Designation: D6376 – 06

Standard Test Method for Determination of Trace Metals in Petroleum Coke by Wavelength Dispersive X-ray Fluorescence Spectroscopy[1]

1. Scope*

1.1 This test method covers the X-ray fluorescence spectrometric determination of total sulfur and trace metals in samples of raw or calcined petroleum coke. Elements determined using this test method are listed in Table 1.

1.2 Detection limits, sensitivity, and optimal element ranges will vary with matrices, spectrometer type, analyzing crystal, and other instrument conditions and parameters.

1.3 All analytes are determined as the element and reported as such. These include all elements listed in Table 1. This test method may be applicable to additional elements or concentration ranges if sufficient standards are available to produce proper calibration equations.

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

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.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

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

D1552 Test Method for Sulfur in Petroleum Products (High-Temperature Method)

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D5056 Test Method for Trace Metals in Petroleum Coke by Atomic Absorption

D5600 Test Method for Trace Metals in Petroleum Coke by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)

E11 Specification for Woven Wire Test Sieve Cloth and Test Sieves

TABLE 1 Applicable Concentration Ranges

Element	Concentration Range, (ppm)
Na	50–500
Al	50–500
Si	20–500
S, %	0.10–7.0
Ca	20–500
Ti	10–200
V	20–2000
Mn	10–200
Fe	20–1000
Ni	20–500

3. Terminology

3.1 *Definitions:*

3.1.1 *calcined petroleum coke, n*—raw petroleum coke that has been thermally treated to drive off the volatile matter and to develop crystalline structure.

3.1.2 *green petroleum coke, n*—same as raw petroleum coke.

3.1.3 *petroleum coke, n*—a solid, carbonaceous residue produced by thermal decomposition of heavy petroleum fractions or cracked stocks, or both

3.1.4 *raw petroleum coke, n*—petroleum coke that has not been calcined.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *alpha, n*—correction factor used to compensate for interferences.

3.2.2 *analytical sample, n*—a representative fraction taken from a larger mass of petroleum coke and reduced by grinding to pass a 75 μm (No. 200 mesh) sieve.

3.2.3 *pellet, n*—a blend of dried sample and binder milled together and then formed into a pellet by pressure.

3.2.4 *reference samples, n*—samples of known concentrations to be used in the calibration of the X-ray fluorescence spectrometer.

4. Summary of Test Method

4.1 A representative sample of petroleum coke is dried to constant mass at 110 ± 10°C and then crushed to pass a 75 μm

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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 D02.05 on Properties of Fuels, Petroleum Coke and Carbon Material.

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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.

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

(No. 200 mesh) sieve. A weighed portion of this analytical sample is mixed with stearic acid, or other suitable binder, and then milled and compressed into a small, smooth pellet suitable for analysis. The pellet is irradiated by an X-ray beam. The characteristic X rays of the elements analyzed are excited, separated, and detected by the wavelength-dispersive X-ray spectrometer. These measured X-ray intensities are converted to elemental concentration through the use of a calibration equation derived from analyses of standard materials. This calibration equation defines the sensitivity and background associated with a particular X-ray spectrometer.

4.2 The K-alpha spectral lines are used for all of the elements determined by this test method.

5. Significance and Use

5.1 The presence and concentration of sulfur and various metallic elements in a petroleum coke are major factors determining the suitability of a coke for various purposes. This test method provides rapid means for measuring sulfur and commercially important metallic elements in coke samples.

5.2 This test method provides a guide for determining conformance to material specifications for use by buyers and sellers in a commercial transfer of petroleum coke.

5.3 Sulfur contents can be used to evaluate the potential formation of sulfur oxides (SO_x), a source of atmospheric pollution.

6. Interferences

6.1 Review all potential spectral interferences for the elements listed in Table 2. Follow your manufacturer's operating guide to develop and apply alphas to compensate for these interferences.

6.2 Compensate for inter-element effects by using alphas as part of the regression procedure provided with spectrometer software.

6.3 Changes in the sulfur concentration in the sample affects analyte X-ray intensities. Therefore, determine the magnitude of the sulfur effect on each metallic element and apply in appropriate correction.

