Designation: D7757 – 17

Standard Test Method for
Silicon in Gasoline and Related Products by Monochromatic Wavelength Dispersive X-ray Fluorescence Spectrometry[1]

1. Scope*

1.1 This test method covers the determination of total silicon by monochromatic, wavelength-dispersive X-ray fluorescence (MWDXRF) spectrometry in naphthas, gasoline, gasoline-ethanol blends, reformulated gasoline (RFG), ethanol and ethanol-fuel blends, and toluene at concentrations of 3 mg∕kg to 100 mg∕kg. The precision of this test method was determined by an interlaboratory study using representative samples of the liquids described in 1.1 and 1.2. The pooled limit of quantitation (PLOQ) was estimated to be 3 mg∕kg.

Note 1—Volatile samples such as high-vapor-pressure gasolines or light hydrocarbons might not meet the stated precision because of the evaporation of light components during the analysis.

Note 2—Aromatic compounds such as toluene are under the jurisdiction of Committee D16 on Aromatic Hydrocarbons and Related Chemicals. However, toluene can be a contributor to silicon contamination in gasoline (see 4.4), thus its inclusion in this test method.

1.2 Gasoline samples containing ethanol and other oxygenates may be analyzed with this test method provided the matrix of the calibration standards is either matched to the sample matrices or the matrix correction described in Annex A1 is applied to the results. The conditions for matrix matching and matrix correction are provided Section 5, Interferences.

1.3 Samples with silicon concentrations above 100 mg∕kg can be analyzed after dilution with appropriate solvent. The precision and bias of silicon determinations on diluted samples have not been determined and may not be the same as shown for neat samples (Section 16).

1.4 A fundamental assumption in this test method is that the standard and sample matrices are well matched, or that the matrix differences are accounted for (see 13.5). Matrix mismatch can be caused by C/H ratio differences between samples and standards or by the presence of other interfering heteroatoms; observe the cautions and recommendations in Section 5.

1.5 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.6 *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.*

1.7 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products

D4806 Specification for Denatured Fuel Ethanol for Blending with Gasolines for Use as Automotive Spark-Ignition Engine Fuel

D5798 Specification for Ethanol Fuel Blends for Flexible-Fuel Automotive Spark-Ignition Engines

D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance

D6300 Practice for Determination of Precision and Bias Data for Use in Test Methods for Petroleum Products and Lubricants

D7343 Practice for Optimization, Sample Handling, Calibration, and Validation of X-ray Fluorescence Spectrometry Methods for Elemental Analysis of Petroleum Products and Lubricants

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[1] This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, 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.

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

3. Summary of Test Method

3.1 A monochromatic X-ray beam with a wavelength suitable to excite the K-shell electrons of silicon is focused onto a test specimen contained in a sample cell (see Fig. 1). The fluorescent Kα radiation at 0.713 nm (7.13 Å) emitted by silicon is collected by a fixed monochromator (analyzer). The intensity (counts per second) of the silicon X-rays is measured using a suitable detector and converted to the concentration of silicon (mg/kg) in a test specimen using a calibration equation.

4. Significance and Use

4.1 This test method provides rapid and precise measurement of total silicon in naphthas, gasoline, gasoline-ethanol blends, RFG, ethanol and ethanol-fuel blends, and toluene with minimum sample preparation. Typical analysis time is 5 min to 10 min per sample.

4.2 Excitation by monochromatic X-rays reduces background, simplifies matrix correction, and increases the signal/background ratio compared to polychromatic excitation used in conventional WDXRF techniques.[3]

4.3 Silicone oil defoamer can be added to coker feedstocks to minimize foaming in the coker. Residual silicon in the coker naphtha can adversely affect downstream catalytic processing of the naphtha. This test method provides a means to determine the silicon content of the naphtha.

4.4 Silicon contamination of gasoline, gasoline-ethanol blends, denatured ethanol, and their blends has led to fouled vehicle components (for example, spark plugs, exhaust oxygen sensors, catalytic converters) requiring parts replacement and repairs. Finished gasoline, gasoline-ethanol blends, and ethanol-fuel blends can come into contact with silicon a number of ways. Waste hydrocarbon solvents such as toluene can be added to gasoline. Such solvents can contain soluble silicon compounds. Silicon-based antifoam agents can be used

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[3] Bertin, E. P., *Principles and Practices of X-ray Spectrometric Analysis*, Plenum Press, New York, 1975, pp. 115–118.

in ethanol plants, which then pass silicon on to the finished ethanol-fuel blend. This test method can be used to determine if gasoline, gasoline-ethanol blends, and ethanol-fuel blends meet specifications with respect to silicon content of the fuel, and for resolution of customer problems.

4.5 Some silicon compounds covered by this test method are significantly more volatile than the silicon compounds typically used for the preparation of the calibration standards. Volatile compounds may not meet the stated precision from this test method because of selective loss of light materials during the analysis.

5. Interferences

5.1 Differences between the elemental composition of test samples and the calibration standards can result in biased silicon determinations. For fuels within the scope of this test method, the only important elements contributing to bias resulting from differences in the matrices of calibrants and test samples are hydrogen, carbon, and oxygen. A matrix-correction factor (C) may be used to correct this bias; the calculation is described in Annex A1. For general analytical purposes, the matrices of test samples and the calibrants are considered to be matched when the calculated correction factor C is within 0.95 to 1.05. No matrix correction is required within this range. A matrix correction is required when the value of C is outside the range of 0.95 to 1.05. For most testing, matrix correction can be avoided with a proper choice of calibrants. For example, Fig. 2 and the calculation in Annex A1 show that a calibrant with 87.5 % by mass carbon and 12.5 % by mass hydrogen can cover non-oxygen containing samples with C/H ratios from 5.0 to 11.0, which corresponds to a correction factor range of 0.95 to 1.05.

