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Standard Practice for Sample Preparation of Petroleum and Lubricant Products for Elemental Analysis¹

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1. Scope

1.1 This practice covers different means by which petroleum product and lubricant samples may be prepared before the measurement of their elemental content using different analytical techniques.

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

1.3 This practice is not a substitute for a thorough understanding of the actual test method to be used, caveats the test method contains, and additional sample preparation that may be required.

1.4 The user should not expand the scope of the test methods to materials or concentrations outside the scope of the test methods being used without thoroughly understanding the implications of such deviations.

1.5 This practice may also be applicable to sample preparation of non-petroleum based bio-fuels for elemental analysis. Currently, work is ongoing in ASTM Subcommittee D02.03; as information becomes available, it will be added to this standard.

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

1.7 *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.*

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

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2. Referenced Documents

2.1 ASTM Standards:²

- D86 Test Method for Distillation of Petroleum Products at Atmospheric Pressure
- D129 Test Method for Sulfur in Petroleum Products (General High Pressure Decomposition Device Method)
- 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
- 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 (High-Temperature Method)
- 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
- 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)

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.

- 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
- 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
- D3701** Test Method for Hydrogen Content of Aviation Turbine Fuels by Low Resolution Nuclear Magnetic Resonance Spectrometry
- D3831** Test Method for Manganese in Gasoline By Atomic Absorption Spectroscopy
- D4045** Test Method for Sulfur in Petroleum Products by Hydrogenolysis and Rateometric Colorimetry
- D4047** Test Method for Phosphorus in Lubricating Oils and Additives by Quinoline Phosphomolybdate Method
- D4057** Practice for Manual Sampling of Petroleum and Petroleum Products
- D4177** Practice for Automatic Sampling of Petroleum and Petroleum Products
- D4294** Test Method for Sulfur in Petroleum and Petroleum Products by Energy Dispersive X-ray Fluorescence Spectrometry
- 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 Petroleum Hydrocarbons by Syringe/Inlet Oxidative Combustion and Chemiluminescence Detection
- D4808** Test Methods for Hydrogen Content of Light Distillates, Middle Distillates, Gas Oils, and Residua by Low-Resolution Nuclear Magnetic Resonance Spectroscopy
- 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 Methods 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 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 Determination of Additive Elements, Wear Metals, and Contaminants in Used Lubricating Oils and Determination of Selected Elements in Base Oils by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)
- 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 Petroleum and Petroleum Products by Boat-Inlet Chemiluminescence
- 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
- D6920** Test Method for Total Sulfur in Naphthas, Distillates, Reformulated Gasolines, Diesels, Biodiesels, and Motor Fuels by Oxidative Combustion and Electrochemical Detection

- D7039** Test Method for Sulfur in Gasoline and Diesel Fuel 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
- 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 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
- WK16905** Practice for Sampling, Storage, and Handling of Hydrocarbon Samples for Mercury Analysis

3. Summary of Practice

3.1 This practice covers alternate ways of preparing a petroleum product or lubricant sample for elemental analysis measurements. The means of preparation of samples may vary from no special steps to extensive detailed procedures dependent on the sample matrix and the measurement technique to be used.

3.2 This practice may also be applicable to non-petroleum based biofuels. Work is underway to validate the applicability to these types of materials.

4. Significance and Use

4.1 Crude oil, petroleum, petroleum products, additives, and lubricants are routinely analyzed for their elemental content such as chlorine, nitrogen, phosphorus, sulfur, and various metals using a variety of analytical techniques. Some of these test methods require little to no sample preparation; some others require only simple dilutions; while others require elaborate sample decomposition before the product is analyzed for its elemental content.

4.2 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.

4.3 Uniform practice for sample preparation is beneficial in standardizing the procedures and obtaining consistent results across the laboratories.

5. Gross Sample Preparation

5.1 Collection of a meaningful and representative sample is often the most critical step in an analytical procedure. In trace element analysis, in particular, extreme care must be taken to avoid contamination of the samples during the sampling and all subsequent analysis steps. Good laboratory practices in this area can include:

5.1.1 The sample received by the laboratory for analysis needs to be stored in a designated specific storage location while awaiting analysis. This area, whenever possible, shall not contain materials with high levels of specific elements that could contaminate other samples requiring trace element analysis.

5.1.2 All laboratory equipment used specifically for trace element analysis need to be free of any source of contamination. This may require that specific equipment be used only for trace element analysis.

5.1.3 Use working surfaces that can be decontaminated easily if a spillage occurs. The atmosphere needs to be free of interfering gases and dust particles.

5.1.4 Wear clean, fresh, protective, and impermeable gloves for sample preparation for trace element analysis, appropriate for the materials being handled. Test the gloves to confirm that they do not contain interfering elements or elements of interest, since they may cause contamination. The development of clean area sample handling protocols is encouraged.

5.2 All laboratory samples should be collected in accordance with Practices **D4057** and **D4177**. The personnel collecting the samples should be properly trained in sampling, since invalid sampling can lead to invalid results. The responsibility of the laboratory starts on receipt of the sample in the laboratory.

5.2.1 It would be useful for the laboratory personnel to assist the plant personnel in securing a representative contamination-free sample. Often inappropriate or unclean containers are used to collect the samples in plant or field. It would help if the laboratory can provide pre-cleaned sample containers to the plant personnel collecting the samples.

5.2.1.1 The clean container, lid, liner seal, and liner adhesive shall not contaminate the sample, and the sample shall not compromise the integrity of the container.