7. Apparatus

7.1 *Balance*, capable of weighing 50 ± 0.01 g.

TABLE 2 Suitable Instrument Operating Conditions

Element	2Θ Angle, Degrees[A]	Background, Degrees[A]	Analyzing Crystal[A]
Sodium	25.05	26.75, 24.35	Multilayer, 2d ~50Å
Aluminum	145.13	143.13	PET
Silicon	144.95	147.05, 142.85	InSb
Sulfur	110.68	113.18	Ge
Calcium	113.08	116.00	LiF (200)
Titanium	86.13	84.13	LiF (200)
Vanadium	76.93	78.93	LiF (200)
Manganese	62.97	60.97	LiF (200)
Iron	57.52	59.02	LiF (200)
Nickel	48.66	49.92, 47.40	LiF (200)

[A] The wavelength angles and analyzing crystals listed are suitable due to their sensitivity and general industry acceptance. These choices are made based on the element to be determined. Other instrument operating conditions can be used, but an attempt should always be made to use only those conditions yielding optimal sensitivity with minimum interferences. The instrument manufacturer should be consulted for recommendations on optimal targets, crystal options, and any concentration limit restrictions on your unit.

7.2 *Hydraulic Press*, capable of exerting a force of not less than 276 MPa (40 000 psi).

7.3 *Mill or Grinder*, capable of reducing 20 g of petroleum coke to a sample passing 75 µm (No. 200 mesh) in less than 10 min, without introducing contamination.

7.4 *Mixer/Mill*, for blending sample and binder.

7.5 *Pellet Cup, Aluminum* (optional), tapered to hold pressed pellets.

7.6 *Pelletizing Die*, for forming pellets of a diameter suitable for use in the spectrometer.

7.7 *Sieves*, 75 µm (No. 200 mesh) as specified in Specification E11.

7.8 *Drying Oven*, capable of maintaining a minimum temperature of 110 ± 10°C.

7.9 *X-ray Spectrometer*, equipped for soft X-ray detection of the K-alpha spectral lines for all of the elements determined by this test method. For increased sensitivity, this instrument shall be equipped with the following:

7.9.1 *Analyzing Crystals*—This choice is made based on the element to be determined. The crystal selected should yield optimal sensitivity with minimum interferences. The same crystal shall be used for both standards and unknowns. See Table 2 for recommended crystals.

7.9.2 *Detector*, suitable for the determination of elements in question. Choices include gas-flow proportional, sealed proportional, and scintillation detectors.

7.9.3 *Optical Path*, in a vacuum.

7.9.4 *Pulse-Height Analyzer*, or other means of energy discrimination.

7.9.5 *Suitable X-ray Tube*—Chromium, molybdenum, platinum, rhodium, or tungsten target and dual targets have been found suitable. The scandium tube is very advantageous for light elements.

8. Reagents and Materials

8.1 *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.[3,4] Other grades may be used, provided they are of sufficiently high purity to permit use without diminishing the accuracy of the determination.

8.2 *Detector Gas*—P-10 gas (90 % argon, 10 % methane) is used with gas-flow proportional detectors.

8.3 *Pellet Binder Material*—Stearic acid, or other suitable binder, providing no spectral interferences shall be used.

8.4 *Reference Samples*, of petroleum coke bracketing the element ranges of the analytical samples. Commercial reference samples of this type are available from several sources.

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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 *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.

[4] For the testing of reagents not listed by the American Chemical Society, see *Reagent Chemicals and Standards*, by Joseph Rosin, D. VanNostrand Co., Inc., New York, NY.

9. Sampling and Preparation of Test Specimens

9.1 *Basic Assumptions*—All petroleum coke samples examined using this test method shall be analytical samples representative of a green or calcined coke production lot or shipment. Practices D4057 and D346 shall be followed. The analytical sample shall pass a 75 µm (No. 200 mesh) sieve and shall be of sufficient quantity to provide sample for all testing and analyses planned for the particular lot of petroleum coke. To provide for possible replicate determinations of the sulfur and metallic contents by this test method and for a retain sample, an analytical sample shall be 50 g or more for this test alone.