5.2 Fuels containing large quantities of ethanol, such as ethanol fuel blends, denatured fuel ethanol, and gasoline-ethanol blends (see Specifications D4806 and D5798), can have a high oxygen content leading to significant absorption of silicon Kα radiation and low silicon results. Such fuels may be analyzed using this test method provided either that correction

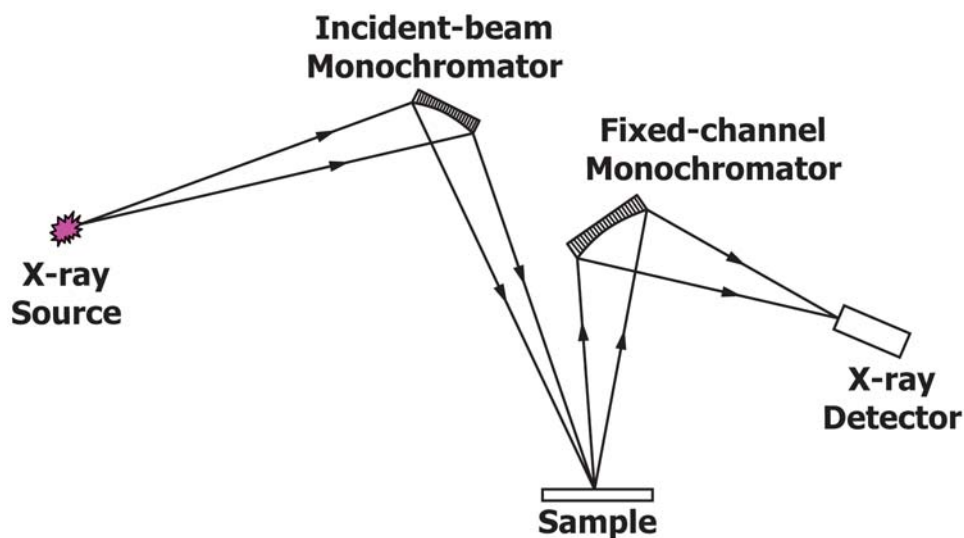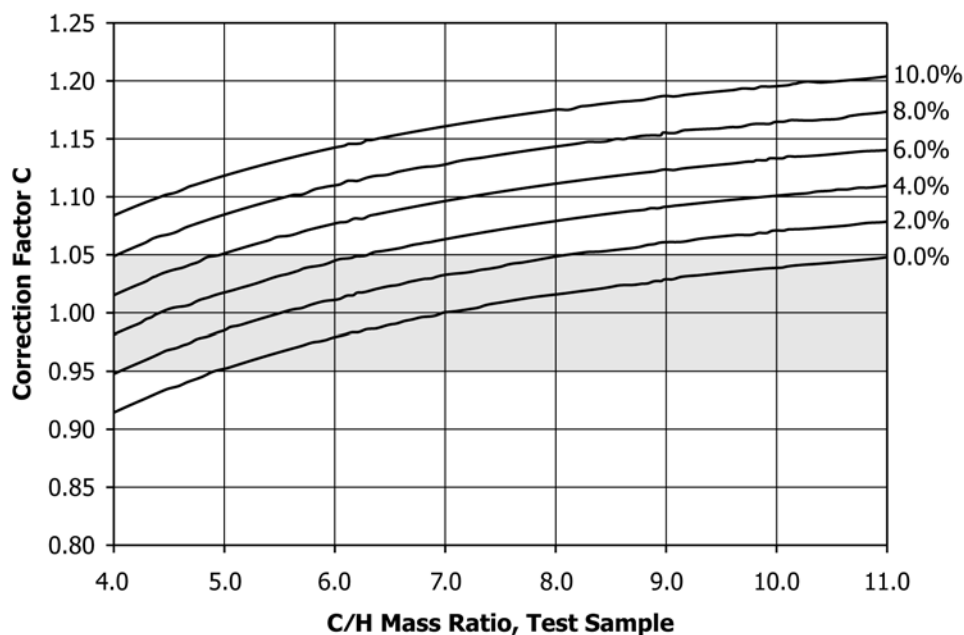**FIG. 1 Schematic of the MWDXRF Analyzer**

FIG. 2 Matrix Correction for a Test Sample versus C/H and Total Oxygen Content Using Chromium Kα for the Excitation Beam

factors (see Table 1 and Table 2) are applied to the results or by using calibration standards that are matrix matched to the test sample. For gasoline samples with oxygenates, up to 3.1 % by mass oxygen can be tolerated for test samples with the same C/H ratio as the calibrants.

5.2.1 For test samples with high oxygenate content, such as denatured fuel ethanol and ethanol fuel blends (see Specifications D4806 and D5798), ethanol-based calibrants may be used provided the correction factors as described in 5.1 are applied to the results. Table 1 and Table 2 show the correction factor that should be applied to the measurement results of the gasoline-ethanol and ethanol fuel blends if they are measured using either an *iso*octane or ethanol calibration curve.

