



Designation: D 5184 – 00

Standard Test Methods for Determination of Aluminum and Silicon in Fuel Oils by Ashing, Fusion, Inductively Coupled Plasma Atomic Emission Spectrometry, and Atomic Absorption Spectrometry¹

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1. Scope

1.1 These test methods cover the determination of aluminum and silicon in fuel oils at concentrations between 5 and 150 mg/kg for aluminum and 10 and 250 mg/kg for silicon.

1.2 *Test Method A*—Inductively coupled plasma atomic emission spectrometry is used in this test method to quantitatively determine aluminum and silicon.

1.3 *Test Method B*—Flame atomic absorption spectrometry is used in this test method to quantitatively determine aluminum and silicon.

1.4 The values given in SI (metric) units are to be regarded as the standard.

1.5 *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.* Specific precautionary statements are given in 10.1 and 11.5.

2. Referenced Documents

2.1 ASTM Standards:

D 1193 Specification for Reagent Water²

D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products³

D 4177 Practice for Automatic Sampling of Petroleum and Petroleum Products³

D 6299 Practice for Applying Statistical Quality Assurance Techniques to Evaluate Analytical Measurement System Performance⁴

E 135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials⁵

¹ These test methods are under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and are the direct responsibility of Subcommittee D02.03.0B on Spectrometric Methods.

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² *Annual Book of ASTM Standards*, Vol 11.01.

³ *Annual Book of ASTM Standards*, Vol 05.02.

⁴ *Annual Book of ASTM Standards*, Vol 05.04.

⁵ *Annual Book of ASTM Standards*, Vol 03.05.

3. Terminology

3.1 Definition:

3.1.1 *emission spectroscopy*—Refer to Terminology E 135.

3.2 Definitions of Terms Specific to This Standard:

3.2.1 *calibration*—the process by which the relationship between signal intensity and elemental concentration is determined for a specific element analysis.

3.2.2 *check standard*—in calibration, an artifact measured periodically, the results of which typically are plotted on a control chart to evaluate the measurement process.

4. Summary of Test Methods

4.1 A weighed quantity of homogenized sample is heated in a clean platinum dish, the combustible material is removed by burning and the carbon finally removed by heating in a muffle furnace at a temperature of $550 \pm 25^\circ\text{C}$. The residue is fused with a lithium tetraborate/lithium fluoride flux. The fused mixture is digested in a solution of tartaric acid and hydrochloric acid and diluted to volume with water. The resulting solution is aspirated into an inductively-coupled plasma and the emission intensities of aluminum and silicon lines are measured. Standard calibration solutions are also aspirated and aluminum and silicon intensities are measured for comparison. Alternatively, the resulting solution is aspirated into the flame of an atomic absorption spectrometer and the absorptions of the resonance radiation of aluminum and silicon are measured. Standard calibration solutions are also aspirated and aluminum and silicon absorption intensities are measured for comparison.

5. Significance and Use

5.1 Catalyst fines in fuel oils can cause abnormal engine wear. These test methods provide a means of determining silicon and aluminum, the major constituents of the catalysts.

6. Apparatus

6.1 *Balance*, capable of weighing to 0.1 g, capacity of 150 g.

6.2 Choice of Instrument:

6.2.1 *Inductively-Coupled Plasma Atomic Emission*

Spectrometer—Either a sequential or simultaneous spectrometer is suitable, if equipped with an ICP torch and RF generator to form and sustain the plasma.

6.2.2 *Atomic Absorption Spectrometer*—A suitable instrument will consist of modulated hollow cathode lamps or other sources of resonance radiation of aluminum and silicon, a nitrous oxide/acetylene burner, and a spectrometer with a suitable detection and read-out system.

6.3 *Homogenizer*, non-aerating, high-speed shear mixer to homogenize the sample.

NOTE 1—Ultrasonic bath and ultrasonic probe type homogenizers were not evaluated in the development of these test methods.

6.4 *Electric Muffle Furnace*, capable of being maintained at temperatures of $550 \pm 25^\circ\text{C}$ and $925 \pm 25^\circ\text{C}$. The furnace preferably having suitable apertures at front and rear to allow a slow, natural draft of air to pass through.

6.5 *Electric Hot Plate*, with or without magnetic stirring capability.

6.6 *Electric Oven*, maintained at a temperature of 50 to 60°C .

6.7 *Graduated Cylinders*, 10, 25, 50 and 100 mL.

6.8 *Pipettes*, 1, 2, 5, 10, 20 and 25 mL.

6.9 *Platinum Dish*, 100 mL capacity, cleaned with fused potassium hydrogen sulfate.

6.10 *Volumetric Flasks*, 100 and 1000 mL.

6.11 All glassware must be carefully cleaned with 1 + 1 hydrochloric acid and rinsed thoroughly with water to minimize contamination. The use of chromic acid cleaning solution is not recommended.