NOTE 1—Results are particle dependent, and erroneous data may be collected if analytical samples contain particles varying significantly in size from those in reference samples. Measurements may be necessary to ensure the equivalence of analytical samples and reference samples. The most difficult problems occur when there are coarse petroleum coke samples and finely ground reference samples. In this case, it is best to grind the analytical samples, achieving a size distribution similar to the reference samples.

9.2 *Types of Samples*:

9.2.1 *Reference Samples*—These samples shall be similar to the analytical samples in composition and physical properties. A wide range of concentrations is required for inter-element effect detection when regression software is used to analyze reference data. Elemental concentrations shall bracket the values expected in the analytical samples.

9.2.2 *Analytical Samples*—Samples whose sulfur and metallic contents are to be determined.

9.3 *Typical Preparation of Standards and Test Specimens*:

9.3.1 Dry a sufficient portion of the analytical sample to constant mass in an oven at 110 ± 10°C to obtain at least 5 g.

9.3.2 Weigh 5 ± 0.01 g of the dried analytical sample.

9.3.3 Add 1 ± 0.01 g of binder and mill for a minimum of 20 s. Binder/coke ratio shall remain constant for samples and standards.

9.3.3.1 Suitable grinding times to produce particles passing a 75 µm (No. 200 mesh) sieve depends on the type of grinder used and coke variations. Further grinding time impacts element intensities. It is important that grinding time be thoroughly investigated and optimized.

NOTE 2—It is essential that the same sample preparation procedure (including sample mass, binder mass and ratio, grinding, and so forth) be followed precisely for all analytical and reference samples. Even a small change in procedure requires making all new reference samples match the changed procedure. All reference samples and analytical samples used with them shall be prepared in exactly the same manner. All weighings are to be made to the nearest 0.01 g.

9.3.4 Place the pellet cup in the die mounted on the hydraulic press. Transfer sufficient ground mix to this cup to produce a pile of maximum height above the cup lip. Hand pack with a flat spatula until the ground mix is level with the cup lip.

9.3.5 Apply adequate pressure to achieve a stable pellet. Allow adequate time to reach a pressure of approximately 276 MPa (40 000 psi) and hold for a minimum of 5 s.

9.3.6 Release the pressures slowly, and remove the pellet from the die. (**Warning—**Release the pressure slowly to avoid possible damage to the pressure gauge.)

9.3.7 Inspect the pellet surface to ensure that it is smooth and free of cracks. The cylindrical pellets should be 3 to 7 mm thick.

9.3.8 When the pellet is too thin, repeat 9.3.2-9.3.7 using about 20 % more ground mix.

9.3.9 Clean the outside surface of the pellet cup, using a clean cloth or tissue. If the pellet is to be stored, it is important to properly identify it and store it in a dry place.

9.3.10 Unused test specimens prepared and stored as above are generally stable for years. Reference sample pellets can be used daily for establishing instrument conditions. If changes greater than 3 % (10 % for silicon) are observed for the calculated concentrations for any element in a used pellet, the reference sample pellets shall be prepared again. If deviations persist, recalibrate the instrument.

10. Preparation of Apparatus

10.1 Follow manufacturer's instructions for the initial assembly, conditioning, and preparation of the XRF unit.

10.2 Follow the manufacturer's control setting and operation instructions.

10.3 *Peak and Background Intensity Measurements*—A decision on counting time is made after analyzing all required reference samples and after the sensitivity is known. A suggested strategy for counting time based on reference samples is as follows:

10.3.1 Counting time is derived from:

$$\text{Relative error, \%} = 100/(T_t)^{1/2} \times 1/((R_p)^{1/2} - (R_b)^{1/2}) \quad (1)$$

where:

T_t = the total counting time for the peak and the background. T_t can be calculated as all other terms, either known or measured,

R_p = the count rate for the peak, and

R_b = the count rate for the background.

10.3.2 The partitioning of counting time based on the peak and background is estimated from:

$$T_p/T_b = (R_p/R_b)^{1/2} \quad (2)$$

where:

T_p = the peak count time,

T_b = the background count time, and

R_p and R_b = values used to reflect intensity data from a mid to low concentration standard reference material.