NOTE 3—Alcohol based calibration standards may be preferred for test samples containing a high oxygenate content.

5.3 To minimize any bias in the results, use calibration standards prepared from silicon-free base materials of the same or similar elemental composition as the test samples.

5.3.1 When diluting samples, use a diluent with an elemental composition the same or similar to the base material used for preparing the calibration standards.

5.3.2 A base material for gasoline may be simulated by mixing 2,2,4-trimethylpentane (*iso*octane) and toluene in a ratio that approximates the expected aromatic content of the samples to be analyzed.

6. Apparatus

6.1 *Monochromatic Wavelength Dispersive X-ray Fluorescence (MWDXRF) Spectrometer*[4], equipped for X-ray detection at 0.713 nm (7.13 Å). Any spectrometer of this type may be used if it includes the following features, and the precision

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[4] The sole source of supply of the apparatus known to the committee at this time is XOS, Inc., 15 Tech Valley Drive, Suite 1, East Greenbush, NY 12061. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

TABLE 1 Correction Factors for Gasoline-Ethanol and Ethanol Fuel Blends Measured on an *Iso*octane Calibration Curve

NOTE 1—Determine the correction factor in the table below by finding the known ethanol content of the test specimen (for example, 15 % by mass) as the sum of the value in the first column and the value in the first row (for example, 15 = 10+5). The intersection of these two values is the correction factor (for example, 1.0844). Apply the correction according to 13.5. Refer to 7.7 and 11.1 for *iso*octane calibration.

Ethanol, % by mass	0 %	1 %	2 %	3 %	4 %	5 %	6 %	7 %	8 %	9 %
0 %	1.0000	1.0056	1.0112	1.0169	1.0225	1.0281	1.0337	1.0394	1.0450	1.0506
10 %	1.0562	1.0619	1.0675	1.0731	1.0787	1.0844	1.0900	1.0956	1.1012	1.1069
20 %	1.1125	1.1181	1.1237	1.1294	1.1350	1.1406	1.1462	1.1519	1.1575	1.1631
30 %	1.1687	1.1744	1.1800	1.1856	1.1912	1.1969	1.2025	1.2081	1.2137	1.2194
40 %	1.2250	1.2306	1.2362	1.2419	1.2475	1.2531	1.2587	1.2644	1.2700	1.2756
50 %	1.2812	1.2868	1.2925	1.2981	1.3037	1.3093	1.3150	1.3206	1.3262	1.3318
60 %	1.3375	1.3431	1.3487	1.3543	1.3600	1.3656	1.3712	1.3768	1.3825	1.3881
70 %	1.3937	1.3993	1.4050	1.4106	1.4162	1.4218	1.4275	1.4331	1.4387	1.4443
80 %	1.4500	1.4556	1.4612	1.4668	1.4725	1.4781	1.4837	1.4893	1.4950	1.5006
90 %	1.5062	1.5118	1.5175	1.5231	1.5287	1.5343	1.5400	1.5456	1.5512	1.5568

TABLE 2 Correction Factors for Gasoline-Ethanol and Ethanol Fuel Blends Measured on an Ethanol (E100) Calibration Curve

Note 1—Determine the correction factor in the table below by finding the known ethanol content of the test specimen (for example, 85 % by mass) as the sum of the value in the first column and the value in the first row (for example, 85 = 80+5). The intersection of these two values is the correction factor (for example, 0.9460). Apply the correction according to 13.5. Refer to 7.6 and 11.1 for ethanol calibration.

Ethanol, % by mass	0 %	1 %	2 %	3 %	4 %	5 %	6 %	7 %	8 %	9 %
0 %	0.6400	0.6436	0.6472	0.6508	0.6544	0.6580	0.6616	0.6652	0.6688	0.6724
10 %	0.6760	0.6796	0.6832	0.6868	0.6904	0.6940	0.6976	0.7012	0.7048	0.7084
20 %	0.7120	0.7156	0.7192	0.7228	0.7264	0.7300	0.7336	0.7372	0.7408	0.7444
30 %	0.7480	0.7516	0.7552	0.7588	0.7624	0.7660	0.7696	0.7732	0.7768	0.7804
40 %	0.7840	0.7876	0.7912	0.7948	0.7984	0.8020	0.8056	0.8092	0.8128	0.8164
50 %	0.8200	0.8236	0.8272	0.8308	0.8344	0.8380	0.8416	0.8452	0.8488	0.8524
60 %	0.8560	0.8596	0.8632	0.8668	0.8704	0.8740	0.8776	0.8812	0.8848	0.8884
70 %	0.8920	0.8956	0.8992	0.9028	0.9064	0.9100	0.9136	0.9172	0.9208	0.9244
80 %	0.9280	0.9316	0.9352	0.9388	0.9424	0.9460	0.9496	0.9532	0.9568	0.9604
90 %	0.9640	0.9676	0.9712	0.9748	0.9784	0.9820	0.9856	0.9892	0.9928	0.9964

and bias of test results are in accordance with the values described in Section 16.

6.1.1 *X-ray Source,* capable of producing X-rays to excite silicon. X-ray tubes with a power >20 W capable of producing Rh Lα, Pd Lα, Ag Lα, Ti Kα, Sc Kα, or Cr Kα radiation are recommended for this purpose.

