Designation: D6376 – 09

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

This standard is issued under the fixed designation D6376; 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 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. No other units of measurement are included in this standard.

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.*

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

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

3. Terminology

3.1 *Definitions:*

3.1.1 *calcined petroleum coke*, *n*—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

[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.

[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.