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, RFG, ethanol and ethanol-fuel blends, and toluene at concentrations of 3 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.*

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

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, RFG, ethanol and ethanol-fuel blends, and toluene with minimum sample preparation. Typical analysis time is 5 to 10 min per sample.

4.2 Excitation by monochromatic X-rays reduces background, simplifies matrix correction, and increases the signal/

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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 D02.03 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.
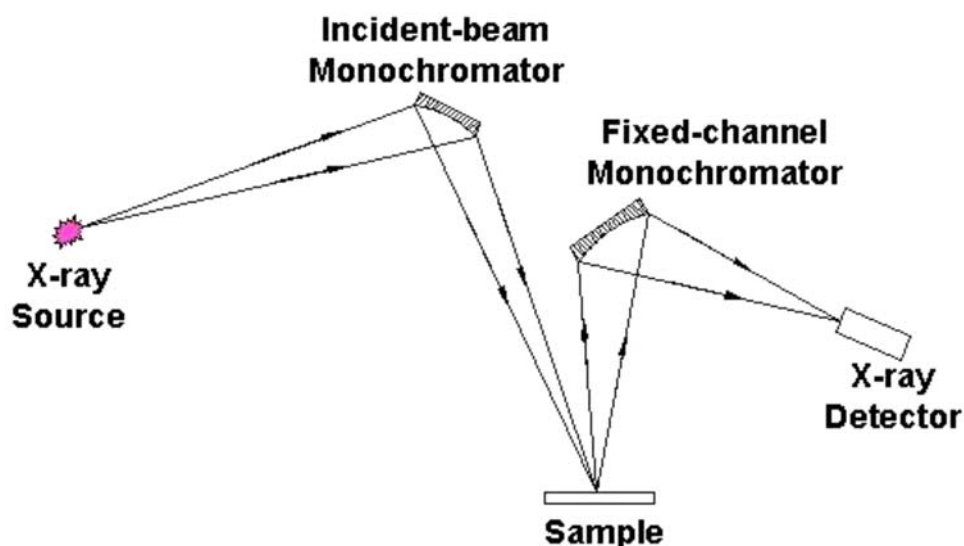
FIG. 1 Schematic of the MWDXRF Analyzer

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, 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 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 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 (for example, hexamethyldisiloxane with a boiling point of 101°C), which typically have boiling points below 170°C can give higher silicon sensitivities than the standard.

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 mass % carbon and 12.5 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 fuel ethanol, 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 Figs. 3 and 4) 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 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 fuel ethanol, denatured fuel ethanol, and gasoline-ethanol 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 Figs. 3 and 4 show the correction factor that should be applied to the measurement results of the gasoline-gasoline ethanol 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.

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[3] Bertin, E. P., *Principles and Practices of X-ray Spectrometric Analysis*, Plenum Press, New York, 1975, pp. 115-118.
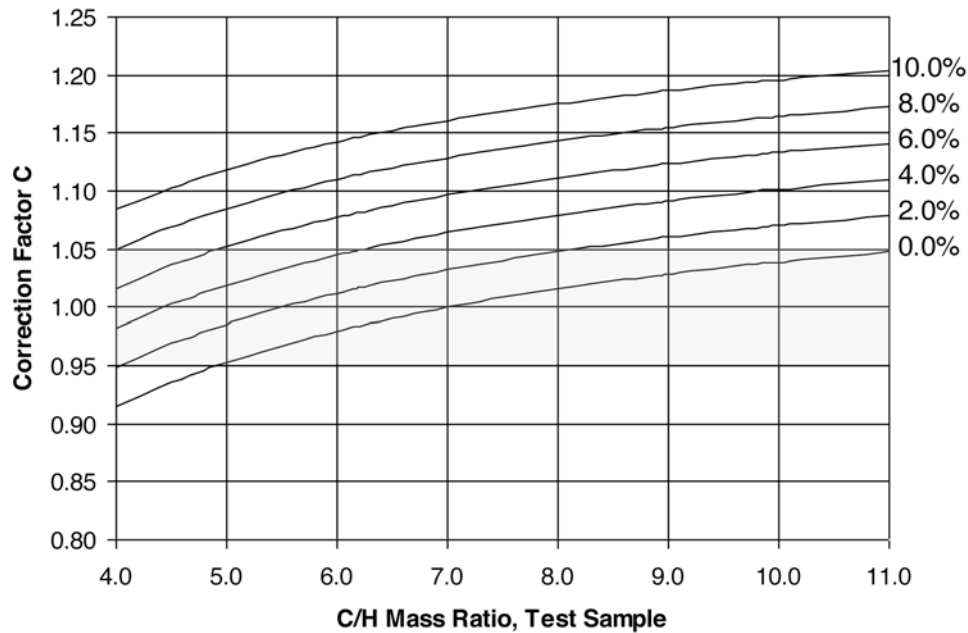
FIG. 2 Matrix Correction for a Test Sample versus C/H and Total Oxygen Content Using Chromium Kα for the Excitation Beam

TABLE 1 Gasoline-Ethanol Blend Correction Factors

Isooctane Calibration Curve		Ethanol (E100) Calibration Curve	
Ethanol in Test Sample, wt%	Correction Factor C[A]	Gasoline in Test Sample, wt%	Correction Factor C[A]
0%	1.00	0%	1.00
2%	1.01	2%	0.99
4%	1.02	4%	0.99
6%	1.03	6%	0.98
8%	1.04	8%	0.97
10%	1.06	10%	0.96
20%	1.11	20%	0.93
30%	1.17	30%	0.89
40%	1.22	40%	0.86
50%	1.28	50%	0.82

[A] Correction factor is for gasoline-ethanol blend test sample measured on either an isooctane calibration curve or an ethanol calibration curve.

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 (isooctane) 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 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 >20W capable of producing Rh Lα, Pd Lα, Ag Lα, Ti Kα, Sc Kα, and 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.

[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.