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Standard Guide for Calibration Requirements for Elemental Analysis of Petroleum Products and Lubricants¹

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

1.9 *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

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 Oil¹ (Withdrawn 1997)³

D1552 Test Method for Sulfur in Petroleum Products by High Temperature Combustion and Infrared (IR) Detection or Thermal Conductivity Detection (TCD)

D1839 Test Method for Amyl Nitrate in Diesel Fuels (Withdrawn 2019)³

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

D2784 Standard Test Method for Sulfur in Liquefied Petroleum Gases (Oxy-Hydrogen Burner or Lamp) (Withdrawn 2016)³

¹ This guide 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.

³ The last approved version of this historical standard is referenced on www.astm.org.

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

- D3120** Test Method for Trace Quantities of Sulfur in Light Liquid Petroleum Hydrocarbons by Oxidative Microcoulometry
- D3228** Test Method for Total Nitrogen in Lubricating Oils and Fuel Oils by Modified Kjeldahl Method
- D3230** Test Method for Salts in Crude Oil (Electrometric Method)
- D3231** Test Method for Phosphorus in Gasoline
- D3237** Test Method for Lead in Gasoline by Atomic Absorption Spectroscopy
- D3246** Test Method for Sulfur in Petroleum Gas by Oxidative Microcoulometry
- D3340** Test Method for Lithium and Sodium in Lubricating Greases by Flame Photometer (Withdrawn 2013)³
- D3341** Test Method for Lead in Gasoline—Iodine Monochloride Method
- D3348** Test Method for Rapid Field Test for Trace Lead in Unleaded Gasoline (Colorimetric Method)
- D3605** Test Method for Trace Metals in Gas Turbine Fuels by Atomic Absorption and Flame Emission Spectroscopy
- D3831** Test Method for Manganese in Gasoline By Atomic Absorption Spectroscopy
- D4045** Test Method for Sulfur in Petroleum Products by Hydrogenolysis and Rateometric Colorimetry
- D4046** Test Method for Alkyl Nitrate in Diesel Fuels by Spectrophotometry (Withdrawn 2019)³
- D4047** Test Method for Phosphorus in Lubricating Oils and Additives by Quinoline Phosphomolybdate Method
- D4294** Test Method for Sulfur in Petroleum and Petroleum Products by Energy Dispersive X-ray Fluorescence Spectrometry
- D4307** Practice for Preparation of Liquid Blends for Use as Analytical Standards
- D4628** Test Method for Analysis of Barium, Calcium, Magnesium, and Zinc in Unused Lubricating Oils by Atomic Absorption Spectrometry
- D4629** Test Method for Trace Nitrogen in Liquid Hydrocarbons by Syringe/Inlet Oxidative Combustion and Chemiluminescence Detection
- D4927** Test Methods for Elemental Analysis of Lubricant and Additive Components—Barium, Calcium, Phosphorus, Sulfur, and Zinc by Wavelength-Dispersive X-Ray Fluorescence Spectroscopy
- D4929** Test Method for Determination of Organic Chloride Content in Crude Oil
- D4951** Test Method for Determination of Additive Elements in Lubricating Oils by Inductively Coupled Plasma Atomic Emission Spectrometry
- D5056** Test Method for Trace Metals in Petroleum Coke by Atomic Absorption
- D5059** Test Methods for Lead and Manganese in Gasoline by X-Ray Spectroscopy
- 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)
- D5291** Test Methods for Instrumental Determination of Carbon, Hydrogen, and Nitrogen in Petroleum Products and Lubricants
- D5384** Test Methods for Chlorine in Used Petroleum Products (Field Test Kit Method)
- D5453** Test Method for Determination of Total Sulfur in Light Hydrocarbons, Spark Ignition Engine Fuel, Diesel Engine Fuel, and Engine Oil by Ultraviolet Fluorescence
- D5600** Test Method for Trace Metals in Petroleum Coke by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)
- D5622** Test Methods for Determination of Total Oxygen in Gasoline and Methanol Fuels by Reductive Pyrolysis
- D5708** Test Methods for Determination of Nickel, Vanadium, and Iron in Crude Oils and Residual Fuels by Inductively Coupled Plasma (ICP) Atomic Emission Spectrometry
- D5762** Test Method for Nitrogen in Liquid Hydrocarbons, Petroleum and Petroleum Products by Boat-Inlet Chemiluminescence
- D5800** Test Method for Evaporation Loss of Lubricating Oils by the Noack Method
- D5863** Test Methods for Determination of Nickel, Vanadium, Iron, and Sodium in Crude Oils and Residual Fuels by Flame Atomic Absorption Spectrometry
- D6334** Test Method for Sulfur in Gasoline by Wavelength Dispersive X-Ray Fluorescence
- D6443** Test Method for Determination of Calcium, Chlorine, Copper, Magnesium, Phosphorus, Sulfur, and Zinc in Unused Lubricating Oils and Additives by Wavelength Dispersive X-ray Fluorescence Spectrometry (Mathematical Correction Procedure)
- D6445** Test Method for Sulfur in Gasoline by Energy-Dispersive X-ray Fluorescence Spectrometry (Withdrawn 2009)³
- D6470** Test Method for Salt in Crude Oils (Potentiometric Method)
- D6481** Test Method for Determination of Phosphorus, Sulfur, Calcium, and Zinc in Lubrication Oils by Energy Dispersive X-ray Fluorescence Spectroscopy
- D6595** Test Method for Determination of Wear Metals and Contaminants in Used Lubricating Oils or Used Hydraulic Fluids by Rotating Disc Electrode Atomic Emission Spectrometry
- D6667** Test Method for Determination of Total Volatile Sulfur in Gaseous Hydrocarbons and Liquefied Petroleum Gases by Ultraviolet Fluorescence
- D6728** Test Method for Determination of Contaminants in Gas Turbine and Diesel Engine Fuel by Rotating Disc Electrode Atomic Emission Spectrometry
- D6732** Test Method for Determination of Copper in Jet Fuels by Graphite Furnace Atomic Absorption Spectrometry

- D6792** Practice for Quality Management Systems in Petroleum Products, Liquid Fuels, and Lubricants Testing Laboratories
- D6920** Test Method for Total Sulfur in Naphthas, Distillates, Reformulated Gasolines, Diesels, Biodiesels, and Motor Fuels by Oxidative Combustion and Electrochemical Detection (Withdrawn 2018)³
- 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 Liquid Hydrocarbons and Hydrocarbon-Oxygenate Blends by 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
- D8110** Test Method for Elemental Analysis of Distillate Products by Inductively Coupled Plasma Mass Spectrometry (ICP-MS)
- D8127** Test Method for Coupled Particulate and Elemental Analysis using X-ray Fluorescence (XRF) for In-Service Lubricants
- D8150** Test Method for Determination of Organic Chloride Content in Crude Oil by Distillation Followed by Detection Using Combustion Ion Chromatography
- 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*—in *QC testing*, material having an accepted reference value used to determine the accuracy of a measurement system.

⁴ Available from National Institute of Standards and Technology (NIST), 100 Bureau Dr., Stop 1070, Gaithersburg, MD 20899-1070, <http://www.nist.gov>.

⁵ Available from International Organization for Standardization (ISO), 1, ch. de la Voie-Creuse, Case postale 56, CH-1211, Geneva 20, Switzerland, <http://www.iso.ch>.

3.1.3.1 *Discussion*—This standard is not used to calibrate the measurement instrument or system (see *calibration standard*).

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

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

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- 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.
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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 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

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		

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 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.