6.1.2 *Incident-beam Monochromator,* capable of focusing with an effective collection solid angle greater than 0.05 sr and selecting a single wavelength of characteristic X-rays from the source onto the specimen. A monochromatic beam is considered to be monochromatic when it has an energy bandwidth (Full Width Half Maximum) less than ±1.5 % relative to the selected energy and containing more than 98 % flux of the spectrum of the excitation beam which is incident on the sample.

6.1.3 *Optical Path,* designed to minimize the absorption along the path of the excitation and fluorescent beams using a helium or vacuum atmosphere.

6.1.4 *Fixed-Channel Monochromator,* suitable for dispersing silicon Kα X-ray photons with an effective collection solid angle greater than 0.3 sr.

6.1.5 *Detector,* designed for efficient detection of silicon Kα X-ray photons.

6.1.6 *Single-Channel Analyzer,* an energy discriminator to monitor only silicon radiation.

6.1.7 *Removable Sample Cell,* compatible with the sample and the geometry of the MWDXRF spectrometer. A disposable cell is recommended.

6.1.8 *X-Ray Transparent Film,* for containing and supporting the test specimen in the sample cell (see 6.1.7) while providing a low-absorption window for X-rays to pass to and from the sample. Use an X-ray transparent film resistant to chemical attack that does not contain a listed silicon impurity. Follow manufacturer's recommendations for appropriate film types.

7. Reagents and Materials

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents 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.

7.2 *Calibration-Check Samples,* for verifying the accuracy of a calibration. The check samples shall have known silicon content and not be used in determining the calibration curve. A standard from the same reliable and consistent source of calibration standards used to determine the calibration curve is convenient to validate the calibration.

7.3 *Octamethylcyclotetrasiloxane (D4),* a high-purity material (typical purity 98 %), is known to be suitable for making silicon calibration standards. Use the known silicon concentration and the material purity when calculating the exact concentrations of silicon in calibration standards. (**Warning**—Octamethylcyclotetrasiloxane is harmful if swallowed or absorbed through skin. It is an eye irritant and may cause skin irritation.)

7.4 *Drift Correction Monitor(s) (Optional)*—, to determine and correct instrument drift over time (see 11.4, 12.1, and 13.1). Various forms of stable (with respect to repeated exposure to X-rays) silicon-containing materials are suitable drift correction monitors; for example, liquid petroleum, solid, pressed powder, metal alloy, and fused glass. The count rate displayed by the monitor sample, in combination with a convenient count time (T), shall be sufficient to give a relative standard deviation (RSD) of less than 1 % (see Appendix X1).

7.4.1 Calibration standards may be used as drift correction monitors. Because it is desirable to discard test specimens after each determination, a lower cost material is suggested for use over time. Any stable material meeting the recommendations of 7.4 or 7.4.1 may be used for monitoring of drift on a given day when samples are being analyzed.

[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 4—The effect of drift correction on the precision and bias of this test method has not been studied.

7.4.2 Drift correction may be done automatically if the instrument embodies this option, although the calculation may be readily done by conventional methods of data reduction and processing.

7.5 *Quality-Control (QC) Samples,* for use in establishing and monitoring the stability and precision of an analytical measurement system (see Section 15). Use homogeneous materials, similar to samples of interest and available in sufficient quantity to be analyzed regularly for a long period of time.

7.5.1 Verification of system control through the use of QC samples and control charting is highly recommended.

NOTE 5—Suitable QC samples can be prepared by combining retains of typical samples.

7.6 *Ethanol,* use a high purity grade and account for its silicon content when calculating the silicon concentrations of the calibration standards. (**Warning—**Ethanol is flammable and harmful if swallowed or inhaled. It is an eye irritant and may cause skin irritation.)

7.7 *2,2,4-Trimethylpentane (Isooctane),* use a high purity grade and account for its silicon content when calculating the silicon concentration of the calibration standards. (**Warning—***Iso*octane is flammable and harmful if swallowed or inhaled. It is an eye irritant and may cause skin irritation.)

7.8 *Toluene,* use a high purity grade and account for its silicon content when calculating the silicon concentration of the calibration standards. (**Warning—**Toluene is flammable and harmful if swallowed or inhaled. It is an eye irritant and may cause skin irritation.)

7.9 *Helium,* (for units that require helium per manufacturer), minimum purity 99.9 %, for use as an optical path.

8. Hazards

8.1 (**Warning—**Exposure to excessive quantities of X-ray radiation is injurious to health. The operator needs to take appropriate actions to avoid exposing any part of his/her body, not only to primary X-rays, but also to secondary or scattered radiation that might be present. The X-ray spectrometer should be operated in accordance with local and national regulations governing the use of ionizing radiation.)

8.2 Consult current health and safety regulations such as OSHA, suppliers' Material Safety Data Sheets and local regulations for all materials used in this test method.

9. Sampling and Sample Handling

9.1 Sample fuel according to the procedures in Practices D4057 or D4177.

9.2 Use the utmost care in sampling and handling gasoline to prevent evaporation of light ends which could change the concentration of silicon in the sample. Store gasoline in a leak tight container at 0 °C to 4 °C until ready for analysis. If possible, maintain at this temperature throughout any transfer and handling processes. Allow samples maintained at 0 °C to 4 °C to come to room temperature before testing, and expose these materials to ambient conditions only as long as necessary to obtain a sample for analysis. Analyze test specimens as soon as possible after sub-sampling from bulk container. Do not allow bulk container to remain uncovered any longer than is needed to obtain desired sub-samples.

