Designation: D1318 − 16

Standard Test Method for
Sodium in Residual Fuel Oil (Flame Photometric Method)[1]

1. Scope*

1.1 This test method covers the determination of sodium in residual fuel oil by means of a flame photometer. Its precision in low ranges limits its application to samples containing more than 15 mg/kg sodium. Other elements commonly found in residual fuel oil do not interfere.

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

1.3 *This standard does not purport to address all of the safety problems 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.* For specific hazard statements see 6.3, 6.5, 6.7, 8.2, 6.8, 6.9, and Note 3.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1193 Specification for Reagent Water
D4057 Practice for Manual Sampling of Petroleum and Petroleum Products
D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products
D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance

3. Summary of Test Method

3.1 A weighed sample is reduced to a carbonaceous ash under controlled conditions. The residual carbon is removed by heating in a muffle furnace at 550 °C. The ash is dissolved, diluted to volume, and the sodium determined by means of a flame photometer.

4. Significance and Use

4.1 Excessive amounts of sodium can indicate the presence of materials that cause high wear of burner pumps and valves, and contribute to deposits of boiler heating surfaces.

5. Apparatus

5.1 *Flame Photometer,* capable of isolating the sodium doublet at 589 nm and stable enough to give repeatable measurements that do not vary more than 5 % of their mean in the 2 mg/kg to 20 mg/kg range of sodium.

5.2 *Platinum Dish,* 100 mL capacity, approximately 35 mm in depth.

5.3 *Electric Muffle Furnace,* capable of operating over a variable range from 200 °C to 600 °C and of maintaining a temperature of 550 °C ± 50 °C.

6. Reagents and Materials

6.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[3] Other grades can 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.

6.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type II or III of Specification D1193.

6.3 *Hydrochloric Acid* (sp gr 1.19)—Concentrated hydrochloric acid (HCl). (**Warning—**Poison. Causes severe burns. Harmful or fatal if swallowed or inhaled.)

6.4 *Hydrochloric Acid* (1+9)—Mix 1 volume of HCl (sp gr 1.19) with 9 volumes of water.

6.5 *Hydrofluoric Acid* (48 %)—Concentrated hydrofluoric acid (HF). (**Warning—**Poison. Causes severe burns. Harmful or fatal if swallowed or inhaled.)

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

Current edition approved July 1, 2016. Published July 2016. Originally approved in 1954. Last previous edition approved in 2011 as D1318 – 00 (2011). DOI: 10.1520/D1318-16.

[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] *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.

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

6.6 *Sodium Solution, Standard* (1000 mg Na/L)—Dissolve 3.088 g ± 0.005 g of dried sodium sulfate (Na_2SO_4) in water and dilute to 1 L in a volumetric flask. Store in a polyethylene bottle.

6.7 *Sulfuric Acid* (1+1)—Carefully add, while stirring, 1 volume of concentrated sulfuric acid (H_2SO_4, sp gr 1.84) to 1 volume of water. (**Warning—**Poison. Causes severe burns. Harmful or fatal if swallowed or inhaled.)

6.8 *Ethyl Alcohol,* C_2H_6O, 95 % reagent grade. (**Warning—**Flammable.)

6.9 *2-Propanol,* C_3H_8O, 99 % reagent grade (**Warning—**Flammable.)

7. Sampling

7.1 Sampling shall be done in accordance with Practices D4057 or Test Method D4177.

7.2 Use a clear, clean glass pint bottle, previously rinsed twice with HCl (1+9) and once with water and allowed to dry, for sampling the bulk material or plant streams. Obtain a representative sample but do not fill the bottle more than about two-thirds full. Warm viscous samples until they can be mixed readily. Stir up any material that has settled out and shake the sample for 3 min just prior to weighing it out.

7.3 Optimum sample size for most instruments is that which contains from 0.5 mg to 1.0 mg of sodium. Estimate the sample size as follows (see Note 1):

$$\text{Sample size, g} = 750/\text{estimated sodium content, mg/kg} \quad (1)$$

NOTE 1—An estimate of the maximum amount of sodium in a sample can be obtained from its ash value. For example, an ash of 0.01 % would undoubtedly have less than 0.005 % sodium (50 ppm). If there is no estimate as to the probable sodium range in a sample, it is more expedient to weigh out a large amount, for example 60 g, because the test method provides for dilution of sample solutions that are more concentrated than the standards.

8. Calibration

8.1 Dilute the sodium solution (1000 mg Na⁄L) so as to obtain solutions containing 2 mg⁄L, 4 mg⁄L, 6 mg⁄L, 8 mg⁄L, 10 mg⁄L, 12 mg⁄L, 15 mg⁄L, 18 mg⁄L, and 20 mg⁄L (approximately equivalent to mg/kg). Store all dilute sodium solutions in polyethylene bottles.

