



Standard Test Method for Trace Metals in Petroleum Coke by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)¹

This standard is issued under the fixed designation D 5600; 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

1.1 This test method covers the analysis for commonly determined trace metals in test specimens of raw and calcined petroleum coke by inductively coupled plasma atomic emission spectroscopy.

1.2 Elements for which this test method is applicable are listed in Table 1. Detection limits, sensitivity, and optimum ranges of the metals will vary with the matrices and model of spectrometer.

1.3 This test method is applicable only to samples containing less than one mass % ash.

1.4 Elements present at concentrations above the upper limit of the working ranges can be determined with additional, appropriate dilutions.

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.*

1.6 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

2. Referenced Documents

2.1 *ASTM Standards:*

D 346 Practice for Collection and Preparation of Coke Samples for Laboratory Analysis²

¹ This test method is under the jurisdiction of ASTM Committee D-2 D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.03 on Elemental Analysis.

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TABLE 1 Elements Determined and Suggested Wavelengths

Element	Wavelengths, nm ^{A,B}	Concentration Range, mg/kg ^C
Aluminum	237.313, 256.799, 308.216, 396.152	15–110
Barium	455.403, 493.410	1–65
Calcium	317.933, 393.367, 396.847	10–140
Iron	259.940	40–700
Magnesium	279.079, 279.553	5–50
Manganese	257.610, 294.920	1–7
Nickel	231.604, 241.476, 352.454	3–220
Silicon	212.412, 251.611, 288.159	60–290
Sodium	588.995, 589.3, 589.592	30–160
Titanium	334.941, 337.280	1–7
Vanadium	292.402	2–480
Zinc	202.548, 206.200, 213.856	1–20

^A The wavelengths listed were utilized in the round robin because of their sensitivity. Other wavelengths can be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference (see 6.1). In time, other elements may be added as more information becomes available and as required.

^B Alternative wavelengths can be found in references such as “Inductively Coupled Plasma Atomic Emission Spectroscopy,” Winge, R. K., Fassel, V. A., Peterson, V. J., and Floyd, M. A., Elsevier, 1985.

^C Based on this round robin study. This method can be applicable to other elements or concentration ranges but precision data is not available.

D 1193 Specification for Reagent Water³

E 11 Specification for Wire- Cloth and Sieves for Testing Purposes⁴

3. Terminology

3.1 Definitions of Terms Specific to This Standard:

3.1.1 *petroleum coke*—~~a solid, carbonaceous residue produced by thermal decomposition of heavy petroleum fractions and cracked stocks.~~

3.1.2 *gross sample*—the original, uncrushed, representative portion taken from a shipment or lot of coke.

3.1.32 *ICP-AES*—Inductively Coupled Plasma—Atomic Emission Spectrometry.

3.1.3 *petroleum coke*—a solid, carbonaceous residue produced by thermal decomposition of heavy petroleum fractions and cracked stocks.

4. Summary of Test Method

4.1 A test sample of the petroleum coke is ashed at 700°C. The ash is fused with lithium borate. The melt is dissolved in dilute hydrochloric acid (HCl), and the resultant solution is analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES) using simultaneous, or sequential multielemental determination of elements. The solution is introduced to the ICP instrument by free aspiration or by an optional peristaltic pump. The concentrations of the trace metals are then calculated by comparing the emission intensities from the sample with the emission intensities of the standards used in calibration.

5. Significance and Use

5.1 The presence and concentration of various metallic elements in a petroleum coke are major factors in determining the suitability of the coke for various end uses. This test method provides a means of determining the concentrations of these metallic elements in a coke sample.

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

6. Interferences

6.1 *Spectral*—Follow the instrument manufacturer’s operating guide to develop and apply correction factors to compensate for the interferences. To apply interference corrections, all concentrations shall be within the previously established linear response range of each element.

6.2 Spectral interferences are caused by: (1) overlap of a spectral line from another element; (2) unresolved overlap of molecular band spectra; (3) background contribution from continuous or recombination phenomena; and (4) stray light from the line emission of high-concentration elements. Spectral overlap can be compensated for by computer-correcting the raw data after monitoring and

² Annual Book of ASTM Standards, Vol 05.05.

