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.

Designation: D7757 – 22

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

This standard is issued under the fixed designation D7757; 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 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 5.4), 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 6, 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 17).

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 14.5). 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 6.

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, health, and environmental 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

D4175 Terminology Relating to Petroleum Products, Liquid Fuels, and Lubricants

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, Liquid Fuels, and Lubricants

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

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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.

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

Products and Lubricants

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms used in this test method, refer to Terminology D4175.

4. Summary of Test Method

4.1 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.

5. Significance and Use

5.1 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.

5.2 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]

5.3 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.

5.4 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 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.

5.5 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.

6. Interferences

6.1 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

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

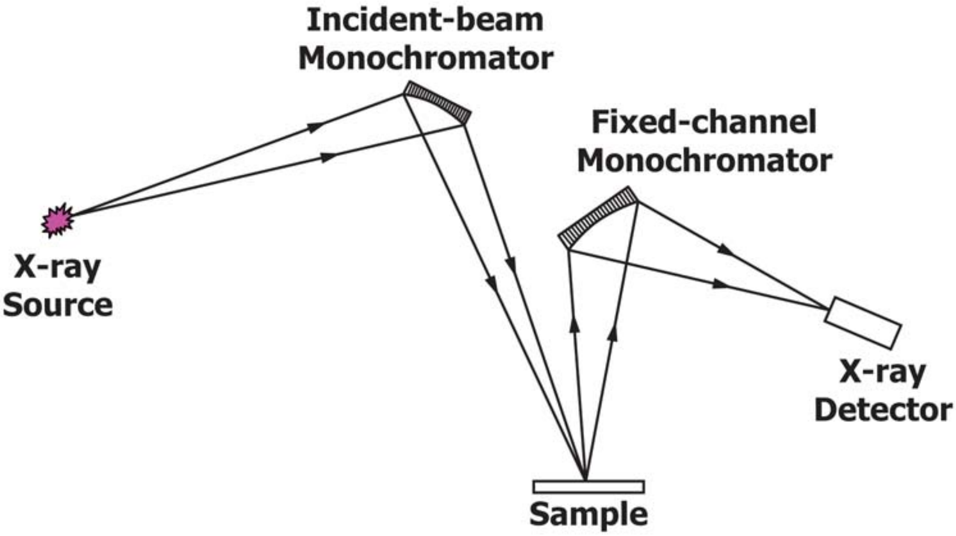

FIG. 1 Schematic of the MWDXRF Analyzer

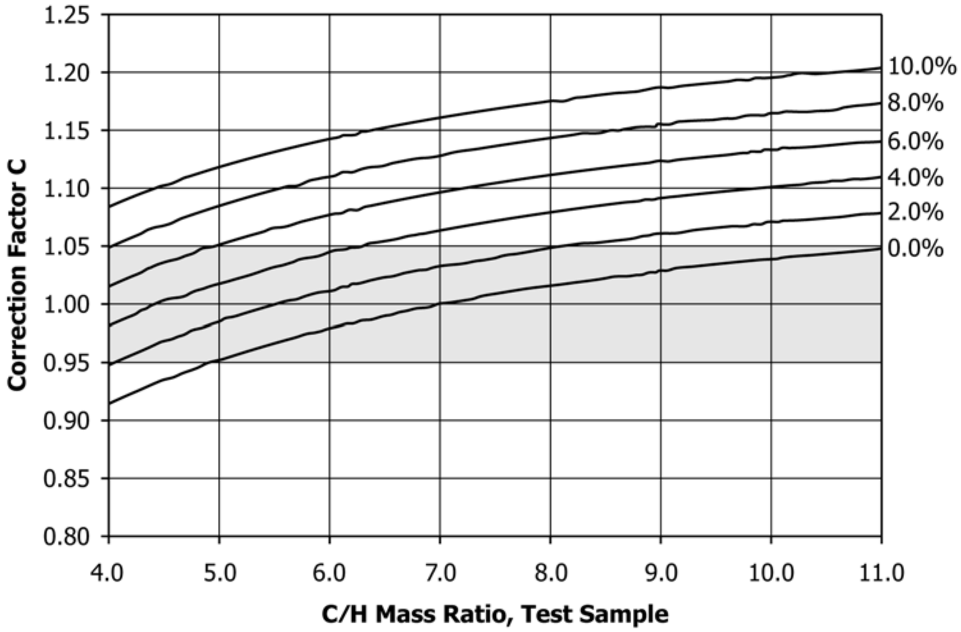

FIG. 2 Matrix Correction for a Test Sample versus C/H and Total Oxygen Content Using Chromium Kα for the Excitation Beam

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.

