



# Standard Test Method for Trace Metals in Petroleum Coke by Atomic Absorption<sup>1</sup>

This standard is issued under the fixed designation D 5056; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 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 hazard statements, see Sections 8, 9 and 10.

## 2. Referenced Documents

### 2.1 ASTM Standards:

D 346 Practice for Collection and Preparation of Coke Samples for Laboratory Analysis<sup>2</sup>

D 1193 Specification for Reagent Water<sup>3</sup>

## 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 ( $\text{Li}_2\text{B}_4\text{O}_7$ ), or lithium metaborate ( $\text{LiBO}_3$ ). 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.

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.03.0B on Spectrometric Methods.

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<sup>2</sup> Annual Book of ASTM Standards, Vol 05.05.

<sup>3</sup> Annual Book of ASTM Standards, Vol 11.01.

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

4.2 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  $\pm$  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  $\pm$  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

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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.<sup>4</sup> 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 D 1193.

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<sub>3</sub> in water and dilute to 1 L with water).

7.5 *Lanthanum Chloride (LaCl<sub>3</sub>) powder* (high purity).

7.6 *Lithium Tetraborate (Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub>) powder* (high purity), or *Lithium Metaborate (LiBO<sub>3</sub>) powder* (high purity).

7.7 *Standard and Sample Dilution Additive, Solution 3*—Weigh 40.0 g, to the nearest 0.1 g, of Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub> 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<sub>2</sub>B<sub>4</sub>O<sub>7</sub>, 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<sub>2</sub>B<sub>4</sub>O<sub>7</sub>, 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.

## 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 D 346, Section 9.

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.

NOTE 3—**Caution:** 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.

NOTE 4—**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.

NOTE 5—**Precaution:** 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 desiccator 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<sub>2</sub>B<sub>4</sub>O<sub>7</sub> powder. Mix the ash and lithium tetraborate by sprinkling Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub> 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<sub>2</sub>B<sub>4</sub>O<sub>7</sub> melts in about 30 s. Using the platinum-tipped tongs, gently swirl the melt to dissolve the ash. Continue 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<sub>2</sub>B<sub>4</sub>O<sub>7</sub> melts.

NOTE 6—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 7—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

<sup>4</sup> *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. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.