5.2.1.2 Consult Department of Transportation packaging guidelines or other appropriate sources, such as placing in a Hazmat-Pak, taping caps in place after securing tightly container/liner compatibility, judicious use of vermiculite as a packing material considering contamination as well as user safety from inhaled dust, etc.

5.2.2 To preserve sample integrity and prevent the loss of volatile components, which can be present in some samples, they shall not be kept uncovered any longer than necessary. Samples need to be analyzed as soon as possible after taking from the bulk supplies to prevent loss of volatile species or contamination.

5.3 Before taking an aliquot of the bulk sample, ensure that the sample is well-mixed and homogenous. This can be ensured, if necessary, by the use of an ultrasonic device or vigorously stirring with a magnetic or mechanical stirrer or shaker. Purge the sampling port lines on tanks properly before collecting the samples.

5.4 Care must be taken during the homogenization procedure that the sample is not contaminated with dust, particles, or by contact with other sources of metals.

5.4.1 Stabilized crude oils typically contain multiple phases, particulates, and volatiles. Decisions whether to separate the phases and analyze them separately, or homogenize the whole sample need to be made prior to analysis.

5.5 Many samples contain volatile components. Hence, it is prudent to keep the sample refrigerated until ready for analysis. This is particularly true for products such as gasoline, diesel, reformulated gasoline, jet fuel, etc. Vessel pressure integrity and permeability need to be considered.

5.5.1 Unless a given test method procedure states otherwise, refrigerated samples should be warmed to ambient temperature before taking an aliquot for analysis. During warming, condensation of moisture on the sample containers is a concern.

5.5.2 Potential overpressure hazard, just like heating a sealed container in an oven needs to be lessened by loosening the cap to prevent rupture. However, this can result in loss of light ends, depending on the material composition.

5.5.3 If the sample does not readily flow at room temperature, heat it to a sufficiently high and safe temperature to ensure adequate fluidity.

5.5.4 Great care needs to be exercised in heating the viscous samples prior to analysis. Changes in chemical composition, loss of volatile elements, etc. are causes for concern.

5.6 Fuel samples can contain particulate matter and free water. In order to be representative, always shake vigorously prior to taking a test specimen for analysis.

5.6.1 Samples that have been in transit for several days, idle in storage, or viscous may be placed in a heated ultrasonic bath to break up clusters of particles and to bring them back into suspension. The samples may be vigorously shaken with a power mixer after being in an ultrasonic bath and prior to pouring a test specimen for analysis. The bath temperature should be 60°C for very viscous fuels and below the flash point for non-viscous fuels. The total agitation time for a sample should be at least 2 min.

5.6.2 Impeller mixers can be a source of contamination as well. Air-driven motors (for example, oil or dust), bearing wear contaminants, leaching of metals from impellers, impeller abrasion contact with container, etc., are some of the points that need to be thought of as potential contamination sources.

5.6.3 From a safety perspective, electric motors present an ignition hazard with flammables. Long term use of ultrasonic

baths can overheat samples. To prevent fire or explosion, an operator should always remain present during these preparations and never leave any of these operations unattended.

6. Contamination Control

6.1 Samples that are used for the determination of metals shall be scrupulously kept away from contact with metal containers and laboratory utensils. Wherever possible, plastic or other inert materials shall be used.

6.2 Reagents and solvents used in chemical processing of the samples need to be free of trace elements. For example, laboratory wipe tissues commonly used in many laboratories for wiping laboratory glassware has been reported to contain 48 ppm of zinc, and could be a potential source of contamination.

6.3 Trace elements in the sample can interact with the wall containers and subsequently will result in low biased results. On the other hand, if the sample matrix is reacting with the containers, metals will leach out in the sample leading to high biased results. However, in both cases, the results will not represent the true elemental concentration in the original sample.

6.4 Acid-washed glass containers lined with inert substances and polyethylene-polypropylene-PTFE, or both, containers are the best containers for storage of petroleum products and lubricants.

6.5 Materials used in dilutions, solubilizations, or adjusting pH, etc. need to be screened for possible contamination, especially in trace element analysis.

7. Methods Requiring No Sample Preparation

7.1 There are a number of test methods that essentially require no sample preparation. Mostly these test methods are X-ray fluorescence (XRF) test methods, and they include Test Methods **D2622**, **D4294**, **D6334**, **D6445**, **D7039**, **D7212**, and **D7220** for sulfur; Test Methods **D3348** and **D5059** for lead; Test Method **D3605** for trace metals; and Test Methods **D6443** and **D6481** for metals.

7.1.1 However, in some procedures such as **D2622**, dilution is needed for samples containing >4.6 m% sulfur or for samples containing >5 m% oxygen or other metals. Similarly, in Test Method **D4294**, it may be necessary to remove certain interfering elements from the matrix before measurements.

7.2 For some X-ray fluorescence test methods given above, mixing with the internal standard is necessary before the analysis (for example, Test Method **D5059** for lead).

7.3 Other non-XRF test methods that do not need special sample treatment include Test Method **D3230** for salt in crude oil; Test Methods **D3701**, **D4808**, and **D7171** for hydrogen by NMR; Test Method **D5291** for carbon-hydrogen-nitrogen by combustion; Test Methods **D6595** and **D6728** for contaminants by rotrode atomic emission spectrometry; Test Method **D6732** for copper by graphite furnace atomic absorption spectrometry, and Test Methods **D7318**, **D7319**, and **D7328** for chloride and sulfate by potentiometry and ion chromatography.