Designation: D5056 – 04

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

1. 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 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.

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

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 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.

6. Apparatus

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

6.2 *Magnetic Stirring Hot Plate.*

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

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

6.5 *Platinum-Tipped Tongs.*

6.6 *Furnace*, electric, capable of regulation of temperature at 950 ± 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.

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

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[1] This test method 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] 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.

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 of concentrated HCl diluted to 100 mL with Type II reagent water).

7.4 *Lanthanum Additive, Solution 2*, 100 g/L lanthanum (dissolve 175 g $LaCl_3$ in water and dilute to 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, to the nearest 0.1 g, of $Li_2B_4O_7$ into a 150 to 200 mL platinum dish, fuse with a Meker type burner to form a liquid, and cool. Alternatively, heat in a furnace at 950 ± 10°C for 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 beaker. Add 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 flask. To avoid crystallization add about 100 mL of water; stir the solution and cool to room temperature. Add 400 mL of Solution 2 (lanthanum additive) and mix. Dilute to 2000 mL with water, mix thoroughly, and vacuum filter the entire solution through Dow filter paper.

NOTE 2—Fifty millilitres of Solution 3 contains 1 g $Li_2B_4O_7$, 25 mL of Solution 1, 20 % HCl, and 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 (mg/L) for each metal are needed for preparation of dilute standards in the range from <1.0 to 50 ppm (mg/L). Working standards containing aluminum, calcium, iron, nickel, silicon, sodium, and vanadium in concentration ranges below 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) sieve by the procedure in Practice D346, Section 10 on Preparation of Coke Sample for Laboratory Analysis.

8.2 Crush approximately a 30 g of representative portion of the minus No. 60 sieve analysis sample to pass a No. 200 (0.075 mm) sieve. Use a tungsten carbide mill to minimize metal contamination. Dry this sample to constant weight at 110 to 115°C (approximately 8 h) and store in a desiccator until cool. (**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.)

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) of the dried coke prepared in 8.2 into 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 with the furnace door opened approximately 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) 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. Using the platinum-tipped tongs, gently swirl the melt to dissolve the ash. Continue

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[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.

heating over the burner for 2 to 3 min or until a clear, transparent melt is obtained. Alternatively, heat in a furnace at 950 ± 10°C for 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 to 10 min on a silica plate. Add a 25.4 mm (1 in.) TFE-fluorocarbon coated magnetic stirring bar, and 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 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 flask. Add 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.

10.7 Establish the AAS operating conditions (see Section 9). Select the flame gases and spectral lines from the requirements presented in Table 2.

NOTE 7—Each analyst determines the sensitivity and linear range of calibration of his own equipment and chooses concentration ranges for standards compatible with the samples and instrument specific to his own work. Sample dilutions can be required for the determination of some elements. Table 2 lists the oxidant gases used in the analyses for determining the precision of this method. However, nitrous oxide can be used as the oxidant for all of the elements of interest to reduce errors due to chemical interferences.

10.8 Prepare calibration standards, including a calibration blank, using 50 mL of Solution 3 per 100 mL. Dilute with water (see Note 6).

NOTE 8—Standard and sample solutions are of similar composition to minimize errors due to matrix effects.

10.9 Using the AAS, determine the concentration of each metal in the sample solution. Standards must bracket the sample concentration.

11. Calculation

11.1 Calculate parts per million (milligram per kilogram) of each metal in the sample as follows:

TABLE 2 Experimental Conditions

Element	Fuel	Oxidant	Wavelength (nm)
Aluminum	C_2H_2	N_2O	309.3
Calcium	C_2H_2	air	422.7
Iron	C_2H_2	air	248.3
Nickel	C_2H_2	air	232.0
Silicon	C_2H_2	N_2O	251.6
Sodium	C_2H_2	air	589.0
Vanadium	C_2H_2	N_2O	318.3

TABLE 3 Repeatability and Reproducibility Ranges

NOTE—x = The average value of two results in parts per million (milligrams per kilogram)

Metal, Range mg/kg	Repeatability	Reproducibility
Aluminum, 15 to 105	15	40
Calcium, 20 to 225	21	36
Iron, 150 to 500	$0.39\ x^{3/4}$	$1.18\ x^{3/4}$
Nickel, 5 to 200	$1.27\ x^{1/2}$	$1.69\ x^{1/2}$
Silicon, 90 to 420	$1.94\ x^{1/2}$	$9.41\ x^{1/2}$
Sodium, 15 to 115	$0.19\ x$	$0.61\ x$
Vanadium, 5 to 500	$1.19\ x^{1/2}$	$2.93\ x^{1/2}$

$$\text{M, ppm (mg/kg)} = \frac{A \times V}{W} \times C/D \tag{1}$$

where:

M = metal,
A = metal in solution analyzed, ppm (mg/L),
V = volume of sample solution, mL,
W = weight of sample, g, and
C/D = dilution factor (amount of dilution of the sample solution in 10.6 needed to bring the metal concentrations into the range of standard solutions).

11.2 Calculations used and results reported are on a dried original sample basis.

12. Report

12.1 Report results for each element as parts per million (milligram per kilogram) or mass percent (1000 ppm (mg/kg) = 0.1 %).

12.1.1 Use three significant figures if the duplicate values do not vary in the first two figures. Use two significant figures when only single values are determined.

13. Quality Control (QC)

13.1 Confirm the performance of the instrument or the test procedure by analyzing a QC sample (see 7.9).

13.1.1 When QC/Quality Assurance (QA) protocols are already established in the testing facility, these may be used when they confirm the reliability of the test result.

13.1.2 When there is no QC/QA protocol established in the testing facility, Appendix X1 can be used as the QC/QA system.

14. Precision and Bias

14.1 The values in the following statements were determined in a cooperative program following ASTM D02-1007.[4] The calibration blank used during this program was not matrix matched.

14.1.1 *Precision*—The precision of this test method as determined by the statistical examination of interlaboratory test results appears in Table 3.

14.1.2 *Repeatability*—The difference between successive results obtained by the same operator with the same apparatus under constant operating conditions on identical test material

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[4] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report D02-1007.

would, in the long run, in the normal and correct operation of the test method, exceed the values in Table 3 only in one case in twenty.

14.1.3 *Reproducibility*—The difference between the two single and independent results obtained by different operators working in different laboratories on identical test material would, in the long run, exceed the values in Table 3 only in one case in twenty.

14.2 *Bias Statement*—The bias for this test method can not be determined since a suitable reference material is not available.

15. Keywords

15.1 ash; atomic absorption; metals; petroleum coke; spectroscopy

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 (see Practice D6299 and MNL7[5]).

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[6] (see Practice D6299 and MNL7[5]). Investigate any out-of-control data for root cause(s). The results of this investigation may, but not necessarily, result in instrument recalibration.

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 MNL7[5]).

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 homogeneous and stable under the anticipated storage conditions.

X1.6 See Practice D6299 and MNL7[5] for further guidance on QC and Control Charting techniques.

SUMMARY OF CHANGES

Subcommittee D02.03 has identified the location of selected changes to this standard since the last issue (D5056–02) that may impact the use of this standard.

(1) Added Note 3 allowing the use of commercially prepared standards and reagent solutions.

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[5] MNL7, *Manual on Presentation of Data Control Chart Analysis*, 6th Ed., Section 3, ASTM International, W. Conshohocken, PA.

[6] In the absence of explicit requirements given in the test method, this clause provides guidance on QC testing frequency.