INTERNATIONAL

Designation: ~~D5056 – 04 (Reapproved 2010)~~ D5056 – 15

Standard Test Method for Trace Metals in Petroleum Coke by Atomic Absorption[1]

This standard is issued under the fixed designation D5056; 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~~ Scope*

1.1 This test method covers the analysis for the commonly determined trace metals (aluminum, calcium, iron, nickel, silicon, sodium, and vanadium) in laboratory analysis samples of raw and calcined petroleum coke by atomic absorption spectroscopy.

1.2 The elemental concentration ranges for which this test method is applicable and the limits of detection of this test method are listed in Table 1.

1.3 The values stated in SI units are to be regarded as the standard.

1.4 *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.* For warning statements, see Sections 8 – 10.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D346 Practice for Collection and Preparation of Coke Samples for Laboratory Analysis

D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance

D1193 Specification for Reagent Water

3. Summary of Test Method

3.1 A representative sample of the petroleum coke is ashed at ~~525°C~~525 °C under specified conditions. The ash is fused with lithium tetraborate ($Li_2B_4O_7$), or lithium metaborate ($LiBO_3$). The melt is dissolved in dilute hydrochloric acid (HCl), and the resultant solution is analyzed by atomic absorption spectroscopy for the following elements: aluminum, calcium, iron, nickel, silicon, sodium, and vanadium.

4. Significance and Use

4.1 The presence and concentration of various metallic elements in a petroleum coke are major factors in the suitability of the coke for various uses. This test method provides a means of measuring the amounts of those metallic elements in the coke sample.

4.2 The concentration of these elements is one factor in determining the economic value of the coke. Coke used for production of electrodes will have different specification requirements dependent on what service the electrodes will be used in. Generally the fuel cokes are highest in metallic element concentration and have the least economic value.

4.3 The test method provides a standard procedure for use by the purchaser and seller in the commercial transfer of petroleum coke to determine whether the lot of coke meets the specifications of the purchasing party.

5. Interferences

5.1 Spectral interferences can occur when using other than the recommended wavelength for analysis or when using multi-elemental hollow cathode lamps.

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

Current edition approved ~~May 1, 2010~~June 1, 2015. Published ~~May 2010~~June 2015. Originally approved in 1990. Last previous edition approved in ~~2004~~2010 as ~~D5056~~D5056 – 04 (2010).~~–04.~~ DOI: ~~10.1520/D5056-04R10.~~10.1520/D5056-15.

[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.

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

TABLE 1 Applicable Concentration Ranges and Limits of Detection on a Dried Original Sample Basis

Element	Concentration Range (mg/kg)	Limit Detection (mg/kg)
Aluminum	15 to 105	5.0
Calcium	20 to 225	1.0
Iron	150 to 500	1.5
Nickel	5 to 200	1.5
Silicon	90 to 420	20
Sodium	15 to 115	0.2
Vanadium	5 to 500	2.0

6. Apparatus

6.1 *Furnace,* electric, capable of regulation of temperature at ~~525°C~~525 °C ± ~~10°C.~~10 °C.

6.2 *Magnetic Stirring Hot Plate.*

6.3 *Platinum Dish,* ~~50~~50 mL to ~~58-mL~~58 mL capacity.

6.4 *Platinum Dish,* ~~150~~150 mL to ~~200-mL~~200 mL capacity.

6.5 *Platinum-Tipped Tongs.*

6.6 *Furnace,* electric, capable of regulation of temperature at ~~950~~950 °C ± ~~10°C~~10 °C or a Meker type forced air burner.

6.7 *Atomic Absorption Spectrophotometer (AAS),* equipped as follows:

6.7.1 *Background Correction,* using either a deuterium (D_2) arc background corrector or other comparable simultaneous background correction system.

6.7.2 *Burner Head,* capable of supporting a nitrous oxide-acetylene flame.

6.7.3 *Burner Head,* single or multiple-slot, capable of supporting an air-acetylene flame.

6.7.4 *Hollow Cathode Lamps,* one for each of the elements to be analyzed: aluminum, calcium, iron, nickel, silicon, sodium, and vanadium.

