Fuels
D7040	Phosphorus	Lube Oils
D7111	Trace Elements	Middle Distillate Fuels
D7303	Metals	Lubricating Greases
D7691	Multiple Elements	Crude Oils

elements, the analysis may be continued. Otherwise, any necessary adjustments to the instrument need to be made and the calibration repeated.

11.6 The calibration curves can be constructed differently, depending on the implementation of internal standard compensation.

11.6.1 When analyte intensities are ratioed to internal standard intensities, the calibration curve, in effect, is a plot of intensity ratio for analyte versus the analyte concentration.

11.6.2 When the internal standard compensation is handled by multiplying all results for a test specimen by the ratio of the actual internal standard concentration to the determined internal standard concentration, the calibration curve is, in effect, a plot of (intensity for analyte – intensity of the blank for the analyte) versus analyte concentration.

11.7 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.

11.8 Detailed discussion of calibration and all other pertinent protocols for use of ICP-AES for analyzing petroleum products and lubricants is given in Practice D7260.

11.9 Some of the test methods available for analysis of petroleum products and lubricants using ICP-AES appear in Table 7.

12. Calibration in XRF Test Methods

12.1 Similar to ICP-AES, XRF has the capability of multi-element analysis, even with a better precision. A large number of XRF test methods have been written for the determination of low levels of sulfur in fuels because of its importance in environmental and regulatory affairs.

12.1.1 Detailed discussion about the sample handling, calibration and validation using XRF methods can be found in Practice D7343.

12.2 Some of the test methods utilizing XRF technique for the analysis of petroleum products and lubricants appear in Table 8.

12.3 The calibration standards used in XRF analysis are similar to those used in ICP-AES analysis. Since for petroleum products analysis usually XRF is a solution analysis, the standards are prepared from pure organometallic compounds or organic sulfur compounds in base oil or other suitable organic solvents. Particular attention needs to be paid to the purity of

the solvent used. Otherwise a blank correction may be necessary for the contaminants in the solvent.

12.3.1 Working calibration standards can be prepared by careful mass dilution of a certified organic compound with an analyte-free white oil or other suitable base material such as toluene, iso-octane, xylene, etc. The concentration of the unknown samples shall lie within the calibration range that is used.

12.4 Some of the calibration standards suggested and widely used include:

12.4.1 *Di-n-Butyl Sulfide, Thiophene, 2-Methyl Thiophene*—Used for sulfur analysis.

12.4.2 *Polysulfide Oil*—Generally, nonyl polysulfides containing a known percentage of sulfur (as high as 50 m%) diluted in a hydrocarbon matrix. They exhibit excellent physical properties such as low viscosity, low volatility, and durable shelf life while being completely miscible in white oil. The sulfur content of the polysulfide oil concentrate is determined via mass dilution in sulfur-free white oil followed by a direct comparison analysis against NIST (or other primary standard body) reference materials.

12.4.3 *Metal Sulfonates, Octoates, Ethylhexanoates, or Cyclohexanebutyrates*—Used for metal analysis such as Ba, Ca, Cu, Mg, P, Zn.

12.5 The calibration standards and check samples should be stored in glass bottles in a cool dark place until required. The glass bottles should be either dark or wrapped in opaque material and closed with glass stoppers, inert plastic lined screw caps, or other equally inert, impermeable enclosures. As soon as any sediment or change of concentration is observed, the standard should be discarded.

12.6 The calibration curve is established by determining the net intensity of the emitted radiation from the metal of interest in each of the standards. Usually five to ten calibration standards may be employed; these may be in the mg/kg or 0.x mass% levels depending on the level of the analyte to be determined in the samples. Usually a calibration model is prepared by the software in the XRF instrument.

