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CAN/CGSB-3.0
No./N° 16.0-2004

ICS 71.040.50

WITHDRAWAL

October 2011

Methods of testing petroleum and associated products Sulphur in diesel fuel and similar middle distillates by energy dispersive X-ray fluorescence spectrometry (EDXRF)

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RETRAIT

Octobre 2011

Méthodes d'essai des produits pétroliers et produits connexes Soufre dans le carburant diesel et les distillats moyens similaires par spectrométrie de fluorescence X à dispersion d'énergie (EDXRF)

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CAN/CGSB-3.0
No. 16.0-2004

Supersedes CAN/CGSB-3.0
No. 16.0-95

Withdrawn/Retirée

Methods of Testing Petroleum and Associated Products

Sulphur in Diesel Fuel and Similar Middle Distillates by Energy Dispersive X-Ray Fluorescence Spectrometry (EDXRF)

ICS 71.040.50

National Standard of Canada

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NATIONAL STANDARD OF CANADA

CAN/CGSB-3.0
No. 16.0-2004

Supersedes CAN/CGSB-3.0
No. 16.0-95

METHODS OF TESTING PETROLEUM AND ASSOCIATED PRODUCTS

SULPHUR IN DIESEL FUEL AND SIMILAR MIDDLE DISTILLATES BY ENERGY DISPERSIVE X-RAY FLUORESCENCE SPECTROMETRY (EDXRF)

Withdrawn/Retiree

Prepared by the
Canadian General Standards Board CGSB

Approved by the
Standards Council of Canada

Published July 2004 by the
Canadian General Standards Board
Gatineau, Canada K1A 1G6

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National Standard of Canada

CGSB Gatineau Canada K1A 1G6	METHODS OF TESTING PETROLEUM AND ASSOCIATED PRODUCTS	CAN/CGSB-3.0
	Sulphur in Diesel Fuel and Similar Middle Distillates by Energy Dispersive X-Ray Fluorescence Spectrometry (EDXRF)	No. 16.0-2004

Supersedes CAN/CGSB-3.0
No. 16.0-95

1. SCOPE

1.1 This test method covers the determination of total sulphur concentrations in diesel fuel and similar middle distillates such as kerosene and aviation jet fuel in the range from 0.010 to 0.500% by mass (100 to 5000 mg/kg), using energy dispersive X-ray fluorescence spectrometry.

1.2 The testing and evaluation of a product against this method may require the use of materials and/or equipment that could be hazardous. This document does not purport to address all of the safety aspects associated with its use. Anyone using this method has the responsibility to consult the appropriate authorities and to establish appropriate health and safety practices in conjunction with any applicable regulatory requirements prior to its use. Please refer to the manufacturer's material safety data sheet (MSDS) for safety requirements for the specific chemicals used in this method.

2. REFERENCED PUBLICATIONS

2.1 The following publications are referenced in this method:

2.1.1 ASTM International

RR D02:1007 Vol. 5.03 1998 — Manual in Determining Precision Data for ASTM Methods on Petroleum Products and Lubricants

RR D02:1418 — Round Robin Data for ASTM D4294, Standard Test Method for Sulfur in Petroleum Products by Energy-Dispersive X-Ray Fluorescence Spectroscopy

D4057 — Standard Practice for Manual Sampling of Petroleum and Petroleum Products

D4177 — Standard Practice for Automatic Sampling of Petroleum and Petroleum Products

D5854 — Standard Practice for Mixing and Handling of Liquid Samples of Petroleum and Petroleum Products

D6299 — Standard Practice for Applying Statistical Quality Assurance Techniques to Evaluate Analytical Measurement System Performance

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

E691 — Standard Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method.

2.1.2 International Organization for Standardization (ISO)

ISO 4259 — Petroleum products — Determination and application of precision data in relation to methods of test.

2.2 A dated reference in this method is to the issue specified. An undated reference in this method is to the latest issue, unless otherwise specified by the authority applying this method. The sources are given in the Notes section.