6.12 Zirconium crucible with close fitting zirconium lid, 30 to 50 mL capacity.

7. Reagents

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.⁶ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 *Purity of Water*—Unless otherwise indicated, reference to water shall be understood to mean reagent water conforming to Type II of Specification D 1193.

7.3 *Flux*—Mixture of 90 % lithium tetraborate and 10 % lithium fluoride.

NOTE 2—Lithium fluoride is necessary to prevent heavy metal corrosion of the platinum dish and to lower the fusion temperature.

7.4 *Hydrochloric acid* (36 % (m/m))—concentrated hydrochloric acid.

7.5 *Potassium Hydrogen Sulfate*, fused solid.

⁶ *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

7.6 *2-Propanol (Isopropyl Alcohol)* (**Warning**—Flammable; can be explosive when evaporated to or near dryness.)

7.7 *Aqueous Standard Solutions*.

7.7.1 *Aluminum Standard Solutions*—Obtain a ready made, aqueous standard or prepare a standard from aluminum wire.

7.7.1.1 *Aluminum Solution* (1000 mg/L)—Aqueous, ready made commercial standard.

7.7.1.2 *Aluminum Solution* (1000 mg/L)—Dissolve 1.000 ± 0.005 g of aluminum metal (wire form, 99.99 % purity) in 50 mL of concentrated hydrochloric acid. Heat gently. Cool and transfer the solution to 1000 mL volumetric flask. Dilute to the mark with water.

7.7.2 *Silicon Standard Solutions*—Obtain a ready made, aqueous standard or prepare a standard from silicon dioxide.

7.7.2.1 *Silicon Solution* (1000 mg/L)—Aqueous, ready made commercial standard.

7.7.2.2 *Silicon Solution* (1000 mg/L)—Using a zirconium crucible with a close fitting lid, fuse 2.140 ± 0.0107 g of silicon dioxide (99.99 % purity) with 8 g of sodium hydroxide until a clear melt is obtained. Cool and dissolve the melt in 100 mL of a solution of 1 part hydrochloric acid by volume and 2 parts water by volume. Transfer this solution to a 1000 mL volumetric flask and dilute to the mark with water. Immediately, transfer the contents of the flask to a plastic bottle.

7.8 *Tartaric Acid/Hydrochloric Acid Solution*—Dissolve 5 g of tartaric acid in about 500 mL of water acidified with 40 mL of concentrated hydrochloric acid and dilute to 1000 mL with water.

7.9 *Toluene/2-Propanol Solution* (1 + 1)—Mix one volume of toluene with one volume of 2-propanol.

7.10 *Quality Control (QC) Samples*, preferably are portions of one or more liquid petroleum materials that are stable and representative of the samples of interest. These QC samples can be used to check the validity of the testing process as described in Section 18.

8. Quality Control (QC) Sample Preparation

8.1 Preparation of QC Samples shall follow the same protocol as defined for the test specimen (Sections 9, 10 and 11).

9. Sampling

9.1 The objective of sampling is to obtain a sample for testing purposes that is representative of the entire quantity. Thus, take samples in accordance with the instructions in Practice D 4057 or D 4177. Typically, a gallon size container filled to approximately three-fourths of capacity is satisfactory.

10. Sample Handling

10.1 *Homogenization*—It is extremely important to homogenize the fuel oil in the sample container in order to obtain a representative specimen. (**Warning**—Failure to use this homogenization procedure can invalidate the results because non-representative aliquots could be obtained and this could lead to erroneous results.)

10.2 Place the sample container in an oven at a temperature of 50 to 60°C . Keep the container in the oven until the sample comes to temperature. Insert the shaft of a high speed homogenizer into the sample container so that the head of the shaft is

immersed to approximately 5 mm from the bottom of the sample vessel. Mix the sample for about 5 min.

11. Specimen Preparation

11.1 Weigh a clean platinum dish to the nearest 0.1 g. Immediately transfer up to 50 g (but not less than 20 g) of the well-mixed sample, preferably containing about 1.3 mg aluminum, to the platinum dish and re-weigh the dish and contents to the nearest 0.1 g to obtain the weight of the specimen.

NOTE 3—The specimen mass proposed, based on the aluminum content will suffice for silicon as both elements are usually found in fuel oils at similar concentrations.

11.2 Warm the dish and contents gently with a bunsen flame until the sample can be ignited. Maintain the contents of the basin at a temperature such that most of the combustible material is removed and only carbon and ash remain.

NOTE 4—If the specimen contains considerable amounts of moisture, foaming and frothing can cause loss of material. If this is the case, discard the specimen and to a fresh portion add 1 to 2 mL of 2-propanol before heating. If this is not satisfactory, add 10 mL of a mixture of equal parts of toluene and 2-propanol and mix thoroughly. Place several strips of ashless filter paper in the mixture and warm gently. When the paper begins to burn, the greater part of the water will have been removed.