12.7 Respective X-ray cups are filled at least half full with the calibration standard solutions. No wrinkle or bulges should appear in the film which shall be flat. The filled cups with a vent hole punched in the top of the cell are placed in the X-ray beam in order to measure and record the net intensity (that is, peak intensity – background intensity) for the analyte signal. Although many XRF instruments can count for times even

TABLE 8 Test Methods Using XRF Technique

Test Method	Analyte	Matrix	XRF Type
D2622	Sulfur	Petroleum Products	WD-XRF
D4294	Sulfur	Petroleum Products	ED-XRF
D4927	Additive Elements	Additives and Lube Oils	WD-XRF
D5059	Lead	Gasoline	WD-XRF
D6334	Sulfur	Gasoline	WD-XRF
D6443	Additive Elements	Additives and Lube Oils	WD-XRF
D6445	Sulfur	Gasoline	ED-XRF
D6481	Additive Elements	Lube Oils	ED-XRF
D7039	Sulfur	Gasoline and Diesel	MWD-XRF
D7212	Sulfur	Automotive Fuels	ED-XRF
D7220	Sulfur	Automotive Fuels	ED-XRF
D7751	Multiple Elements	Lube Oils	ED-XRF
D7757	Silicon	Gasoline Products	MWD-XRF

WD-XRF: Wavelength Dispersive X-Ray Fluorescence
ED-XRF: Energy Dispersive X-Ray Fluorescence
MWD-XRF: Monochromatic Wavelength Dispersive X-Ray Fluorescence

greater than 15 min, in petroleum products analysis a counting period up to 60-s may be used at each wavelength position. This is done for each of the calibration standards for each of the elements measured. A regression analysis is performed for each calibration element by plotting on a linear graph paper or by the way of instrument computer system. It is recommended that a multiple linear regression be performed for each calibration. The regression analysis will determine a slope and an intercept for each calibration element that will be used to determine elemental concentrations in the samples to be analyzed.

12.8 The initial calibration to obtain the slope, intercept, and interelement correlation factors is performed initially when the test method is set up, after any major instrumental maintenance is performed that can affect the calibration (for example, new X-ray tube installed, new crystal added, and so forth), and as deemed necessary by the operator (for example, triggered by quality control sample results). Subsequently re-calibration is performed with a minimum of three standards containing each of the calibration elements at nominal concentrations across the respective calibration ranges in order to check the values of the slope and the intercept.

12.9 Immediately after completing the calibrations, the sulfur concentration of one or more of the calibration check standards is determined. The difference between the two measured values should be within the repeatability of the test method being used. When this is not the case, the stability of the instrument and the repeatability of the sample preparation may be suspect, and corrective measures should be taken. The degree of matrix mismatch should also be considered when evaluating a calibration.

12.10 *Drift Correction Monitors*—The use of drift correction monitors for determination and correction of instrument drift can be advantageous. Monitors are stable, solid disks or pellets containing all elements of interest in the test method used. Two disks are preferred to correct for both sensitivity and base line drifts. The high-concentration drift monitor provides high-count rates, so that for each analyte, counting error is less than 0.25% relative. The low-concentration drift monitor provides low-count rats, so that for each element, count rate is similar to that obtained with the calibration blank, or zero mass % standard.

13. Blank Determination

13.1 Although every attempt is made during an analysis to use pure reagents and maintain a clean working environment, often there will be contamination from unknown quantity of analyte of interest in an analytical sequence. To minimize such effects, a blank should always be subtracted from the sample and standard measurement responses. The blank sample in such cases should contain same quantities of reagents or solvents added to the samples and undergo through the same processing steps to mimic a sample treatment.

14. Keywords

14.1 atomic absorption spectrometry; balances; calibration; calibration standard; check standard; electrometric methods; ICP-AES methods; lubricants; petroleum products; photometric methods; reference material; temperature measuring devices; timers; verification; XRF methods

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SUMMARY OF CHANGES

Subcommittee D02.03 has identified the location of selected changes to this standard since the last issue (D7578 – 10$^{\varepsilon 1}$) that may impact the use of this standard. (Approved June 1, 2015.)

(1) Added new references to Section 2, expanded sections 10.9.1, 10.10, and Tables 6-8.