3. SUMMARY OF TEST METHOD

3.1 The liquid sample to be analyzed is transferred to a sample cup fitted with a transparent window. The cup is placed in the beam of an exciting radiation emitted from an X-ray source, which may be an X-ray tube or a radioisotope. The exciting radiation generates characteristic X-ray radiation of the elements in the fuel sample. The intensity of

Withdrawn/Retiree

the resulting characteristic X-ray radiation of sulphur is compared to that measured on previously prepared calibration standards to obtain the sulphur concentration in mass percent.

3.2 The calibration range is from 0.010 to 0.500% by mass of sulphur. It is applicable to diesel fuel and similar middle distillates such as kerosene and aviation jet fuel in which the sulphur concentration does not exceed 0.500% by mass.

4. SIGNIFICANCE AND USE

4.1 During combustion, the sulphur content in fuels results in SOx emissions and can contribute to particulate emissions. Both of these emissions degrade air quality. Certain jurisdictions may restrict the amount of sulphur in fuel to prevent or limit pollution of the environment.

5. INTERFERENCES

5.1 Spectral interferences are those caused by the closeness of the X-ray characteristic lines of the elements present in a sample and the limited detector ability to completely resolve them. As a result, the lines produce spectral peaks that overlap with each other. Spectral interferences are expected from the elements mentioned in par. 5.4. Follow the manufacturer's operating-guide to compensate for the interferences.

5.2 Matrix effects are caused by concentration variations of the elements in the sample. These variations directly influence X-ray absorption and change the measured intensity of each element. This type of interference is always present in X-ray fluorescence analysis and is completely unrelated to spectral interferences.

5.3 Both types of interferences may be compensated for in contemporary instruments with the use of built-in software for spectra deconvolution and inter-element correction by multiple regression.

5.4 Samples containing heavy metal additives, lead alkyls, etc., may interfere with the sulphur determination. Elements such as silicon, phosphorus, calcium, potassium, and halides will interfere if present at concentrations greater than one tenth of the measured concentration of sulphur.

6. APPARATUS

6.1 **Energy Dispersive X-ray Fluorescence Analyzer** — An energy dispersive X-ray fluorescence spectrometer may be used if its design incorporates, as a minimum, the following features and if test results from these are shown to be equivalent on the samples of interest. The required design features shall include:

a. A source of exciting radiation with significant energy output above the 2.5 keV energy level.

b. A removable sample cup with replaceable transparent plastic film window and providing a sample depth of at least 5 mm.

c. An X-ray detector with high detection sensitivity for the sulphur K-alpha radiation, at the energy of 2.3 keV.

d. An energy resolution capable of discriminating between sulphur K-alpha radiation and the X-rays from other elements. Filters or other means may be used to eliminate extraneous X-rays from striking the detector, thus achieving better detector resolution.

e. A signal conditioning and data handling electronics that include the functions of X-ray intensity counting and converting it into percent of sulphur concentration.

f. A display or printer capable of direct readout of X-ray counts, or sulphur concentration.

6.1.1 The relative standard deviation of the counting statistics at the 0.050 mass % sulphur level shall be less than 2%.

6.2 **Analytical Balance** — A balance capable of weighing to the nearest 0.1 mg.

7. REAGENTS

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 whenever such specifications are available. Other grades may be used, provided that the reagent is pure enough to permit its use without lowering the accuracy of the analysis.

Withdrawn/Retiree

7.2 **Di-n-Butyl Sulphide (DBS)** — Obtain the lot analysis of DBS and calculate the actual mass percentage of total sulphur.

7.3 **Mineral Oil** — An oil, such as a white oil, having a viscosity similar to that of diesel fuel, ACS grade or grade containing less than 0.0020% by mass (20 ppm) of sulphur.

8. SAMPLING

8.1 Samples shall be taken in accordance with ASTM D4057, D4177 and D5854, as appropriate.

9. SAFETY PRECAUTIONS

9.1 Commercially available instruments employing radioisotopes as sources of exciting radiation are as a rule constructed to international standard requirements of radiation safety and, therefore, should not present any imminent radiation hazard, whether in use or not.