³ Annual Book of ASTM Standards, Vol 11.01.

⁴ Annual Book of ASTM Standards, Vol 14.02.

measuring the interfering element. Unresolved overlap requires selection of an alternate wavelength. Background contribution and stray light can usually be compensated for by a background correction adjacent to the analyte line.

6.3 Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If physical interferences are present, they shall be reduced by diluting the sample, by using a peristaltic pump, or by using the standard additions method. Another problem that can occur with high dissolved solids is salts buildup at the tip of the nebulizer, which can affect aerosol flow rate and cause instrumental drift. This problem can be controlled by wetting the argon prior to nebulization, using a tip washer, or diluting the sample.

7. Apparatus

- 7.1 *Balance*, top loading, with automatic tare, capable of weighing to 0.0001 g, 150 g capacity.
- 7.2 *Ceramic Cooling Plate*, desiccator plates have been found effective.
- 7.3 *Crucible Support*, nichrome wire triangles.
- 7.4 *Furnaces*, electric, capable of regulation of temperature at $700^{\circ}\text{C} \pm 10^{\circ}\text{C}$ and $1000^{\circ}\text{C} \pm 100^{\circ}\text{C}$, with allowances for exchange of combustion gases and air.
- 7.5 *Inductively Coupled Plasma Atomic Emission Spectrometer*—Either sequential or simultaneous spectrometer is suitable.
- 7.6 *Magnetic Stirring Bars*, polytetrafluoroethylene (PTFE) coated, approximately 12 mm ($\frac{1}{2}$ in.) in length.
- 7.7 *Magnetic Stirring Hot Plate*.
- 7.8 *Meker Type Forced Air Burner*.
- 7.9 *Nebulizer*—A high-solids nebulizer is strongly recommended. This type of nebulizer reduces the possibility of clogging and minimizes aerosol particle effects.
- 7.10 *Peristaltic Pump*—A peristaltic pump is strongly recommended to provide a constant flow of solution.
- 7.11 *Platinum Dish*, 50 to 58 mL capacity.
- 7.12 *Platinum Dish*, 100 to 200 mL capacity.
- 7.13 *Platinum-tipped Tongs*.
- 7.14 *Ring Stand*, with crucible support.
- 7.15 *Sieves*, 0.250 mm (No. 60) and 0.075 mm (No. 200), conforming to Specification E 11.
- 7.16 *Tungsten Carbide Mill*, laboratory size.
- 7.17 *Vacuum Filtration Apparatus*.
- 7.18 *Filter Paper*, sized to fit vacuum filtration apparatus, fine porosity, slow flow rate, 2.5 micron particle retention.

8. Reagents

8.1 *Purity of Reagents*—Reagent-grade chemicals shall be used in all tests. 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.⁵ 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.

8.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean Type II reagent water as defined in Specification D 1193.

8.3 *Argon Gas Supply*, welding grade.

8.4 *Lithium Borate*, either, or a blend containing both.

8.4.1 *Lithium Metaborate* (LiBO_2), powder (high purity).

8.4.2 *Lithium Tetraborate* ($\text{Li}_2\text{B}_4\text{O}_7$), powder (high purity).

8.5 *Solution No. 1, Hydrochloric Acid*, 20 % by volume (400 mL of concentrated HCl diluted to 2000 mL with water).

8.6 *Solution No. 2, Standard and Sample Solution Additive*. Weigh 20.0 grams, ± 0.1 g, ± 0.1 g of lithium borate into a 100 to 200 mL platinum dish. Place in a furnace at 1000°C for 5 min to fuse to a liquid. Remove and cool. Place the cooled platinum dish containing the fused recrystallized lithium borate and a magnetic stirring bar into a 2-L glass beaker. Add 1000 mL of Solution No. 1 (20 % HCl). Heat gently and stir the solution on a magnetic stirring hot plate until the lithium borate 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 volumetric flask. Dilute to about 1800 mL with water to avoid crystallization. Mix the solution and cool to room temperature. Dilute to volume with water, mix thoroughly, and vacuum-filter the entire solution through filter paper.

