

California Environmental Protection Agency



Air Resources Board

**PROCEDURE FOR THE DETERMINATION OF SULFUR IN FUELS BY
ENERGY-DISPERSIVE X-RAY FLUORESCENCE SPECTROMETRY**

Standard Operating Procedure MV-FUEL-150

Revision 2.0

Effective: July 23, 2014

Fuel Analysis and Methods Evaluation Section
Chemical Analysis & Emissions Research Branch
Emissions Compliance, Automotive Regulations & Science Division

9528 Telstar Avenue
El Monte, CA 91731

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1 Introduction

- 1.1 This procedure describes the determination of sulfur content in petroleum products such as marine gas oil and marine diesel oil by energy-dispersive x-ray fluorescence spectrometry.
- 1.2 This method determines total sulfur in liquid hydrocarbons with a boiling point range from approximately 25 to 400 degrees Celsius, with viscosities between approximately 0.2 and 10 cSt (mm/S) at room temperature. This procedure is applicable to products having sulfur contents in the range of 0.01% (*m/m*) to 0.25% (*m/m*). The term “% (*m/m*)” is used to represent the mass fraction of analyte/sample.
- 1.3 The Air Resources Board utilizes this procedure to determine compliance with regulations for fuel sulfur for ocean-going vessels within California waters and 24 nautical miles of the California water baseline (13 CCR 2299.2 and 17 CCR Section 93118.2).
- 1.4 This procedure is based on ISO 8754:2003 (E), Petroleum Products- Determination of Sulfur Content- Energy-dispersive X-Ray Fluorescence Spectrometry.

2 Method

- 2.1 An Energy-dispersive X-ray spectrometer is used to measure sulfur contents in marine gas oil and marine diesel oil.
- 2.2 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 a calibration graph plotting counts against sulfur content as percentage by mass [%(*m/m*)], on a series of calibration samples covering the range of sulfur contents under examination.
- 2.3 This test method provides rapid and precise measurement of total sulfur in petroleum products with a minimum sample preparation. A typical analysis time is 1-4 minutes per sample.

3 Instrumentation and Apparatus

- 3.1 Energy-dispersive X-ray fluorescence analyzer: use any suitable model source of X-Ray excitation (such as Oxford X-Supreme 8000): with significant X-ray flux at energies above 2.5 keV.

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- 3.2 Removable sample cup: providing a sample depth of at least 3 mm, and equipped with replaceable X-ray transparent Mylar film.
- 3.3 X-ray detector: with high sensitivity at 2.3 keV.
- 3.4 Filters: or other means of discriminating between sulfur $K\alpha$ radiation and other X-rays.

4 Reagents and Materials

- 4.1 White oil (light paraffin oil) of high purity grade, with a maximum sulfur content of 20 mg/kg.
- 4.2 Sulfur compounds, of known sulfur content, used for the preparation of the primary standards. Suggested compounds are dibenzothiophene (DBT), dibutylsulfide (DBS), or thionaphthene (TNA).
- 4.3 Quality Control Sample: petroleum product with a sulfur concentration between 0.01%-0.25%.
- 4.4 Carrier gas: helium, high purity grade, 99.998% minimum purity.

5 Calibration Standards Preparation

- 5.1 Use either certified reference materials, or primary standards prepared from sulfur compounds dissolved in white oil as a basis for preparation of the appropriate range of calibration standards.
- 5.2 Certified Reference Materials: Use materials from a national standards body or accredited supplier, with a range of certified traceable sulfur contents for the production of calibration curves for routine analysis. An example of such supplier is ASTM D4294 Calibration Standard Mixture Set in mineral oil with sulfur weight values of 0.0100%, 0.0250%, 0.0500%, 0.1000%, and 0.2500% from Spectrum Quality Standards, LTD.
- 5.3 Prepared Standards
 - 5.3.1 Prepare a range of at least five primary standards. Either use primary standards to prepare the calibration standards by dilution with white oil, or prepare the complete range of calibration standards.

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- 5.3.2 Weigh the appropriate quantity of white oil (Table 1), into a 100 ml container and add the corresponding quantity of the selected sulfur compound. Mix the contents of the container thoroughly at room temperature.
- 5.3.3 Calculate the exact sulfur content, w_s , expressed as a percentage by mass [%(m/m)] to three decimal places in each case, from the amounts of white oil and sulfur compounds used as below:

$$w_s = m_1 * w_{s,c} / (m_1 + m_2)$$

where

m_1 is the mass of sulfur compound, expressed in grams;

$w_{s,c}$ is the sulfur content of the sulfur compound, expressed as a percentage by mass;

m_2 is the mass of the white oil, expressed in grams.