8.2 Prepare the flame photometer for use as described in the manufacturer's instruction manual. Carefully adjust the pressure of the gases (**Warning—**Dangerous.) used for flame combustion in the order described by the manufacturer until optimum control is achieved. Select a standard approximately in the middle of the optimum range of the instrument being used. While atomizing this medium-range standard, adjust the wavelength selector to the greatest response for the sodium doublet at about 589 nm and adjust all controls of the instrument to optimum performance. Finally, adjust the sensitivity control to give a proper scale reading.

8.3 Atomize each of the standard solutions and record the scale response for each. Run repeat checks on the medium-range standard selected in 6.2 after each of these standards to determine whether the flame photometer is functioning properly. Make the indicated adjustments, if required, and rerun the standards.

8.4 Prepare a working curve by plotting the milligrams of sodium per litre against the scale readings.

9. Procedure

9.1 *Preparation of Sample:*

9.1.1 Weigh into a thoroughly clean, dry 100 mL platinum dish the appropriate size sample (7.3) with an accuracy of at least 1 part per 100 parts of sample (Note 2). Samples larger than 75 g require a second filling of the platinum dish; for such samples, obtain the sample weight from the difference between the initial and final weights of the sample bottle. Place the platinum dish containing the fuel oil on a silica triangle properly supported, and heat with a bunsen burner until the contents ignite and burn readily (Note 3). Continue heating with the burner in such a manner that the sample burns at a uniform and moderate rate and only ash and carbon remain after burning ceases. For samples larger than 75 g, cool the dish and fill it approximately two-thirds full with additional well-shaken sample, and burn as above.

NOTE 2—Handle the platinum dish only with platinum-tip tongs and do not touch it with the fingers during the test. Carefully dust the bottom of the dish with a clean camel-hair brush before each weighing.

NOTE 3—If sample contains an appreciable amount of water, as indicated by spattering when heated, add a few millilitres of ethyl-alcohol (95 %) (**Warning—**Flammable) or isopropyl alcohol (99 %) (**Warning—**Flammable) before heating. Include the alcohol in the blank determination.

9.1.2 Place the dish in a muffle furnace at no more than 200 °C (Note 3). Slowly raise the temperature to 550 °C ± 50 °C. Leave the muffle door slightly ajar until only a little carbon remains in the dish; then close the door and continue the ignition until no carbon is visible.

NOTE 4—The platinum dishes should be placed on silica plates or silica triangles on the floor of the muffle furnace. Particular care must be exercised to avoid contamination of the sample with particles from the roof, walls, and the door of the furnace. During the initial ignition, the opening of the muffle door must be carefully adjusted so that the air flow into the muffle is not excessive. Too great an air flow causes high temperatures in the burning carbon and also possible loss of ash from the dish.

9.1.3 Cool the dish to room temperature, add 1 mL of H_2SO_4 (1+1) and about 1 mL of HF to the platinum dish (Note 5), evaporate to dryness under a hood, and replace the dish in the muffle furnace at 550 °C ± 50 °C for 15 min.

NOTE 5—Unless the silica is removed, low values will result from the occlusion of sodium in the insoluble residue.

9.1.4 Cool the platinum dish, wash down its sides with about 10 mL of water and, by means of a dropper, add 2 drops of H_2SO_4 (1+1). Heat the dish on a steam bath, to effect the solution of the sodium salts, until approximately 1 mL of liquid remains. Remove from the steam bath, add 5 mL to 10 mL of water, and filter the solution through an acid-washed filter paper or an acid-washed, sintered-glass filter into a 100 mL volumetric flask. Wash the dish and filter with water, collecting the wash water in the volumetric flask. Dilute to 100 mL with water and mix. If the ashed sample is known to contain less than 0.5 mg of sodium, make a proportionately smaller dilution to obtain 5 mg to 10 mg of sodium per litre in the final solution.

9.2 *Photometric Measurement:*

9.2.1 Put the flame photometer into operation, using the identical burner and instrument settings that were determined during calibration in accordance with 8.2. Vaporize the medium-range standard solution (8.2) and adjust the sensitivity control to give the same scale reading that was obtained when the calibration curve was prepared.

9.2.2 Atomize a portion of the sample solution prepared in 9.1.4 in the flame photometer. If it is in the optimum range for the instrument in use, proceed as directed in 9.2.3. If it is too concentrated, place a few millilitres in a graduated cylinder, dilute to a known volume with water, and atomize. If necessary, repeat this operation to determine the correct dilution. When this is established, make the proper accurate dilution by pipetting an aliquot from the original 100 mL volumetric flask into another volumetric flask and dilute to the mark with water.