9.3 For specimen preparation, see 10.2.

9.3.1 Because impurities and thickness variations can occur in commercially available transparent films and vary from lot to lot, use calibration-check samples (see 7.2) to verify calibration integrity after starting each new batch of film or if the type and thickness of the window film is changed.

9.4 When reusable sample cells are used, thoroughly clean and dry cells before each use.

9.4.1 Disposable sample cells shall not be reused.

10. Preparation of Apparatus and Specimens for Analysis

10.1 *Analyzer Preparation*—Ensure that the MWDXRF analyzer has been installed and put into operation according to manufacturer's instructions. Allow sufficient time for instrument electronics to stabilize. Perform any instrument checkout procedures required. When possible, the instrument should be run continuously to maintain optimum stability.

10.1.1 Use the count time (T) recommended by the instrument manufacturer for the lowest silicon concentration expected. The typical time for each measurement is five to ten minutes.

10.1.2 Alternatively, determine T expected for a desired count precision by following the procedure in Appendix X1.

10.2 *Specimen Preparation*—Prepare a specimen of a test sample or a calibration standard as follows:

10.2.1 Carefully transfer a sufficient portion of the liquid to fill a sample cell above a minimum depth beyond which additional liquid does not affect the count rate. In a XRF sample cup, filling the sample cell to two thirds of the cell's depth is generally adequate.

10.2.2 Fit an unused piece of X-ray-transparent film over the sample-cell opening and attach securely. Use the same batch of film for the analysis of test samples and the calibration standards used for constructing the calibration curve. Avoid touching the inside of the sample cell, any portion of the film exposed to the liquid or the X-ray beam, and also avoid touching the instrument window. (It is highly recommended that clean, disposable rubber or plastic gloves be used when preparing test specimens.) Oil from fingerprints can generate errors in the analysis of silicon. Ensure the film is clean, taut, wrinkle-free, and the test specimen is not leaking to ensure reliable results.

10.2.3 Provide a small vent to prevent bowing of the window film caused by the accumulating vapor. Many commercially available sample cells provide a means to vent the space above the liquid.

10.2.4 Perform the analysis of the specimen promptly after preparing the specimen. Do not let the specimen remain in the sample cell any longer than necessary before collecting the data.

11. Calibration

11.1 Obtain or prepare a set of calibration standards by careful mass dilution of octamethylcyclotetrasiloxane (D4) with a suitable base material (BM) (see Section 5). The concentrations of the unknown samples shall lie within the calibration range that is used. All standards used in the analysis shall be from a reliable and consistent source, which may include commercially available standards. Approximate recommended nominal silicon concentration standards are listed as follows for the range of 3 mg/kg to 100 mg/kg: 0.0 mg/kg (base material), 10 mg/kg, 25 mg/kg, 100 mg/kg, and 250 mg/kg.

11.1.1 Take into account any silicon in the base materials when calculating the silicon content (mg/kg) in each of the calibration standards as shown in Eq 1:

$$Si = [(D4 * Si_{D4}) + (BM * Si_{BM})]/(D4 + BM) \quad (1)$$

where:

Si = mass fraction of silicon in the prepared standards, mg/kg,

$D4$ = actual mass of octamethylcyclotetrasiloxane, g,

Si_{D4} = mass fraction of silicon in D4, mg/kg, typically 37.838%,

BM = actual mass of base material, g, and

Si_{BM} = mass fraction of silicon in the base material, mg/kg.

11.2 Following instrument manufacturer's instructions and the instructions in 12.2, measure the silicon fluorescence intensity (total silicon count rate) for each of the calibration standards. Convert total counts (N) to count rate (R_S) in counts per second by dividing N by the count time (T) using units of seconds (see 10.1.1, 10.1.2, and Eq 2).

$$R_S = N/T \quad (2)$$

R_S = measured total count rate of the silicon fluorescence from 11.2, counts per second,

N = total counts collected at 0.713 nm, and

T = seconds required to collect N counts.

11.3 Construct a linear calibration model by either:

11.3.1 Using the software supplied by the instrument manufacturer, or

11.3.2 Perform a linear regression of the calibration measurements. The following linear equation (Eq 3) describes the regression:

$$R_S = Y + E \times Si \quad (3)$$

R_S = measured total count rate of the silicon fluorescence from 11.2, counts per second,

Y = y-intercept of the calibration curve, counts per second,

E = slope of the calibration curve, counts kg s^{-1} mg^{-1}, and

Si = silicon concentration, mg/kg.

11.4 When using drift correction, measure the total counts of silicon fluorescence from the drift-monitor sample during the calibration procedure. Determine R_S by dividing the total counts by T. The factor, R_S, determined on the drift-monitor sample at the time of calibration, is factor A in Eq 4.

11.5 Immediately after analyzing the calibration standards, determine the silicon concentration of one or more calibration-check samples (see 7.2). The determined value shall be in the range defined by the certified concentration plus or minus the repeatability of this test method. If this criterion is not met, the calibration process and calibration standards are suspect, corrective measures shall be taken, and the calibration repeated. The degree of matrix mismatch between calibration check samples and standards should be considered when evaluating a calibration.

