Designation: D7455 – 14

Standard Practice for
Sample Preparation of Petroleum and Lubricant Products for Elemental Analysis[1]

This standard is issued under the fixed designation D7455; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope*

1.1 This practice covers 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.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

C1234 Practice for Preparation of Oils and Oily Waste Samples by High-Pressure, High-Temperature Digestion for Trace Element Determinations
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 Oil[1] (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

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

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[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**

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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

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 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 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, 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

D7482 Practice for Sampling, Storage, and Handling of Hydrocarbons for Mercury Analysis

D7620 Test Method for Determination of Total Sulfur in Liquid Hydrocarbon Based Fuels by Continuous Injection, Air Oxidation and Ultraviolet Fluorescence Detection

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

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

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, and Test Method D7751 for additive elements in lubricating oils.

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.

7.1.2 A monochromatic wavelength dispersive XRF method has been developed for the determination of trace amounts of silicon in gasoline and related products. This Test Method D7757 was in response to an industry need to counter the silicon contamination of gasolines.

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.

8. Methods Requiring Solvent Dilution

8.1 For several test methods, the only sample preparation required is a simple dilution with appropriate organic solvent. Most of these test methods are based on atomic absorption spectrometry (AAS) or inductively coupled plasma atomic emission spectrometry (ICP-AES) measurement of analytes of interest. The reason for this step could be that either the sample is too viscous to flow through the nebulizer or the viscosity of the sample needs to match that of the calibration standards. In both cases this is achieved by appropriate dilution with an organic solvent or a solvent mixture.

8.2 A variety of organic solvents have been used for this purpose: methyl iso-butyl ketone, heavy distillate, kerosene, xylenes, acetone, etc.

8.3 The test methods that require such solvent dilutions include:

8.3.1 Atomic absorption spectrometry Test Methods D3237 and D3341 for lead, Test Method D3831 for manganese, Test Method D4628 for additive metals, and Test Method D5863 B for nickel, vanadium, iron, and sodium in crude oils.

8.3.2 ICP-AES Test Methods D4951 for additive elements, Test Method D5185 for additive elements and wear metals, Test Method D5708 for nickel, vanadium, and iron in crude oils, Test Method D7040 for phosphorus, Test Method D7111 for trace metals, and Test Method D7691 for multielement analysis of crude oils.

8.3.3 XRF Test Methods D4927 for additive elements.

8.3.4 Miscellaneous Test Method D5384 for chloride by coulometric titration, and Test Method D6470 for salt in crude oil by potentiometric titration.

9. Ash and Sulfated Ash Procedures

9.1 The fundamental and empirical procedures used for destroying organic materials and converting all inorganic components to oxides or sulfates are a cornerstone of many analyses.

9.1.1 In ash Test Method D482, a sample is ignited and later heated in a muffle furnace at 775°C to constant weight. All nonvolatile inorganic species are converted to oxides. The resultant ash can be used for the dissolution in acid(s) and the determination of metals by spectroscopy or other means.

9.1.1.1 Examples of procedures using preliminary treatment by ashing step include Test Methods D1318 for sodium, Test Method D5056 for trace metals, Test Method D5184 for aluminum and silicon, and Test Method D5600 for metals in coke.

9.1.2 In the sulfated ash (SASH) Test Method D874, a sample is ignited and the residue is treated with concentrated sulfuric acid and finally heated in a muffle furnace at 775°C to a constant weight. Although it is presumed that all metals are converted to sulfates in this procedure, experimental evidence definitively shows that the resultant residue contains a number of sub-stoichiometric compounds, phosphates and pyrophosphates in addition to sulfates. As a result, the theoretical sum of total sulfates calculated from metal concentrations in the sample does not match the experimental weights of residues obtained by this procedure.[4]

9.1.2.1 There are a number of notes in Test Method D874 that caution about the interaction of various metal species during this procedure.

9.1.3 In both ash and SASH procedures, platinum, quartz or high purity silica crucibles are preferable. However, most of the time many laboratories use porcelain or quartz crucibles. Platinum ware should not be used if the sample contains

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[4] Nadkarni, R. A., Ledesma, R. R., and Via, G. H., "Sulfated Ash Test Method: Limitations of Reliability and Reproducibility," *SAE Technical Paper Series 952548*, SAE, Warrendale, PA.

phosphorus, since it can react with the platinum and contaminate the ash residue. Similarly, alkalies present in crude oil during field treatment can react with platinum or silica crucibles.

9.1.3.1 Platinum, silica, quartz, porcelain or other crucibles being used should be placed on silica plates or silica triangles on the floor of the muffle furnace.

9.1.4 Microwave ovens have also been used for dry ashing of petroleum products. However, all volatile organic-based products need to be handled in this step with extreme care to prevent fire hazards. See extensive warning notes given in Test Method D7303 regarding the use of microwave ovens/furnaces/digestion devices.