6.2 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 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.

6.2.1 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 6.1 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.

6.3 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.

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 14.5. Refer to 8.7 and 12.1 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 14.5. Refer to 8.6 and 12.1 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

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

6.3.2 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.

7. Apparatus

7.1 *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 and bias of test results are in accordance with the values described in Section 17.

7.1.1 *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.

7.1.2 *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.

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

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

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

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

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

7.1.8 *X-Ray Transparent Film,* for containing and supporting the test specimen in the sample cell (see 7.1.7) 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.

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 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 *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.

8.3 *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.)

8.4 *Drift Correction Monitor(s) (Optional)*—, to determine and correct instrument drift over time (see 12.4, 13.1, and

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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.

[5] *ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials*, 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.

14.1). 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).

8.4.1 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 8.4 or 8.4.1 may be used for monitoring of drift on a given day when samples are being analyzed.

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

8.4.2 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.

8.5 *Quality-Control (QC) Samples,* for use in establishing and monitoring the stability and precision of an analytical measurement system (see Section 16). Use homogeneous materials, similar to samples of interest and available in sufficient quantity to be analyzed regularly for a long period of time.

8.5.1 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.

8.6 *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.)

8.7 *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.)

8.8 *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.)

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

9. Hazards

9.1 (**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.)

9.2 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.

10. Sampling and Sample Handling

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

10.2 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.

10.3 For specimen preparation, see 11.2.

10.3.1 Because impurities and thickness variations can occur in commercially available transparent films and vary from lot to lot, use calibration-check samples (see 8.2) to verify calibration integrity after starting each new batch of film or if the type and thickness of the window film is changed.

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

10.4.1 Disposable sample cells shall not be reused.

11. Preparation of Apparatus and Specimens for Analysis

11.1 *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.

11.1.1 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.

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

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

11.2.1 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.

11.2.2 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.

11.2.3 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.

11.2.4 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.

12. Calibration

12.1 Obtain or prepare a set of calibration standards by careful mass dilution of octamethylcyclotetrasiloxane (D4) with a suitable base material (BM) (see Section 6). 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.

12.1.1 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:

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

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.

12.2 Following instrument manufacturer's instructions and the instructions in 13.2, 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 11.1.1, 11.1.2, and Eq 2).

$$R_S = N/T \tag{2}$$

R_S = measured total count rate of the silicon fluorescence from 12.2, counts per second,
N = total counts collected at 0.713 nm, and
T = seconds required to collect N counts.

12.3 Construct a linear calibration model by either:

12.3.1 Using the software supplied by the instrument manufacturer, or

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

$$R_S = Y + E \times Si \tag{3}$$

R_S = measured total count rate of the silicon fluorescence from 12.2, 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.

12.4 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.

12.5 Immediately after analyzing the calibration standards, determine the silicon concentration of one or more calibration-check samples (see 8.2). 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.

13. Procedure

13.1 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.

13.2 Analyze each sample of interest as follows:

13.2.1 Prepare a test specimen of the sample of interest according to 11.2.

13.2.2 Place the sample cell containing the test specimen in the X-ray beam, as directed by the instrument manufacturer's instructions (see Analyzer Preparation, 11.1).

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

13.3 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 13.2 on a test specimen of the diluted sample.

13.4 Calculate the concentration of silicon in the test specimen as instructed in Section 14.

14. Calculation

14.1 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.

$$F = A/B \tag{4}$$

where:

A = R_S for the drift monitor sample determined at the time of calibration (12.4), and

B = R_S for the drift monitor sample determined at the time of analysis (13.1).

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

$$R_{cor} = F \times R_S \tag{5}$$

F = drift correction factor, calculated by Eq 4, and
R_S = total count rate for test specimen.

14.3 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.

14.4 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:

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

Si_d = concentration of silicon in test specimen of the diluted sample (from 14.3), 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.

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

15. Report

15.1 Report silicon concentration of the test sample calculated from Section 14 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.

16. Quality Control

16.1 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 8.5). 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.

16.2 In addition to running a quality control sample (see 8.5), 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.

16.2.1 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.

16.3 *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.

16.4 *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.

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

16.6 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 noncompliance should a current monitor measurement prove to be outside acceptable levels.

17. Precision and Bias[7]

17.1 *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.

17.1.1 *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:

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

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[6] *ASTM MNL 7, Manual on Presentation of Data and Control Chart Analysis, Section 3, Control Chart for Individuals*, ASTM International, W. Conshohocken, PA.

[7] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1735. Contact ASTM Customer Service at service@astm.org.