NOTE 1—Multi-elemental lamps can also be used; however, spectral interferences are possible (see 5.1).

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 shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.[3] 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, references to water shall be understood to mean reagent water as defined by Type II of Specification D1193.

7.3 *Hydrochloric Acid, Solution 1,* 20 % by volume ~~(20 mL~~ (20 mL of concentrated HCl diluted to ~~100 mL~~ 100 mL with Type II reagent water).

7.4 *Lanthanum Additive, Solution 2,* ~~100~~100 g/ ~~g/L~~ L lanthanum (dissolve ~~175 g~~ 175 g $LaCl_3$ in water and dilute to ~~1 L~~ 1 L with water).

7.5 *Lanthanum Chloride* ($LaCl_3$) *powder* (high purity).

7.6 *Lithium Tetraborate* ($Li_2B_4O_7$), *powder* (high purity), or *Lithium Metaborate* (LiBO3), *powder* (high purity).

7.7 *Standard and Sample Dilution Additive, Solution 3*—Weigh ~~40.0 g,~~ 40.0 g, to the nearest ~~0.1 g,~~ 0.1 g, of $Li_2B_4O_7$ into a ~~150~~150 mL to ~~200 mL~~ 200 mL platinum dish, fuse with a Meker type burner to form a liquid, and cool. Alternatively, heat in a furnace at ~~950~~950 °C ± ~~10°C~~10 °C for ~~10 min~~ 10 min or until a liquid forms. Place the cooled platinum dish containing the fused recrystallized $Li_2B_4O_7$, and a magnetic stirring bar into a ~~2-L~~2 L beaker. Add ~~1000 mL~~ 1000 mL of Solution 1 (20 % HCl). Heat and stir the solution on a magnetic stirring hot plate until the melt completely dissolves. After dissolution, remove the platinum dish with a glass rod. Rinse the platinum dish and glass rod with water into the lithium borate solution. Immediately transfer the warm solution quantitatively to a ~~2-L~~2 L flask. To avoid crystallization add about ~~100 mL~~ 100 mL of water; stir the solution and cool to room temperature. Add ~~400 mL~~ 400 mL of Solution 2 (lanthanum additive) and mix. Dilute to ~~2000 mL~~ 2000 mL with water, mix thoroughly, and vacuum filter the entire solution through Dow filter paper.

[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 *Annual 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.

NOTE 2—Fifty millilitres of Solution 3 contains ~~1 g~~ 1 g $Li_2B_4O_7$, ~~25 mL~~ 25 mL of Solution 1, 20 % HCl, and ~~10 mL~~ 10 mL of Solution 2, lanthanum additive.

7.8 *Standard Stock Solutions*—Prepare standard stock solutions from high purity (99.9 % or better) metals, oxides, or salts. Stock solutions of ~~1000 ppm~~1000 ppm (mg/~~ (mg/L)~~ L) for each metal are needed for preparation of dilute standards in the range from ~~<1.0~~<1.0 ppm to ~~50 ppm~~ 50 ppm (mg/L). Working standards containing aluminum, calcium, iron, nickel, silicon, sodium, and vanadium in concentration ranges below ~~10 ppm~~ 10 ppm (mg/kg) are to be prepared daily to ensure stability.

7.9 *Quality Control (QC) Samples,* preferably are portions of one or more petroleum coke samples 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 13.

NOTE 3—Commercially available standards and other reagent solutions may be used in place of laboratory preparations.

8. Sample Preparation

8.1 Crush and divide the initial sample to obtain a laboratory analysis sample. Crush to pass a No. 60 ~~(0.250 mm)~~ (0.250 mm) sieve by the procedure in Practice D346, Section 10 on Preparation of Coke Sample for Laboratory Analysis.