11. Reference Samples and Calibration

11.1 *Samples Used for Calibration*:

11.1.1 Reference samples for calibration can be purchased or prepared in-house.

NOTE 3—It is recommended that reference samples used for calibration be verified by Test Method D1552 for sulfur, by Test Method D5600 or D5056 for metals, or by using other techniques considered standards in the industry, such as spectrophotometry.

11.1.2 Reference sample concentrations shall bracket the concentrations of the analytical samples. The minimum number of reference samples is as follows:

$$\text{No. of stds} = 3\,(2 + N) \quad (3)$$

where:

N = the number of corrections calculated by the regression analysis program.

11.1.2.1 Using too few reference samples may result in lines that are over defined, that is, sulfur and vanadium, which can be highly correlated.

11.2 *Calibration*:

11.2.1 Collect data using the procedure in Section 12.

11.2.2 Sulfur correction factors, the slope, and the intercept of the calibration line are obtained by regression analysis using the spectrometer software or a model similar to the following:

$$C_i = (D_i + E_i R_i)(I + \alpha_{is} C_s) \quad (4)$$

where:

C_i = concentration of the analyte element I,

D_i = intercept of the calibration curve for element I,

E_i = slope of the calibration curve for element I,

R_i = measured net intensity for element I,

α_{is} = interelement correction factor for the effect of sulfur on analyte element I, and

C_s = concentration of sulfur.

11.2.3 A slope, an intercept, and a sulfur correction factor shall be calculated for each metallic element.

11.2.4 Sulfur correction factors (α_{is}) can also be calculated from special software.

11.2.5 A stable pellet (monitor sample) shall be used periodically to monitor instrument drift. A change in the drift factor by more than ±10 % indicates a major change or problem has occurred in the equipment. Checks and possibly recalibration may be necessary. The drift factor d is calculated for each element by the ratio:

$$d = R_1/R_n \quad (5)$$

where:

R_1 = intensity of monitor sample during the calibration procedure, and

R_n = intensity of monitor sample when unknown samples are measured.

12. Procedure

12.1 Place the analytical sample pellet into the sample holder and place both into the X-ray spectrometer. Avoid touching or otherwise contaminating the flat sample surface.

12.2 Evacuate the optical path.

12.3 Collect intensity data at the angles and under the conditions indicated in Table 2 or suitable substitutes.

12.4 Use pulse height discrimination on the gas-flow proportional detector.

12.5 Calculate results by operating the data collection and calculation software to produce analytical results by using the calibration equations developed in Section 11. Calculations are thus hidden within the computer program.

13. Precision and Bias

13.1 The precision of this test method, as obtained by statistical examination of interlaboratory test results, is as follows:

13.1.1 *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 values in Table 3 only in one case in twenty.

13.1.2 *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 values in Table 3 only in one case in twenty.

13.2 *Bias*—A result from this test method does not differ from the actual value by more than the reproducibility of the test method.

14. Keywords

14.1 alpha; aluminum; calcined petroleum coke; calcium; green petroleum coke; iron; manganese; nickel; petroleum coke; raw petroleum coke; silicon; sodium; spectrophotometry; sulfur; titanium; vanadium; X-ray fluorescence

TABLE 3 Repeatability and Reproducibility Values

Analyte	Repeatability	Reproducibility
Sodium	26 ppm	36 ppm
Aluminum	8 ppm	11 ppm
Silicon	45 ppm	66 ppm
Sulfur	0.12 %	0.22 %
Calcium	9 ppm	11 ppm
Titanium	2 ppm	2 ppm
Vanadium	24 ppm	32 ppm
Manganese	2 ppm	3 ppm
Iron	19 ppm	28 ppm
Nickel	10 ppm	14 ppm

SUMMARY OF CHANGES

Subcommittee D02.05 has identified the location of selected changes to this standard since the last issue (D6376–05) that may impact the use of this standard.

(*1*) Revised Section 3 to separate into definitions and definitions of terms specific to this standard.

(*2*) Revised 3.1.2.

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