9.1.5 Most metals will be converted to oxides and sulfates, respectively, in these ash and SASH procedures. The sulfates are preferable because metal sulfates are generally nonvolatile. The residue obtained by this procedure can be used for dissolution in acid(s) such as nitric and hydrochloric acids with water, and the determination of metals by spectroscopy or other means.

9.1.6 Examples of the procedure using sulfated ashing as the preliminary sample treating step include Test Method D3340 for lithium and sodium in greases, Test Method D5708 B for nickel, vanadium, and iron in crude oil, and Test Method D7303 for metals in lubricating greases.

9.1.7 During the initial ignition period, the muffle door should be carefully adjusted so that too great an air flow into the muffle will not cause the ash to be blown from the beaker or to be lost because of too rapid burning of the carbonaceous material.

9.1.8 Contamination from the muffle furnace should be prevented by properly covering the specimen container with a lid of the same type of material as the crucible, to prevent contamination of the samples with particles from the roof, walls, and the door of the furnace. The heating element or furnace walls should be replaced if they show flaking.

10. Test Methods Requiring Decomposition With Acid(s) or Other Reagents

10.1 A variety of decomposing agents have been used based on the analysis requirements for the specific sample types. The most commonly used acids are sulfuric and nitric acids or their mixtures, sometimes supplemented by hydrogen peroxide for faster oxidation of organic materials (see Test Method D1091 for phosphorus). (**Warning—**Poison. Causes severe burn. Harmful or fatal if swallowed or inhaled).

10.2 Other inorganic decomposing agents may have to be used in specific instances, such as zinc oxide in Test Methods D3231 and D4047 for phosphorus, and catalyst mixtures of potassium sulfate + mercuric oxide + copper sulfate for Kjeldahl nitrogen determination in Test Method D3228.

10.2.1 The Kjeldahl Test Method D3228 for nitrogen is not applicable to materials containing N-O or N-N linkage resulting in low results if such compounds are present in the sample. For such materials, alternate nitrogen Test Methods D4629, D5291, or D5762 may be used for obtaining the true estimate of total nitrogen content.

10.3 Silica, if present in the residue, will not be dissolved by acid digestion. If required, silica can be dissolved with a few drops of hydrofluoric acid; the excess can be neutralized or complexed with dilute boric acid solution. However, this may cause later interference in the determination of other metals in the solution.

10.4 Examples of acid decomposition of ash residues of petroleum products include Test Methods D1548 (vanadium in crude oil), D5863 A (nickel, vanadium, iron, and sodium in crude oils), and D7303 (trace metals in lubricating greases).

10.5 Heating in an acid mixture in a microwave oven can be used for effective decomposition such as in Test Method D7303 for trace metals in lubricating grease samples. See the detailed caution statements given in Test Method D7303 in this regard.

10.5.1 A standard practice for sample decomposition using microwave heating, with or without prior ashing, has been described in Practice D7876. The metal determination is completed using atomic spectroscopic techniques.

10.6 A standard practice for preparation of oils and oily waste samples by high-pressure, high-temperature digestion followed by atomic spectroscopic determination is described in Practice C1234.

11. Test Methods Requiring Bomb or Lamp Decomposition

11.1 In several cases, the complete decomposition of organic material is achieved by combusting a small amount of sample in an oxygen atmosphere in a closed vessel. The sample burns in contact with pressurized oxygen converting the organic material into carbon dioxide and water, and the metals to oxides. After the combustion is complete, the residue can be dissolved in suitable acid(s) and the metals determined by various means.

11.2 Examples of such combustion procedures include Test Methods D129 for sulfur and D808 for chlorine, both determined gravimetrically.

11.2.1 Instead of using a pressurized bomb, the following test methods use a lamp for combustion: Test Method D1018 for hydrogen (determined gravimetrically), Test Method D1266 for sulfur (determined gravimetrically), and Test Method D2784 for sulfur in LPG determined by titration or turbidimetry.

11.3 For the determination of sulfur in heavier products that cannot be burned effectively in a lamp, other test methods such as the bomb Test Method D129 or the high temperature Test Method D1552 can be used.

11.4 Strict adherence to all of the provisions prescribed in these test methods ensures against explosive rupture of the bomb, or a blow-out, provided the bomb is of proper design and in good mechanical condition. It is desirable, however, that the bomb be enclosed in a shield of steel plate at least 13-mm thick, or that equivalent protection be provided against unforeseeable contingencies.

11.5 Most of these test methods have been largely supplanted by more modern techniques in the industry laboratories.

12. Test Methods Using Combustion—Adsorbant Trains

12.1 In addition to simple combustion followed by the detection of the analyte of interest described in Section 11, several other test methods use separation of combustion products that may require adsorption on specific reagents for specific gaseous oxides or gas chromatographic separation.