11.3 Place the dish and contents in a muffle furnace maintained at a temperature of $550 \pm 25^\circ\text{C}$. Maintain the muffle furnace at this temperature until all the carbon is removed and only ash remains. This may require more than 10 h in the muffle furnace and may conveniently be done overnight.

11.4 Cool the dish to room temperature, add 0.4 g of flux and mix with the ash. Place the dish in a muffle furnace maintained at a temperature of $925 \pm 25^\circ\text{C}$ for 5 min. Remove the dish and ensure contact of the flux with the ash. Replace the dish in the muffle furnace and maintain at a temperature of $925 \pm 25^\circ\text{C}$ for 10 min.

11.5 Remove the dish, cool the fusion melt to room temperature and add 50 mL of the tartaric acid/hydrochloric acid solution. Place the dish and contents on the hot plate maintained at a temperature of approximately 80°C . Heat until the melt is dissolved. (**Warning**—Vaporization of a significant amount of the liquid can lead to precipitation of an insoluble form of silica leading to erroneous results.)

NOTE 5—Prolonged heating can be necessary to dissolve the melt completely and obtain a solution. Agitation or the use of magnetic stirring can be employed to speed dissolution of the melt.

11.6 Allow the solution to cool and then transfer it to a 100 mL flask with water, washing the dish several times to ensure transfer is complete. Make up to the mark with water. Then, transfer the solution to a plastic bottle.

NOTE 6—Transferring the test solution to a plastic bottle is desirable because the dilute acid solution contains fluoboric acid from dissolution of the flux. Storage tests have shown that there is no significant attack of glassware in the short term (up to one week), and that the solution does not contain fluoride ion above the 5 mg/L concentration.

12. Preparation of Calibration Solutions

12.1 *Blank Solution*—Prepare a blank solution containing only 0.4 g flux and 50 mL of the tartaric acid/hydrochloric acid solution diluted to 100 mL. Transfer it to a plastic bottle.

12.2 *Aluminum*—Prepare a 250 mg/L aluminum working solution by diluting 25 mL of the 1000 mg/L standard solution to 100 mL with water. To each of four clean 100 mL volumetric flasks, add 0.4 g of flux and 50 mL of the tartaric acid/hydrochloric acid solution. To successive flasks add 2, 4, 10 and 20 mL of the 250 mg/L aluminum working solution and dilute to 100 mL with water. The calibration solutions contain 5, 10, 25 and 50 mg/L of aluminum, respectively.

12.3 *Silicon*—Prepare a 250 mg/L silicon working solution by diluting 25 mL of 1000 mg/L standard solution to 100 mL with water. To each of four clean 100 mL volumetric flasks, add 0.4 g of flux and 50 mL of the tartaric acid/hydrochloric acid solution. To successive flasks, add 2, 4, 10 and 20 mL of the 250 mg/L silicon working solution and dilute to 100 mL with water. These calibration solutions contain 5, 10, 25 and 50 mg/L of silicon, respectively.

12.4 Transfer all calibration standards to plastic bottles.

NOTE 7—When both aluminum and silicon are being determined, the 5 to 50 mg/L calibration solutions can be combined providing there are no incompatibility problems caused by the reagents used in the preparation of the standard solutions described in 7.7.1 and 7.7.2.

TEST METHOD A—INDUCTIVELY-COUPLED PLASMA ATOMIC EMISSION SPECTROMETRY

13. Preparation of ICP Instrument

13.1 *Instrument*—Consult the manufacturer's instructions for the operation of the instrument. Design differences between instruments, ICP excitation sources, and different selected analytical wavelengths for individual spectrometers make it impractical to specify the required manipulations in detail.

13.2 *Peristaltic Pump*—If using a peristaltic pump, inspect the pump tubing and replace it, if necessary, before starting each day. Verify the solution uptake rate and adjust it to the desired rate.

13.3 *ICP Excitation Source*—Ignite the ICP excitation source at least 30 min before performing an analysis. During this warm-up period, nebulize water.

NOTE 8—Some manufacturers recommend even longer warmup periods to minimize the variability of the measurements.

13.4 *Wavelength Profiling*—Perform any wavelength profiling that may be called for in the normal operation of the instrument.

13.5 *Operation Parameters*—Assign the appropriate operating parameters to the instrument task file so that the desired elements can be determined. Parameters to be included are element, wavelength, background correction points (optional), interelement correction factors (optional), integration time and three consecutive integrations.

14. ICP Calibration

14.1 Perform a five point calibration consisting of the blank and calibration standards at the beginning of analysis of each batch of specimens. Use the check standard to determine if each element is in calibration. If the result obtained on the check standard is outside 5 % of the expected value for any element, make any adjustments to the instrument that may be necessary and repeat the calibration.

14.2 Alternatively, perform a two point calibration with the