9.2.3 Atomize the properly diluted sample solution, record the scale reading, and obtain the sodium concentration in milligrams per litre by reference to the standard curve prepared in 8.4. Also atomize standards just lower and higher than the unknown to check the validity of the calibration curve.

9.2.4 Perform a blank determination on all of the reagents, including the water, in accordance with the procedure just described.

10. Quality Control

10.1 Confirm the performance of the test procedure by analyzing a quality control sample that is stable and representative of the sample of interest.

10.1.1 When the quality control/quality assurance protocols are already established in the testing facility, these may be used to confirm the reliability of the test results.

10.1.2 When there is no quality control/quality assurance protocol established in the testing facility, Appendix X1 can be used to perform this function.

11. Calculation and Report

11.1 Calculate the sodium concentration, in parts per million as follows:

$$\text{Sodium, mg in sample} = \left[(A - B) \times CE \right] / 1000D \tag{2}$$

$$\text{Sodium, mg/kg} = (\text{mg of sodium} \times 1000) / W$$

where:

A = sodium concentration of the sample solution, mg/L,
B = sodium concentration in the reagent blank, mg/L,
C = volume to which ashed sample was originally diluted, mL,
D = volume of aliquot taken from original dilution, mL
E = volume to which aliquot D was diluted, mL and
W = weight of sample used, g,

11.2 Report the results to the nearest 1 mg/kg.

12. Precision and Bias

12.1 *Precision*—The following criteria should be used for judging the acceptability of results (95 % confidence):

12.1.1 *Repeatability*—The difference between successive test results, obtained by the same operator with the same apparatus under constant operating conditions on identical test material, would, in the long run in the normal and correct operation of the test method, exceed the following values only in one case in twenty:

Sodium, mg/kg	Repeatability, mg/kg
15 to 40	4
40 to 85	6

12.1.2 *Reproducibility*—The difference between two single and independent results, obtained by different operators working in different laboratories on identical test material, would, in the long run in the normal and correct operation of the test method, exceed the following values only in one case in twenty:

Sodium, ppm	Reproducibility, ppm
15 to 25	9
25 to 50	15
50 to 90	23

12.2 *Bias*—Since there is no accepted reference material suitable for determining the bias for the procedure in this test method, no statement on bias is being made.

APPENDIX

(Nonmandatory Information)

X1. QUALITY CONTROL MONITORING

X1.1 Confirm the performance of the instrument or the test procedure by analyzing quality control (QC) sample(s).

X1.2 Prior to monitoring the measurement process, the user of the method needs to determine the average value and control limits of the QC sample.

X1.3 Record the QC results and analyze by control charts or other statistically equivalent techniques to ascertain the statistical control status of the total testing process. See Practice D6299. See Note X1.1. See ASTM MNL 7.[4] Investigate any out-of-control data for root cause(s). The results of this investigation may, but not necessarily, result in instrument recalibration.

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[4] *Manual on Presentation of Data Control Chart Analysis*, ASTM MNL 7, 6th Ed, Section 3.

NOTE X1.1—In the absence of explicit requirements given in the test method, this clause provides a recommendation to the testing facility in quality control and quality assurance of the analyses.

X1.4 The frequency of QC testing is dependent on the criticality of the quality being measured, the demonstrated stability of the testing process, and customer requirements. Generally, a QC sample should be analyzed each testing day with routine samples. The QC frequency should be increased if a large number of samples are routinely analyzed. However, when it is demonstrated that the testing is under statistical control, the QC testing frequency may be reduced. The QC sample testing precision should be periodically checked against the ASTM method precision to ensure data quality. See Practice D6299 and ASTM MNL 7.[4]

X1.5 It is recommended that, if possible, the type of QC sample that is regularly tested be representative of the material routinely analyzed. An ample supply of QC sample material should be available for the intended period of use, and must be homogenous and stable under the anticipated storage conditions.

X1.6 See Practice D6299 and ASTM MNL 7[4] for further guidance on QC and Control Charting techniques. (See Note X1.1.)

SUMMARY OF CHANGES

Subcommittee D02.03 has identified the location of selected changes to this standard since the last issue (D1318 – 00 (2011)) that may impact the use of this standard. (Approved July 1, 2016.)

(1) Added Practice D6299 to Referenced Documents.
(2) Added new reagents in subsections 6.8 and 6.9.
(3) Added a quality control section in Section 11 and Appendix X1.