12.2 On combustion in oxygen, all nonmetallic constituents of the sample are converted to gaseous compounds such as carbon dioxide, chlorine, nitrogen, water vapor, sulfur oxides, etc. A variety of adsorbant columns have been used for the separation of these gaseous products.

12.3 A majority of these test methods are used for the determination of sulfur in a variety of products. In all cases, the separated analyte gas of interest is quantitatively measured by a variety of means of detection such as iodate color or infrared spectrometry (Test Method D1552 for sulfur), UV-fluorescence (Test Methods D5453, D6667, and D7620 for sulfur), chemiluminescence (Test Methods D4629 and D5762 for nitrogen), microcoulometry (Test Methods D3120 and D3246 for sulfur), thermal conductivity (Test Method D5622 for oxygen), rateometric colorimetry (Test Method D4045 for sulfur), electrochemistry (Test Method D6920 for sulfur), and flame photometry (Test Method D7041 for sulfur).

12.4 Various adsorption trains can be used for the removal of undesirable oxidation products. These include removal of water vapor using phosphoric acid dehydration cell (Test Method D3120 for sulfur), anhydrous magnesium perchlorate (Test Methods D4629 and D5762 for nitrogen, and D6920 for sulfur), and membrane drying cell or a permeation dryer tube (D5453, D6667, D6920, and D7620 for sulfur). Test Method D5622 for oxygen determination uses a train of molecular sieve for absorbing carbon dioxide, heated copper column for absorbing sulfur oxides, and a scrubber for absorbing acidic gases. Gas chromatographic separation columns are used to separate carbon dioxide and water vapor for the determination of sulfur as sulfur dioxide in Test Method D7041.

13. Miscellaneous Test Methods

13.1 Organic chloride in crude oil is determined by Test Method D4929 either by sodium biphenyl reduction and potentiometry (Procedure A) or by combustion and microcoulometry (Procedure B). However, before these steps, the crude oil sample is distilled using Test Method D86 and a naphtha cut at 204°C is collected. This naphtha cut is washed with 1M KOH solution to remove hydrogen sulfide, and next with water to remove the inorganic chloride salts.

13.2 *Mercury in Crude Oil*—Determination of mercury in crude oils poses a particular problem in terms of sensitivity for ppb level measurements required, and the volatility of mercury species from crude oils during storage and handling. Mercury is present in various molecular forms in crude oils as metallic Hg(0) and other molecular species including alkyl mercury. Multiphase of analyte and matrix mixtures homogeneity needs to be considered.

13.2.1 The most promising storage containers appear to be quartz, borosilicate glass, titanium, sulfinet-coated cans, epoxy lined cans, and glassy carbon. The most likely preservative for speciation would be freezing in liquid nitrogen. The best preservative for keeping total mercury in solution appears to be dithizone, which forms colored stable complexes with many transition metals.

13.2.2 Many high purity solvents have a significant degree of oxidizing capacity (as defined by the ability to oxidize Hg(0) to Hg+2). Thus, before using any solvent to dilute a hydrocarbon for mercury analysis, the solvent should be "redox-neutralized." See Practice D7482 for details.

13.2.3 While bulk mercury droplets are not highly volatile (vapor pressure <1 mm Hg at 60°F), dissolved mercury readily evaporates with an apparent vapor pressure similar to that of butane or pentane. Also, mercury can easily adsorb on to many metal surfaces. To avoid loss of mercury vapor from the samples, vials should be filled as quickly as possible, and to their total capacity or with only a small (~1 mL) headspace remaining. The vials should be capped immediately.

13.2.4 In no case should the hydrocarbon samples be taken directly or sub-sampled from tin-lined cans. Metal containers in any step of the sampling process are discouraged. Glass is preferred. See Practice D7482 for more details.

13.2.5 Organo-mercury species have been shown to be stable for at least 30 days in glass, aluminum, steel, or PTFE containers, while mercuric oxide was stable in all of these plus stainless steel and polyethylene containers. Mercury (II) was rapidly lost from all containers except those made from aluminum. Total mercury, mercury (II), and mercury methyl chloride in crude oil were stable over the course of more than 3 months in glass containers, but mercury (0) decreased with a half life of about 40 days. These storage experiments indicate that while total mercury, methyl mercury chloride, and dimethyl mercury are quite stable in glass and Teflon containers, for complete speciation, the samples must be analyzed as soon as possible. The metal and polyethylene containers are unsuitable for the collection and storage of mercury in petroleum due either to loss of mercury or species inter-conversion.[5,6]

13.2.6 The volatile species of mercury (0) and dimethyl mercury partition to sample bottle headspace. The volatile forms of mercury can be lost from sample containers when they are opened, lost from aliquots that are removed from the containers, and lost in aliquot processing steps prior to element detection.

