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Designation: D 6445 – 99

An American National Standard

Standard Test Method for Sulfur in Gasoline by Energy-Dispersive X-ray Fluorescence Spectrometry[1]

This standard is issued under the fixed designation D 6445; 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 measurement of sulfur in nonleaded gasoline and gasoline-oxygenate blends. The applicable concentration range is 48 to 1000 mg/kg sulfur.

1.2 The values stated in SI units are to be regarded as the standard. The preferred concentration units are mg/kg sulfur.

1.3 This standard may involve hazardous materials, operations, and equipment. *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.* For specific precautionary statements, see Sections 5 and 7.

2. Referenced Documents

2.1 *ASTM Standards:*

D 3120 Test Method for Trace Quantities of Sulfur in Light Liquid Petroleum Hydrocarbons by Oxidative Microcoulometry[2]

D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products[3]

D 4177 Practice for Automatic Sampling of Petroleum and Petroleum Products[3]

3. Summary of Test Method

3.1 The sample is placed in the beam emitted from an X-ray source. The resultant excited characteristic X radiation is measured, and the accumulated count is compared with counts from previously prepared calibration standards to obtain the sulfur concentration in mg/kg. One group of calibration standards is required to span the concentration 5 to 1000 mg/kg sulfur.

4. Significance and Use

4.1 This test method provides a means of quantifying sulfur content in gasoline. It can be referenced in specification documents as a means to determine if the material meets the desired sulfur content. It is a rapid and precise measurement of total sulfur in petroleum products with a minimum of sample preparation.

4.2 The quality of gasoline is related to the amount of sulfur present. Knowledge of sulfur concentration is necessary for processing purposes. There are also regulations promulgated in federal, state, and local agencies that restrict the amount of sulfur present in gasoline as it affects performance characteristics and potential corrosion problems and emission levels. During combustion, the sulfur content in fuel affects SO_x emissions, which degrade air quality. Certain jurisdictions may restrict the amount of sulfur in gasoline to prevent or limit pollution to the environment.

5. Apparatus

5.1 *Energy-dispersive X-ray Fluorescence Analyzer*—The analyzer needs to have sufficient sensitivity to measure the concentration of sulfur at 500 mg/kg with a one standard deviation value due to counting statistics no greater than 10 mg/kg under optimized conditions. Any energy dispersive X-ray fluorescence analyzer may be used if its design incorporates, as a minimum, the following features:

5.1.1 *Source of X-ray Excitation*—X-ray tube with energy above 2.5 keV.

NOTE 1—Operation of analyzers using X-ray tubes is to be conducted in accordance with the manufacturer's safety instructions and federal state and local regulations.

5.1.2 *Sample Cell*, providing a sample depth of at least 4 mm and equipped with replaceable X-ray transparent film window.

5.1.3 *X-ray Detector*, with a resolution value not to exceed 800 eV at 2.3 keV. A gas filled proportional counter has been found suitable to use.

5.1.4 *Filters*, or other means of discriminating between sulfur K_a radiation and other X rays.

[1] This test method is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.03 on Elemental Analysis.

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[2] *Annual Book of ASTM Standards*, Vol 05.01.

[3] *Annual Book of ASTM Standards*, Vol 05.02.

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5.1.5 Signal conditioning and data handling electronics that include the functions of X-ray intensity counting, spectral overlap corrections, and conversion of sulfur X-ray intensity into mg/kg sulfur concentration. It is also imperative that the instrument has the capability to monitor counts for at least one energy region distinct from the sulfur region to allow compensation for variations in spectral background (that is, calculation of net intensities).

5.1.6 *Display or Printer*, that reads or prints out in mg/kg or masspercent sulfur.

6. Matrix Effects

6.1 Matrix effects refer to changes in measured intensity of sulfur caused by concentration variations of the elements in a sample. These variations directly influence X-ray absorption and change the measured intensity of each element. For example, performance enhancing additives, such as oxygenates in gasoline, can affect the apparent sulfur reading. These types of interferences are always present in X-ray fluorescence analysis and are completely unrelated to spectral interferences.