9.2 The instruments using X-ray tube(s) as excitation source(s) shall be shielded to prevent radiation hazard while in operation (powered on).

9.3 All instruments should be operated with strict adherence to the manufacturers' operational and safety instructions.

10. SAMPLE CUP PREPARATION

10.1 Sample cups must be clean and dry before use. It is strongly recommended that disposable sample cups be used whenever possible. Window material of the cup should exhibit the smallest possible absorption of sulphur X-rays; 6 µm thick polycarbonate or polyester film is usually used as a window material. Samples of high aromatic content are known to react with the film. Therefore, it is essential to renew the film window after each measurement and when the sample is left in the cup for an extended period of time.[1] Avoid touching the inside of the sample cup or portion of the window film that is exposed to the X-rays. Oil from fingerprints can affect the reading when analyzing low levels of sulphur. Wrinkles in the film will affect the number of sulphur X-rays transmitted. The importance of the film's smoothness and cleanliness in ensuring reliable results cannot be over-stressed.

10.2 Other materials besides polycarbonate films may be used for X-ray windows, provided that they do not contain any elemental impurities.

11. CALIBRATION

11.1 **Certified Calibration Standards** — Calibration standards that are certified by a standards organization in accordance with a protocol that is technically equivalent to that used by the U.S. National Institute of Science and Technology (NIST) for certification of standard reference materials may be used.

11.1.1 ***Interlaboratory Tested Standards*** — Material with composition similar to the sample intended to be tested by this test method, and with reference values established in accordance with an interlaboratory testing protocol meeting the technical requirements of ASTM E691, RR D02:1007, D6300 or ISO 4259.

11.1.2 ***Calibration Standards Prepared from Pure Compounds*** — Material prepared in accordance with procedures described in par. 11.2.

11.2 **Preparation of Calibration Standards** (from Pure Compounds) — Prepare the sample matrix in pure light mineral oil. Make up the calibration standards in two ranges:

Range #1: 0.000 to 0.100% by mass of sulphur
Range #2: 0.100 to 0.500% by mass of sulphur.

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[1] *The measured sulphur concentration may vary with the time that the sample/standard contacts the film covering the sample cup. To reduce such possible variation, the length of time that the sample/standard contacts the film should be minimized and consistent.*

Withdrawn/Retirée

The target concentrations for the two calibration ranges are listed in Table 1.

TABLE 1

Calibration Standards, Recommended Target Concentrations

Range Number	Sulphur Content Range (% by Mass)	Sulphur Content (% by Mass)
1	0.000 - 0.100	0.0000 0.0100 0.0300 0.0500 0.0700 0.1000
2	0.100 - 0.500	0.1000 0.2000 0.3000 0.4000 0.5000

Note: *See Table 2 for suggested masses to prepare standards.*

TABLE 2

Calibration Standards, Recommended Target Sulphur Concentrations, Preparation Table[2, 3, 4, 5]

Range Number	Sulphur Content (% by Mass)	Mass of Mineral Oil (grams)[6]	Mass of DBS (grams)
1	0.000	50.00	0.0000
	0.010	50.00	0.0229
	0.030	50.00	0.0686
	0.050	50.00	0.1144
	0.070	50.00	0.1603
	0.099	50.00	0.2224
2	0.100	50.00	0.2293
	0.200	50.00	0.4607
	0.300	50.00	0.6942
	0.400	50.00	0.9298
	0.500	50.00	1.1677

[2] *The calculations in Table 2 are based on a value of 21.91 mass % sulphur in di-n-butyl sulphide and a value of <0.0001 mass % sulphur in the mineral oil used.*

[3] *If the mineral oil being used for the preparation of standards contains sulphur, include this value in the equation to calculate the sulphur content of the prepared standards.*