13.2.7 Contamination from improper sample containers should be guarded against. In general, the sample containers for mercury analysis should not be reused unless specially cleaned and tested as a blank prior to sampling. Uncoated metal containers shall not be used for any sampling step. Stainless steel containers may be used but must be cleaned and rinsed with a mild acid rinse and thoroughly dried before use. Epoxy-lined steel containers may also be used, and are preferred for larger volume (>1 L).

13.2.8 For further discussion on storage and analysis of crude oils for mercury, see Practice D7482.

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[5] Robertson, D. E., *Analytical Chemistry*, Vol 40, 1968, p. 1067.

[6] Bloom, N. S., "Analysis and Stability of Mercury Speciation in Petroleum Hydrocarbons," *Analytical Chemistry*, Fresenius, J., ed., Vol 366, 2000, pp. 438-443.

13.2.9 Methods based on cold vapor atomic absorption spectrometry for determination of mercury in crude oils are available in Test Methods D7622 and D7623.

14. Special Issues

14.1 In the atomic spectroscopic methods it has been shown that the viscosity index (VI) improvers added to lubricating oils give low results when calibrations are performed using standards that do not contain VI improvers.[7] Examples of test methods requiring such considerations in sample preparation include Test Methods D4628 AAS determination of additive elements in lubricating oils; Test Methods D4951, D5185, and D7040 for determination of additive elements in lubricating oils; D5600 for elements in coke; and D7111 for trace elements in mid-distillate fuels, all by ICP-AES.

14.2 To overcome this interference, the standards need to be matched with samples in their VI improver content, if available in analyte-free form and of the same type VI improver as the one being used in the sample, or using the specified solvent-to-sample dilution and an internal standard (IS) such as metal sulfonates of beryllium, cadmium, cobalt (most commonly used), lanthanum, lead, manganese, or silver.

14.2.1 The internal standard shall be added in a stable form to the sample matrix; it should pose no spectral interferences for analyte(s) lines used; should not react or precipitate with the sample matrix or analyte; and must ideally not be present in any of the samples being analyzed or if present, should be at much less than the doping level used (a maximum <1 % of dopant level).

14.3 *Viscosity Effects*—Differences in the viscosities of test specimen solutions and standard solutions can cause differences in the sample uptake rate in ICP-AES measurements. These differences can adversely affect the accuracy of the analysis. The effects can be reduced by using a peristaltic pump to deliver solutions to the nebulizer or by the use of internal standardization, or both. When severe viscosity effects are observed, the test specimen and the standard should be diluted with appropriate solvent to up to twentyfold.

14.4 In several XRF test methods, an internal standard is added to the sample to compensate for the interelement effects of X-ray excitation and fluorescence so that the analytical line is subjected to matrix effects of similar magnitude as the analyte's radiation; thereby rendering the need for interelement correction (other than by using the internal standard) unnecessary. The use of internal standard is to avoid having to use more complicated methods for interelement corrections.. If the interelement correction for the element is not employed, the results can be low due to absorption, or high due to enhancement.

14.4.1 These samples need to be well blended with the added internal standards such as organic sulfonates of nickel, lead, tin, titanium, or zirconium. Examples of such use include Test Method D4927 for additive elements in lubricating oils.

14.5 One needs to consider how small a sample can be taken and still remain a representative of the bulk sample. For example because of the very low detection limits of ICP-AES test methods (such as Test Methods D4951, D5185, etc.) only a few drops of oil sample are necessary for analysis. Even if the weight dilution is accurate using a 3 or 4 place balance, the elemental composition of each drop may not. Thus, if small sample sizes (perhaps < 10 drops) are used, the analyst needs to confirm through multiple measurements that the small sample sizes are giving repeatable results consistent with the precision stated in the test method.

14.6 *End Measurements*—Protocols for spectroscopic measurements for elemental analysis are given in Practice D7260 (ICP-AES), Practice D7343 (XRF), and Practice D7740 (AAS).

15. Keywords

15.1 acid decomposition; ash; atomic absorption spectrometry; bomb combustion; ED-XRF; ICP-AES; lubricants; microwave heating; petroleum products; SASH; sample preparation; WD-XRF

SUMMARY OF CHANGES

Subcommittee D02.03 has identified the location of selected changes to this standard since the last issue (D7455 – 08) that may impact the use of this standard. (Approved May 1, 2014.)

(1) Added new references to subsection 2.1.
(2) Added information about these added standards throughout the practice.

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[7] Bansal, J. G., and McElroy, F. C., "Accurate Elemental Analysis of Multigrade Lubricating Oils by ICP Method: Effect of Viscosity Modifiers," *SAE Technical Paper Series 932694*, SAE, Warrendale, PA.

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