12. Procedure

12.1 When using drift correction, prior to analyzing samples on a given day, analyze the drift-monitor sample measured at the time of calibration. Divide the total counts measured on the drift-monitor sample by T to convert to R_S; this R_S corresponds to factor B in Eq 4.

12.2 Analyze each sample of interest as follows:

12.2.1 Prepare a test specimen of the sample of interest according to 10.2.

12.2.2 Place the sample cell containing the test specimen in the X-ray beam, as directed by the instrument manufacturer's instructions (see Analyzer Preparation, 10.1).

12.2.3 Measure the total counts of silicon fluorescence (N), and divide the total counts by T to calculate R_S (see Eq 2).

12.3 If R_S for a test specimen is greater than the highest count rate in the calibration curve, quantitatively dilute a fresh portion of the sample with the base material used to prepare the calibration standards. Dilute the sample so the resultant count rate is within the limits of the calibration curve. Repeat the procedures described in 12.2 on a test specimen of the diluted sample.

12.4 Calculate the concentration of silicon in the test specimen as instructed in Section 13.

13. Calculation

13.1 When using a drift monitor sample, calculate a drift correction factor (F) for changes in daily instrument sensitivity according to Eq 4. If a drift monitor is not used, F is set equal to 1.

$$F = A/B \quad (4)$$

where:

A = R_S for the drift monitor sample determined at the time of calibration (11.4), and

B = R_S for the drift monitor sample determined at the time of analysis (12.1).

13.2 Calculate the drift-corrected count rate (R_{cor}) for the test specimen as follows:

$$R_{cor} = F \times R_S \quad (5)$$

F = drift correction factor, calculated by Eq 4, and

R_S = total count rate for test specimen.

13.3 Calculate the silicon content (Si) of the test specimen by using the drift-corrected count rate (R_{cor}) in place of R_s in Eq 3.

13.4 If the test specimen was prepared from a quantitatively diluted sample, correct the measured concentration for sample dilution. The silicon concentration (Si_o) in the original, undiluted sample is calculated as follows:

$$Si_o = [Si_d \times (M_o + M_b)/M_o] - [Si_b \times (M_b/M_o)] \qquad (6)$$

Si_d = concentration of silicon in test specimen of the diluted sample (from 13.3), mg/kg,
M_o = mass of original sample, g,
M_b = mass of base material used to dilute sample, g, and
Si_b = concentration of silicon in diluent, mg/kg.

13.5 If a correction factor was used to account for differences in the sample matrix versus the matrix of the calibration standards (see Section 5), apply the factor by multiplying the silicon concentration, Si_o, obtained in Eq 6 by the correction factor.

14. Report

14.1 Report silicon concentration of the test sample calculated from Section 13 using units of mg/kg, rounded to the nearest 0.1 mg/kg for concentrations <100 mg/kg, and rounded to the nearest 1 mg/kg for concentrations ≥100 mg/kg. Indicate that the results were obtained according to Test Method D7757.

15. Quality Control

15.1 It is recommended that each laboratory establish a program to ensure that the measurement system described in this test method is in statistical control. One part of such a program might be the regular use and charting[6] of quality control samples (see 7.5). It is recommended that at least one type of quality control sample be analyzed that is representative of typical laboratory samples as defined in Practice D6299.

15.2 In addition to running a quality control sample (see 7.5), it is strongly recommended that the calibration blank (for example, *iso*octane) be analyzed on a daily basis when samples are being analyzed on a given day.

15.2.1 The measured concentration for the blank should be less than 1 mg/kg silicon. If the measured concentration for the blank is greater than 1 mg/kg, re-standardize the instrument and repeat the measurement of the blank (use a fresh sample and fresh cell). If the result falls outside the acceptable range, carry out a full calibration. If the sample loading port becomes contaminated, especially when analyzing <20 mg/kg silicon level samples, it is necessary to open and clean it according to manufacturer's recommendations before further use.

15.3 *Results Validation*—Once a standard or sample has been measured, a procedure should be carried out to validate that measurement. This requires the operator to check for obvious signs of damage to the sample such as leaking sample cells and inspection of any secondary film.

15.4 *Observation of the Resultant Analysis*—If a result is considered outside normal thresholds, a repeat of the analysis should be carried out to confirm anomalous results.

15.5 Regular checks should be carried out to ensure that purging gas performance is within the instrument manufacturer's specification.

15.6 Drift and quality control standards/monitors shall be run on a regular basis. The tolerance level of the checks made using these monitors should be such that a protocol of either drift correction or total recalibration is carried out if the results fall outside these levels. All measurements should be repeated between the last accepted monitor result and point of non-compliance should a current monitor measurement prove to be outside acceptable levels.

16. Precision and Bias[7]

16.1 *Precision*—The precision of this test method was determined by statistical examination of an interlaboratory study, in accordance with Practice D6300. Precision was calculated by using data from seven laboratories, using seven newly manufactured analyzers, which each analyzed 24 silicon-doped samples in the range of 3 mg/kg to 100 mg/kg. The samples included 6 gasolines, 4 gasolines with 10 % ethanol, 2 naphthas, 2 toluenes, 4 E85, and 6 E100 samples. Samples were analyzed in duplicate and back-to-back. A pooled limit of quantitation (PLOQ) of approximately 3 mg/kg was determined for all sample types.

16.1.1 *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 following values only in one case in 20:

$$Repeatability\ (r) = 0.5582 \cdot X^{\,0.5471} \qquad (7)$$

where:
X = silicon concentration in mg/kg total silicon. See Table 3 for calculated values.