[4] *Weigh the di-n-butyl sulphide (DBS) to the recommended mass as close as possible. It is important that the exact mass is known and thus the exact concentration of the prepared standards can be calculated and entered into the instrument for calibration purposes.*

[5] *A solid certified standard may be used; however, proper orientation must be maintained.*

[6] *The mineral oil is not assumed to be 0.0000% by mass of sulphur. Consult your supplier for an accurate sulphur concentration or test the mineral oil using a low level sulphur analyzing method.*

Withdrawn/Retirée

11.3 **Calculations** — To calculate the exact concentration of the prepared standards, use the following equation:

$D = [(A \times E) + (B \times C)] / (A + B)$

where:

A = actual mass of DBS added (grams)
B = actual mass of mineral oil used (grams)
C = sulphur content of the mineral oil (% by mass)
D = sulphur concentration of the prepared standard (% by mass)
E = percentage of sulphur (% by mass of sulphur) in the DBS

For proper calibration of the instrument, standards meeting the requirements of section 11 and the nominal values in Table 1 should be used.

11.4 **Storage of Standards** — Store standards in dark (amber) tightly closed glass bottles having Teflon-lined caps, in a dark, cool place. After a prolonged period of storage, mix each standard in its storage bottle before use. The standard must be free of air bubbles before it is analyzed. Discard the standard if any sediment, phase separation or discoloration is observed.

12. PREPARATION OF INSTRUMENT

12.1 Set up the instrument according to the manufacturer's instructions. (It is recommended that whenever possible the instrument should be left on continuously to maintain optimum stability.)

13. PROCEDURE

13.1 Prepare the sample cup (sample cell) in accordance with section 10 and fill it with sample to a minimum depth of 5 mm. Provide adequate headspace. Provide a vent hole in the cup on the opposite side of the window to reduce bowing of the cup window during measurement of volatile samples.

13.2 **Instrument Calibration** — Calibrate the instrument for each of the two ranges as listed in Table 1, following the manufacturer's instructions. The calibration procedure involves setting up the instrument for the recording of the net sulphur X-ray intensity, followed by measurement of known standards. Measure each standard three times using a counting time of 200 to 300 s. The average values are used to develop a calibration curve having 6 to 7 data points for each range.

13.3 **Sensitivity Check** — Measure the appropriate certified calibration standard three times immediately after calibration at a given concentration range. Record the individual results and their average. Use the average value obtained as the reference for any future measurements using this calibration curve.

13.3.1 Quality control standards are used to verify instrument stability. These quality control standards must be prepared using the same techniques as the preparation of the calibration standards. An industry-accepted practice to establish measurement process stability is to use control charts on results obtained from testing quality control materials as if they were normal production samples to verify instrument stability. Under this scheme, the control limits are generated by control chart data.[7]

13.4 **Analysis of Unknown Samples** — Fill the cup with the sample to be measured to at least 5 mm depth. Ensure that no air bubbles are present between the cup window and the liquid sample. Measure each sample three times (see Table 3 for the recommended counting times for the specific type of instrument). Obtain the average of the readings for the sulphur content in the unknown sample.

Withdrawn/Retirée

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[7] *The principal factor to consider when determining the frequency of testing the quality control samples are:*

1. *Utilization factor of the analytical measurement system*
2. *Criticality of the quality being measured*
3. *Established system stability and precision performance based on historical data*
4. *Analytical measurement, system method requirements*
5. *Contractual/regulatory obligations*
6. *Business economics*
7. *Instrument design.*

TABLE 3

Counting Times for Sulphur Content Analysis

Sulphur Content Range (% by Mass)	Counting Time (seconds)
Tube Source Instruments	
0.000 - 0.100 0.100 - 0.500	200 to 300 100
Isotope Source Instruments	
0.000 - 0.100 0.100 - 0.500	300 100 to 200

14. RESULTS

14.1 Report the results to the nearest 0.001% by mass in the range from 0.010 to 0.500% mass of sulphur.

14.2 Results for sulphur content may be reported in units of milligrams per kilogram, commonly referred to as parts per million by mass.