8.2 Crush approximately a ~~30 g~~ 30 g of representative portion of the minus No. 60 sieve analysis sample to pass a No. 200 ~~(0.075 mm)~~ (0.075 mm) sieve. Use a tungsten carbide mill to minimize metal contamination. Dry this sample to constant weight at ~~110~~110 °C to ~~115°C~~115 °C (approximately ~~8 h)~~ 8 h) and store in a desiccator until cool. ~~(~~(Note**~~Warning—~~**~~Preparation of the minus 200 mesh analysis samples, from the minus 60 mesh analysis samples, neither remove metals through loss nor increase metals through contamination. Full dissolution of the ash is required.)~~ that preparation of the minus 200 mesh analysis samples, from the minus 60 mesh analysis samples, neither remove metals through loss nor increase metals through contamination. Full dissolution of the ash is required.)

9. Preparation of Apparatus

9.1 Consult the manufacturer's instructions for the operation of the atomic absorption spectrophotometer. The present method assumes that good operating procedures are followed. Design differences between spectrophotometers make it impractical to specify the required manipulations in detail here. (**Warning—**Proper operating procedures are required for safety as well as for reliability of results. An explosion can result from the flame blow-back unless the correct burner head and operating sequence are used.)

10. Procedure

10.1 Weigh ~~10 g (to 0.1 mg)~~ 10 g (to 0.1 mg) of the dried coke prepared in ~~8.2~~8.2into a labeled preignited platinum dish. (**Warning—**In addition to other precautions, to minimize the potential of contamination, prepare the platinum ware by boiling in dilute HCl (5 volume % HCl plus 95 % water) rinsing thoroughly with a reagent-grade water. After this initial cleaning, handle the platinum ware with clean tongs, and protect from all sources of contamination. Clean and protect all the glassware used in analyses.)

10.2 Place the platinum dish in a cold muffle furnace and heat directly to ~~525°C~~525 °C with the furnace door opened approximately ~~7 mm~~ 7 mm to allow exchange of combustion gases and air until all carbonaceous matter is removed. Transfer the platinum dish to a dessicator and cool to room temperature.

10.3 To convert the ash into a solution, weigh on an analytical balance onto a tared weighing paper, ~~1 g (±5 mg, 200 ± 10°C)~~1 g (±5 mg, 200 °C ± 10 °C) of $Li_2B_4O_7$ powder. Mix the ash and lithium tetraborate by sprinkling $Li_2B_4O_7$ evenly over the ash. Place the platinum dish onto a ceramic triangle resting on a ring stand over a Meker type burner and adjust the forced air gas flame so that the $Li_2B_4O_7$ melts in about ~~30 s.~~ 30 s. Using the platinum-tipped tongs, gently swirl the melt to dissolve the ash. Continue heating over the burner for ~~2~~2 min to ~~3 min~~ 3 min or until a clear, transparent melt is obtained. Alternatively, heat in a furnace at ~~950~~950 °C ± ~~10°C~~10 °C for ~~10 min~~ 10 min or until the $Li_2B_4O_7$ melts.

NOTE 4—The ideal fusion after cooling will look like a clear glass inside the platinum dish. An opaque melt indicates poor fusion and some of the ash may remain insoluble during the dissolution step.

10.4 Allow the melt to cool for ~~5~~5 min to ~~10 min~~ 10 min on a silica plate. Add a ~~25.4 mm (1 in.)~~ 25.4 mm (1 in.) TFE-fluorocarbon coated magnetic stirring bar, and ~~25 mL~~ 25 mL of Solution 1, and place immediately on the stirring hot plate. Heat the solution to just below boiling temperature and maintain for not more than ~~30 min~~ 30 min with constant stirring, until the melt has completely dissolved.

NOTE 5—If the stirring is not constantly maintained, some of the ash constituents may precipitate, primarily hydrous silica, due to heating the highly acidic solution. If this occurs, it is necessary to repeat the analysis.

10.5 Remove the dish from the hot plate, rinse down the walls of the dish with water, and quantitatively transfer the solution to a ~~100-mL~~100 mL flask. Add ~~10 mL~~ 10 mL of Solution 2, dilute with water, and mix thoroughly (see Note 5).

10.6 Prepare any required dilution using Solution 3 (7.7), diluted 1:1 with water, as the dilutent.

NOTE 6—Lanthanum is included in the solution as a releasing agent for calcium and as an ionization suppressant for aluminum and vanadium.