16.1.2 *Reproducibility*—The difference between two single and independent results obtained by different operators working in different laboratories on different equipment on identical test material would in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in 20:

TABLE 3 Precision Values, All Sample Types

Si, mg/kg	Repeatability r, mg/kg Eq 7 values	Reproducibility R, mg/kg Eq 8 values
3.0	1.0	1.9
5.0	1.3	2.5
10.0	2.0	3.7
25.0	3.2	6.1
50.0	4.7	9.0
100.0	6.9	13.1

$$Reproducibility\ (R) = 1.0535 \cdot X^{0.5471} \qquad (8)$$

where:

X = silicon concentration in mg/kg total silicon. See Table 3 for calculated values.

16.2 *Bias*—Since there is no accepted reference material suitable for determining the bias in this test method for measuring silicon, bias has not been determined.

17. Keywords

17.1 analysis; ethanol; fuel; gasoline; monochromatic X-ray; MWDXRF; silicon; spectrometry; wavelength dispersive X-ray fluorescence; WDXRF; X-ray

ANNEX

(Mandatory Information)

A1. MATRIX CORRECTION

A1.1 Calculate a matrix-correction factor[8] (C) for differences in the carbon, hydrogen, and oxygen composition between a test sample and the calibration standards according to Eq A1.1. If an absorption correction is not used, C is set equal to 1. The subscript "cal" refers to the calibration samples, and the subscript "test" refers to the test sample. The variable, µ, is the average, mass absorption coefficient.

$$C = \left[{}^{\lambda 0}\mu_{test} + {}^{\lambda Si}\mu_{test}\,G \right] / \left[{}^{\lambda 0}\mu_{cal} + {}^{\lambda Si}\mu_{cal}\,G \right] \qquad (A1.1)$$

$$ {}^{\lambda 0}\mu = {}^{\lambda 0}\mu_C X_C + {}^{\lambda 0}\mu_O X_O + {}^{\lambda 0}\mu_H X_H \qquad (A1.2)$$

$$ {}^{\lambda Si}\mu = 454.7\,X_C + 1034.0\,X_O + 1.18\,X_H \qquad (A1.3)$$

where:

G = a constant determined by the angle between the sample surface and the incident and emitted beams. The instrument manufacturer provides G; 0.87 is a typical value for the analyzer shown in Fig. 1.

${}^{\lambda 0}\mu$ = average, mass absorption coefficient (cm^2/g) for the incident-beam wavelength (λ0),

${}^{\lambda Si}\mu$ = average, mass absorption coefficient (cm^2/g) for silicon radiation at λ = 0.713 nm,

${}^{\lambda 0}\mu_C$ = mass absorption coefficient (cm^2/g) of carbon for λ_0 (=14.8 for Cr Kα excitation),

${}^{\lambda 0}\mu_O$ = mass absorption coefficient (cm^2/g) of oxygen for λ_0 (=37.7 for Cr Kα excitation),

${}^{\lambda 0}\mu_H$ = mass absorption coefficient (cm^2/g) of hydrogen for λ_0 (=0.34 for Cr Kα excitation).

X_C = mass fraction of carbon in calibrant or sample of interest,

X_O = mass fraction of oxygen in calibrant or sample of interest, and

X_H = mass fraction of hydrogen in calibrant or sample of interest.

A1.2 Calculate the absorption-corrected count rate (RC) for the test sample as follows:

$$R_C = C \times R_S \qquad (A1.4)$$

where:

R_C = corrected count rate for test sample,

C = absorption-correction factor, calculated in Eq A1.1, and

R_S = total count rate for test sample.

A1.3 Calculate the silicon content (Si) of the test sample by applying the absorptioncorrected count rate (from Eq A1.4) to the calibration Eq 3.

A1.4 An example is provided in Fig. 2 to illustrate the absorption correction. The example uses a test sample with C/H ratios from 5 to 11 and total oxygen from 0 % to 10 % by mass. The correction factor is calculated for chromium Kα excitation using Eq A1.1 for this test sample and a calibration sample with C/H = 7.0 and no oxygenate.

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[8] Goldstein, J. I., et al., *Scanning Electron Microscopy and X-ray Microanalysis*, Plenum Press, New York, 1992 , pp. 743 –777.

APPENDIXES

(Nonmandatory Information)

X1. DETERMINING COUNT TIME

X1.1 The quality of X-ray fluorescence analyses is a function of count precision,[9] which can be improved by increasing the count time (T). It is recommended to accumulate a sufficient number of silicon counts to achieve a 1.0 % expected relative standard deviation (% RSD) of the net silicon signal, or better, when sensitivity and concentration make it practical (see X1.3).

X1.2 To determine the count time to achieve a desired RSD for a sample, analyze the sample using T = 100 s and determine R_S and R_B. Calculate T for the desired percent RSD using the following equation:

$$\% \, RSD = 100 \, T^{-0.5} \, (R_S + R_B)^{0.5}/(R_S - R_B) \qquad (X1.1)$$

where:
R_S = measured total count rate, counts per second, and
R_B = background count rate measured on a blank sample (see X1.2.2) containing no silicon.

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[9] Bertin, E. P., *Principles and Practices of X-ray Spectrometric Analysis*, Plenum Press, New York, 1975, pp. 472–500.