14.2.1 If units of milligrams per kilogram are desired for the sulphur content, report results to the nearest 10 mg/kg in the range from 100 to 5000 mg/kg.

14.2.2 To convert sulphur results from percent by mass to milligrams per kilogram, multiply a percent by mass result by 10 000 to give the result in milligrams per kilogram.

15. QUALITY CONTROL

15.1 Confirm the performance of the test procedure by analyzing a quality control (QC) sample that is stable and representative of the sample of interest. When the quality control/quality assurance protocols are already established in the testing facility, these may be used to confirm the reliability of the test result. When there is no quality control/quality assurance protocol established in the testing facility, Appendix A can be used to perform this function.

15.2 **Quality Control Standards** — Several additional standards (quality control standards), having sulphur concentrations other than those found in Table 1, may prove useful. (See Table 4 for the recommended quality control standards.) Calibration standards prepared in accordance with par. 11.2, as well as any appropriate certified standard prepared in accordance with par. 11.1, may be used as quality control standards. Control samples may be calibration standards with sulphur levels close to those typically encountered in the normal use of this test method, or aliquot samples prepared from a larger batch of material representative of that normally encountered oth in composition and sulphur level. It is recommended that at least one control sample be of the latter. Samples should be stored in an environment suitable for long-term storage, without degradation. Analysis of results from these samples can be carried out using control chart techniques.[7] It is recommended to discard the test aliquot of the standard after measurement. (See Tables 4 and 5 for recommendations on choosing and preparing the quality control standards.)

TABLE 4

Recommended Quality Control Standards

Range Number	Sulphur Content Range (% by Mass)	Sulphur Content (% by Mass)
1	0.010 - 0.100	0.0150 0.0450 0.0600 0.0800
2	0.100 - 0.500	0.1500 0.3500

Withdrawn/Retirée

TABLE 5

Suggested Quality Control Standards, Preparation Table[2, 3, 4, 5]

Range Number	Sulphur Content (% by Mass)	Mass of Mineral Oil (grams)[6]	Mass of DBS (grams)
1	0.015	50.00	0.0343
	0.045	50.00	0.1029
	0.060	50.00	]0.1373
	0.080	50.00	0.1833
2	0.150	50.00	0.3447
	0.350	50.00	0.8117

TABLE 6

Repeatability and Reproducibility

Sulphur Content (% by Mass)	Repeatability (*r*) (+/- % by Mass of Sulphur)	Reproducibility (*R*) (+/- % by Mass of Sulphur)
0.010	0.0011	0.0031
0.020	0.0016	0.0044
0.030	0.0019	0.0054
0.040	0.0022	0.0062
0.050	0.0025	0.0069
0.060	0.0027	0.0076
0.070	0.0029	0.0082
0.080	0.0031	0.0088
0.090	0.0032	0.0093
0.100	0.0035	0.0098
0.150	0.0043	0.0120
0.200	0.0049	0.0139
0.300	0.0060	0.0170
0.400	0.0070	0.0196
0.500	0.0078	0.0219

TABLE 7

Bias

NIST Standard	Sulphur Content (% by Mass)	Bias	Significant
SRM 1616a	0.0146	0.0009	No
SRM 2724a	0.0430	0.0008	No
SRM 1617a	0.173	0.0003	No
SRM 1623c	0.381	-0.0119	Yes
SRM 1621e	0.948	-0.0198	No
SRM 2717	3.02	0.0072	No

Withdrawn/Retirée

16. PRECISION AND BIAS

16.1 **Precision** — The precision of this test method as obtained by statistical analysis of interlaboratory test results on diesel fuel is as follows:[8]

16.1.1 ***Repeatability*** — The difference between successive test results obtained by the same operator with the same operating conditions on identical test materials would, in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in twenty (Table 6).

Repeatability (r) = $0.011(S^{0.5})$

where:

S = % by mass of sulphur

16.1.2 ***Reproducibility*** — The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would, in the long run, exceed the following values only in one case in twenty (Table 6).