NOTE 1—Fifty millilitres of Solution No. 2 contains exactly 0.5 g lithium borate and 25 mL Solution No. 1.

8.7 *Standard Stock Solutions*—Prepare standard stock solutions from high purity (99.9 % or better) metals, oxides, or salts. Stock solutions of 1000 $\mu\text{g}/\text{mL}$ (ppm) for each metal are needed for preparation of dilute standards in the range from <1.0 to 50 $\mu\text{g}/\text{mL}$ (ppm).

⁵ *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—Caution: To minimize the potential of contamination, prepare the platinum ware by boiling in dilute HCl (5 volume % HCl + 95 volume % water) and rinsing thoroughly with water. After this initial cleaning, handle the platinum ware with clean platinum tipped tongs and protect from all sources of contamination. Similarly acid clean all glassware used in the analyses.

9. Sample Preparation

9.1 Crush and divide the gross sample to obtain a laboratory analysis sample. Crush to pass a 0.250 mm (No. 60) sieve using Practice D 346.

9.2 Use a tungsten carbide mill to crush approximately a 30 g representative portion of the minus 0.250 mm (No. 60) sieve analysis sample, as prepared in 9.1, to pass through a 0.075 mm (No. 200) sieve. Dry this sample to constant mass at 110 to 115°C and store in a desiccator until cool and needed for the analysis.

9.2.1 Preparation of the minus 0.075 mm analysis samples, from the minus 0.250 mm analysis samples, shall neither remove metals through loss nor increase metals through contamination. Full dissolution of the ash is required.

10. Preparation of Apparatus

10.1 *ICP-AES Instrument*—Consult the manufacturer’s instructions for operation of the inductively coupled plasma atomic emission spectrometer.

10.2 *Peristaltic Pump*—When a peristaltic pump is used, inspect the pump tubing and replace it, as necessary, before starting each day. Verify the solution uptake rate and adjust it to the desired rate.

10.3 *ICP Excitation Source*—Initiate the plasma source at least 30 min before performing the analysis. Some manufacturers recommend even longer warm-up periods.

10.4 *Wavelength Profiling*—Perform any wavelength profiling that is required in the normal operation of the instrument.

10.5 *Operating Parameters*—Assign the appropriate operating parameter to the instrument task file so that the desired elements can be determined. Parameters to be included are element, wavelength, background correction points (optional), inter-element correction factors (optional), integration time, and internal standard correction (optional).

10.6 Each analyst shall determine the sensitivity and linear range of calibration of their own equipment and choose concentration ranges for standards compatible with the samples and instrument specific to their own work. Sample dilutions can be required for the determination of some elements (see 11.6).

10.7 The linear response range shall be established for each particular instrument being used. This is accomplished by running intermediate standards between the blank and the calibration standard and by running standards containing higher concentrations than the calibration standard within the linear range of response.

11. Procedure

11.1 Weigh 5 g (to 0.1 mg) of the dried petroleum coke prepared in Section 9 into a labeled 50 to 58 mL platinum dish.

11.2 Place the platinum dish in a cold muffle furnace and heat directly to $700 \pm 10^\circ\text{C}$ until all carbonaceous matter is removed. Transfer the platinum dish to a desiccator and cool to room temperature.

11.3 To convert the ash into a solution, weigh, on an analytical balance, onto a tared weighing paper, 0.5 g (± 0.0005 g) of lithium borate powder. Sprinkle the lithium borate evenly over the ash. Use platinum tipped tongs to place the platinum dish into a muffle furnace at $1000 \pm 10^\circ\text{C}$ for one or two minutes. Use the platinum-tipped tongs to gently swirl the melt to dissolve the ash. Continue heating in the furnace for two to three minutes or until a clear, transparent melt is obtained.

11.3.1 The ideal fusion after cooling will look like clear glass inside the platinum dish. An opaque melt possibly indicates poor fusion and some of the ash can remain insoluble during the dissolution step. Full dissolution of the ash is required.