X1.2.1 A current calibration equation can be used to estimate R_s if the concentration of the test sample is approximately known. The background count rate may be estimated by substituting the y-intercept (Y) from the most recent linear regression calibration (see 11.3.2) for R_B in Eq X1.1.

X1.2.2 The T required to attain the desired precision is applicable to samples with silicon concentrations equal to or greater than the sample used to determine T.

X1.2.3 Because a single-channel analyzer is used to measure the silicon signal, R_B cannot be determined directly on samples containing silicon. Therefore, R_B may be obtained by measuring a blank sample containing no silicon or by substituting the y-intercept from the most recent calibration curve for R_B in Eq X1.1.

X1.3 As silicon concentration decreases, the count time necessary to achieve the desired precision increases. If it is more practical to analyze all samples using the same count time, use the count time determined for the lowest expected silicon concentration.

X2. AIDS TO THE ANALYST

X2.1 Best practices for obtaining quality measurement results include: cleanliness steps to reduce contamination, correct sample preparation and measurement, and analyzer quality control. These steps become increasingly important when measuring low concentration values.

X2.1.1 See Practice D7343 for further guidance on optimization, sample handling, calibration, and validation of X-ray fluorescence spectrometry methods.

X2.2 Maintain a clean sample preparation area to minimize sample contamination. Ensure that removable sample cells, X-ray transparent film, and transfer pipettes are kept covered in a dust free area, such as a plastic bag, covered container, or drawer. If a vent tool is used (not needed for pre-vented sample cups), make sure it is also kept in a dust free environment, and clean reusable vent tools with an appropriate solvent after each use.

X2.3 Consult the manufacturer for instructions on cleaning the analyzer, including acceptable solvents for cleaning. Cleaning procedures for the sample area should be performed once daily or more often if necessary. If a suspicious measurement result is obtained, perform the cleaning procedures.

X2.3.1 Canned or compressed air, though not mandatory, is highly recommended in the cleaning and specimen preparation process. Canned air is used as a drying agent after cleaning and as a means to remove airborne contaminants such as dust. Do

not shake the can before use as this may dislodge a visible propellant stream from the can that may form a contaminant coating. If this happens, perform the cleaning step again to remove the contamination or replace the disposable film as appropriate.

X2.3.2 Generally, it is acceptable to clean the sample chamber area with a clean, lint-free cloth wetted with isopropyl alcohol. This includes the inside of the lid, sample holder, and adjacent area, excluding any window films. Dry the area with canned air.

X2.3.3 Disposable secondary or primary windows should not be cleaned; they should be replaced instead per manufacturer's instructions. Blow the new film off with canned air before assembling, and make sure the completed window is wrinkle free. Make sure to verify calibration integrity after starting a new batch of film.

X2.3.4 Non-disposable primary windows should be cleaned carefully according to the manufacturer's instructions. Polyimide primary windows can be cleaned with a foam tipped (or lint-free) swab wetted with isopropyl alcohol. Shake the swab to remove excess alcohol, then hold the swab parallel to the top of the analyzer and carefully wipe the primary window with the swab. Polyimide primary windows are delicate and care should be taken when cleaning these primary windows to avoid breakage. Dry the primary window with canned air. If canned

air propellant is visible when drying the window, repeat the primary window cleaning process.

X2.4 Follow Section 9 for Sampling and Sample Handling and Section 10 for Preparation of Apparatus and Specimens for Analysis instructions. Additional to these instructions, it is recommended to use canned air in sample preparation. Use canned air to blow out the sample cup before the sample is prepared (not necessary for preassembled, pre-vented sample cells).

X2.4.1 Use appropriate sample storage and mixing procedures. Make sure samples are homogenous before transferring a specimen to the sample cell. Filter the sample if necessary to remove particulate matter. Disposable transfer pipettes are recommended for filling the sample cup rather than pouring from the sample container. Do not reuse disposable pipettes.

X2.4.2 Before placing the film on the sample cup, use canned air to blow off the sample side of the film. When flipping the sample cell over for venting, make sure it rests on a sample stand or on a lint-free cloth to prevent film contamination. These steps are not necessary if using preassembled, pre-vented sample cells.

X2.4.3 Using canned air, blow off the sample cup film and then visually inspect film surface for leaks, wrinkles, or particulate matter before placing the specimen in the analyzer. Make sure to verify calibration integrity after starting a new batch of film. Measure the specimen promptly after preparation, and remove it promptly after analysis. Visually inspect the specimen after analysis for leaks. If the specimen has leaked, clean up the spill, change or clean any primary or secondary windows as necessary, and measure a new specimen.

X2.5 To ensure the analyzer is performing satisfactorily, follow Section 15 for Quality Control, unless quality control/quality assurance protocols are already established in the testing facility.

SUMMARY OF CHANGES

Subcommittee D02.03 has identified the location of selected changes to this standard since the last issue (D7757 – 12) that may impact the use of this standard. (Approved July 1, 2017.)

(1) Added Practice D7343 to Referenced Documents.
(2) Deleted former Fig. 3, Fig. 4, and Table 1.
(3) Added new Table 1 and Table 2.

(4) Revised subsections 1.1, 4.1, 4.4, 4.5, 5.2, 5.2.1, 6.1.1, 6.1.8, 7.9, 9.3, 10.2.2, 12.2.2, and 16.1.2.
(5) Added new Appendix X2.