Reproducibility (R) = $0.031(S^{0.5})$

where:

S = % by mass of sulphur

16.2 **Bias** — An ASTM interlaboratory study included eight NIST reference materials. The certified values and bias are given in Table 7. Supporting data are available from ASTM Headquarters. Request Research Report RR D02:1418.

17. NOTES

17.1 **Related Publications**

17.1.1 Canadian General Standards Board (CGSB)

CAN/CGSB-3.0 No. 16.1 — Sulphur in Gasoline by Energy Dispersive X-Ray Fluorescence Spectrometry (EDXRF).

17.1.2 ASTM International

D4294 — Standard Test Method for Sulfur in Petroleum Products by Energy-Dispersive X-Ray Fluorescence Spectroscopy.

17.2 **Sources of Referenced Publications**

The following addresses were valid at the date of publication.

17.2.1 The publication referred to in par. 17.1.1 may be obtained from the Canadian General Standards Board, Sales Centre, Gatineau, Canada K1A 1G6. Telephone (819) 956-0425 or 1-800-665-2472. Fax (819) 956-5644. E-mail ncr.cgsb-ongc@pwgsc.gc.ca. Web site www.ongc-cgsb.gc.ca.

17.2.2 The publications referred to in par. 2.1.1 and 17.1.2 may be obtained from ASTM International, 100 Barr Harbor Drive, West Conshohocken, PA 19428-2959, U.S.A., telephone (610) 832-9585, fax (610) 832-9555, Web site www.astm.org, or from IHS Canada (par. 17.2.3).

17.2.3 The publication referred to in par. 2.1.2 may be obtained from the IHS Canada, 1 Antares Drive, Suite 200, Ottawa, Ontario K2E 8C4. Telephone (613) 237-4250 or 1-800-854-7179. Fax (613) 237-4251. E-mail gic@ihscanada.ca.

Withdrawn/Retired

[8] *When determining the precision of this method, only diesel fuels were used; therefore, the precision statement does not apply to similar middle distillates such as kerosene and aviation jet fuel.*

APPENDIX A

(This appendix does not form a mandatory part of the method.)

A1. QUALITY CONTROL

A1.1 Confirm the performance of the instrument or the test procedure by analyzing a quality control (QC) sample that is, if possible, representative of the samples typically analyzed.

A1.2 Prior to monitoring the measurement process, the user of the method needs to determine the average value and control limits of the QC sample.[A1, A2, A3]

A1.3 Record the QC results and analyze by control charts or other statistically equivalent techniques to ascertain the statistical control status of the total testing process.[A1, A2, A3] Any out-of-control data should trigger investigation for root cause(s). The results of this investigation may, but not necessarily, result in instrument recalibration.

A1.4 In the absence of explicit requirements given in the test method, the frequency of QC testing is dependent on the criticality of the quality being measured, the demonstrated stability of the testing process, and customer requirements. Generally, a QC sample should be analyzed each testing day with routine samples. The QC frequency should be increased if a large number of samples are routinely analyzed. However, when it is demonstrated that the testing is under statistical control, the QC testing frequency may be reduced. The QC sample precision should be periodically checked against the ASTM method precision to ensure data quality.[A2]

A1.5 It is recommended that, if possible, the type of QC sample that is regularly tested be representative of the samples routinely analyzed. An ample supply of QC material should be available for the intended period of use, and must be homogeneous and stable under the anticipated storage conditions.

See footnotes below for guidance on QC and Control Charting techniques.

Withdrawn/Retired

[A1] *ASTM D6299 Applying SQA Techniques to Evaluate Analytical System Performance.*

[A2] *ASTM MNL7A: Manual on Presentation of Data Control Chart Analysis, 7th ed., Section 3: Control Chart for Individuals.*

[A3] *ASTM DXXXX TQA in the Petroleum and Lubricant Testing Laboratories (currently under development).*

Withdrawn/Retirée