11.3.2 If a $1000 \pm 10^\circ\text{C}$ furnace is not available, the fusion can be performed using a Meker type burner as follows. Place the platinum dish onto the crucible support resting on a ring stand over the burner and adjust the forced air gas flame so that the lithium borate melts in about 30 s. Using platinum-tipped tongs, gently swirl the melt to dissolve the ash. Continue heating over the burner for two or three minutes or until a clear, transparent melt is obtained.

11.4 Allow the melt to cool for 5 to 10 min on a ceramic cooling plate, add stirring bar, add 25 mL of Solution No. 1, and place immediately on the stirring hot plate. Heat the solution to just below boiling temperature and maintain the liquid volume with water for not more than 30 min with constant stirring, until the melt has completely dissolved.

11.4.1 If stirring and liquid volume are not constantly maintained, some of the ash constituents can precipitate, primarily hydrous silica, due to heating the highly acidic solution. Repeat the analysis if this occurs.

11.5 Remove the dish from the hot plate, transfer the solution quantitatively to a 100-mL volumetric flask, rinse the dish into the flask with water, dilute to volume with water, and mix thoroughly.

11.6 Prepare any required dilution using Solution No. 2 diluted 1:1 with water.

11.7 Prepare a calibration standard using 50 mL of Solution No. 2 per 100 mL and containing the desired volume of standard stock solutions. Dilute with water.

NOTE 3—Standard and sample solutions are of similar composition to minimize errors due to matrix effects.

11.8 Calibrate the ICP-AES instrument using the calibration standard prepared in 11.7 in accordance with manufacturer’s directions.

11.9 Determine the concentration of each metal in the sample solution.

12. Calculation

12.1 Calculate concentration of each metal in the sample as follows:

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

$$M, \text{ mass \%} = M, \text{ mg/kg}/10\,000 \quad (2)$$

where:

M = metal being calculated,

A = mg/L (ppm) of metal M in solution analyzed,

V = volume of sample solution mL, and

W = mass of sample, g,

(C/D) = dilution factor if sample dilution is required (C = volume diluted to, D = amount of sample diluted) to bring the metal concentrations into the range of standard solutions).

13. Report

13.1 Report concentration for each element as mg/kg (ppm) or mass % (1000 mg/kg (ppm) = 0.1 %).

14. Precision and Bias

14.1 The values in the following statements were determined in a cooperative program following the research report.⁶

14.1.1 *Precision*—The precision of this test method as determined by the statistical examination of interlaboratory test results appears in Table 2.

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 would, in the long run, in the normal and correct operation of the test method, exceed the values in Table 2 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 2 only in one case in twenty.

14.1.4 *Bias*—The bias for the procedure in Test Method 5600 for measuring the trace metals in petroleum coke cannot be determined since suitable reference materials are not available.

15. Keywords

15.1 aluminum; barium; calcium; elements; ICP-AES; inductively coupled plasma; iron; magnesium; manganese; metals; nickel; petroleum coke; silicon; sodium; spectrometry; atomic emission; titanium; vanadium; zinc

⁶ Available from

⁶ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D02-1007.

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TABLE 2 Repeatability and Reproducibility

NOTE 1— X = the average value of two results in mg/kg, and
* = multiply.

Metal, mg/kg	Repeatability	Reproducibility
Aluminum	0.32*X-(2/3)	0.92*X-(2/3)
Barium	0.19*X-(2/3)	0.71*X-(2/3)
Calcium	7.2	20.8
Iron	1.66*X-(1/2)	3.77*X-(1/2)
Magnesium	0.21*X-(2/3)	0.61*X-(2/3)
Manganese	0.042*(X + 2.55)	0.34*(X + 2.55)
Nickel	0.52*X-(2/3)	0.96*X-(2/3)
Silicon	0.71*(X + 4.80)	0.20*(X + 4.80)
Sodium	1.04*X-(1/2)	3.52*X-(1/2)
Titanium	0.75	1.16
Vanadium	0.20*X-(3/4)	0.35*X-(3/4)
Zinc	1.07*X-(1/3)	2.20*X-(1/3)

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