6.2 Many modern instruments have the capability to correct for matrix effects by ratioing measured sulfur intensities to that of X-ray radiation scattered from the sample (for example, scattered X-ray tube lines). This can be an effective method for compensating for matrix differences between samples and standards, although it can result in some degradation of the measurement precision. It is the user's responsibility, however, to ensure that the matrix corrections applied are accurate. It is recommended that these are checked by analyzing standard reference materials and that the software corrections offered by the manufacturer not be accepted at face value. In addition, corrections should be verified for new formulations.

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.[4] 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. The concentration should be known to at least three significant figures or nearest 1 mg/kg, whichever is higher.

7.2 *Di-n-Butyl Sulfide (DBS)*, a high purity standard, minimum 96 % purity, with a certified analysis for sulfur content. Use the certified sulfur content when calculating the exact concentrations of the calibration standards (see 10.1).

NOTE 2—**Warning:** Di-*n*-butyl sulfide is flammable and toxic.

7.3 *Thiophene*, sulfur content 37.72 mass %, 99 % purity.

7.4 *2-Methylthiophene*, 32.00 % sulfur, 98 % purity.

NOTE 3—Purity on the label for di-*n*-butyl sulfide, thiophene, and 2-methylthiophene is only a nominal value. It is essential to know the concentration of sulfur in the sulfur standard, not the purity, since impurities may also be sulfur containing compounds.

7.5 *Isooctane (2,2,4–trimethylpentane)*, with a certified analysis for sulfur content or checked by Test Method D 3120 or equivalent test method as containing less than 3 mg/kg sulfur.

7.6 *Toluene*, with a certified analysis for sulfur content or checked by Test Method D 3120 or equivalent test method as containing less than 3 mg/kg sulfur.

7.7 *X-ray Transparent Film*—Any film that resists attack by the sample, is free of sulfur, and is sufficiently X-ray transparent may be used. Films found to be suitable are polyester, polypropylene, polycarbonate, and polyimide films. Typical film thicknesses range from 1.5 to 8 µm. Film thickness will affect the transmission of X rays and the films resistance to chemical attack.

7.7.1 Samples of high aromatic content may dissolve polyester and polycarbonate films. In these cases, other materials besides these films may be used for X-ray windows, provided that they do not contain any elemental impurities. An optional window material is polyimide film. While polyimide film absorbs sulfur X rays more than other films, it may be a preferred window material as it is much more resistant to chemical attack by aromatics and exhibits higher mechanical strength.

7.8 *Sample Cells*, resistant to sample attack and meeting geometry requirements of spectrometer. Disposable cells are preferred.

8. Sampling and Specimen Preparation

8.1 Take samples in accordance with the instructions in Practice D 4057 or D 4177 where appropriate. Thoroughly mix and analyze samples immediately after pouring into a sample cell. Inspect the sample for any air bubbles or sediment. Allow air bubbles to escape or resample if necessary.

NOTE 4—The measured sulfur concentration may vary with the time that the sample/standard contacts the film covering the sample cell. By consistently minimizing the length of time the film comes into contact with the sample or standards, possible variations can be reduced.

8.2 If using reusable sample cells, clean and dry cells before use. Do not reuse disposable sample cells. Replacement of the X-ray film of a reused sample cell is essential for the measurement of each sample. Avoid touching the inside of the sample cell or portion of the window film in the cell or in the instrument window that is exposed to X rays. Oil from fingerprints can affect the reading when analyzing for low levels of sulfur. Wrinkles in the film will affect the intensity of sulfur X rays transmitted. Therefore, it is essential that the film be taut and clean to ensure reliable results. The analyzer will need recalibration if the type or thickness of the window material is changed.

8.3 Impurities or thickness variations, which may affect the measurement of low levels of sulfur, have been found in window materials films and may vary from lot to lot. Therefore, check the calibration after starting each new package of film.

[4] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, D.C. 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.

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