Table 1

Approximate sulfur content % (m/m)	White Oil	DBT	DBS	TNA
5	40.0	16.1	11.8	10.6
4	40.0	11.95	8.95	8.05
3	40.0	8.3	6.3	5.75
2	45.0	5.85	4.5	4.1
1.5	45.0	4.25	3.3	3.0
1	45.0	2.75	2.15	1.95
0.5	50.0	1.5	1.15	1.05
0.3	50.0	0.9	0.7	0.65
0.1	50.0	0.3	0.25	0.2
0.07	50.0	0.21	0.18	0.14
0.05	50.0	0.14	0.11	0.1
0.03	50.0	0.09	0.07	0.07
0.01	50.0	0.03	0.025	0.02

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- 5.4 Calibration standards: for analyzer without curvature fitting, use calibration standards in four ranges (Table 2).

Table 2

Range	Sample sulfur content % (m/m)	Standard sulfur content % (m/m)
1	0.01 to 0.25	0, 0.01, 0.03, 0.05, 0.10, 0.25
2	> 0.25 and ≤ 1.5	0, 0.25, 0.5, 0.75, 1.0, 1.5
3	> 1.5 and ≤ 5.0	0, 1.5, 2.0, 3.0, 4.0, 5.0

- 5.5 Prepare the sample cup in accordance with the manufacturer's instructions. Cover the base of the cup with window film, avoiding skin contact, and fill to a depth of between 3 mm and 20 mm, or up to the line indentation on the side of the cup, with the calibration standard. Ensure that the window is smooth and taut and that there are no air bubbles between the window and the liquid. Taking consecutive single readings from the same cup is not recommended.
- 5.6 In regular use, check at least two points on each calibration curve not less frequently than weekly. This shall be accomplished by using set-up standards, which have been assigned and selected from an inspection of the calibration curve.

6 Procedure

- 6.1 Fuel samples are collected in glass bottles or metal canisters and delivered to the laboratory.
- 6.2 Prepare and fill the sample cup with the test portion as described in 5.5.
- 6.3 For volatile samples, care should be taken to prevent window bowing if the sample cup is capped.

7 Calculation of Results

- 7.1 The sulfur concentrations, given in % (m/m), are calculated by the data system using external multipoint calibration standards. The area count is compared with a calibration graph plotting counts against sulfur content on a series of calibration samples covering the range of sulfur contents under examination.

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8 Quality Control

8.1 Calibration Standards Analysis

8.1.1 Calibration standards are prepared as needed. It is estimated that the standards will maintain a shelf life of about one year. This depends on how often the standards are uncapped. The multi-level calibration is run yearly and should be linear. The adjusted r-squared value must be 0.99 or greater. If it falls below 0.99, the calibration should be rerun and/or the instrument should be checked for possible malfunction or required maintenance.

8.2 Quality Control Sample Analysis

8.2.1 An ASTM crosscheck sample with the sulfur content within the calibration range is used as the quality control sample. The QC samples are analyzed at least in the beginning and the end of the sample set. A control chart is maintained for the QC samples. The upper and lower warning levels are set within twice the repeatability of the robust mean of the ASTM crosscheck sample.

8.2.2 The repeatability can be calculated as follows:

$$r = 0.0454 * (X + 0.05), \text{ for values } \geq 0.03\% \text{ (m/m) and } \leq 0.05\% \text{ (m/m);}$$

$$r = 0.0215 * (X + 0.15), \text{ for values } > 0.05\% \text{ (m/m) and } \leq 5.00\% \text{ (m/m);}$$

where X is the average of the results being compared, in %(m/m).

8.2.3 A QC sample is out-of-control when the measured value of sulfur exceeds the 3s limit or when two successive measurements of the control sample exceeds the 2s limit. If a QC sample is out-of-control, the calibration and QC sample must be rerun. If QC samples continue to be out-of-control, determine the cause of the problem before analyzing any samples.

8.3 A NIST SRM sample will be analyzed on a quarterly basis. The control limit must be within twice the repeatability value.

9. Safety Precautions

9.1 Prepare fuel samples and standards under a fume hood.

9.2 Wear safety glasses and disposable gloves when handling fuels or solvents.

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- 9.3 Fuels and solvents may be harmful or fatal if ingested or inhaled.
- 9.4 All fuels and solvents should be treated as extremely flammable and explosive.
- 9.5 The instrument produces high intensity x-ray radiation when energized.
- 9.6 Beryllium present inside instrument, avoid contact.
- 9.7 Additional safety procedures can be found in the X-Supreme instrument user's guide.

10. Revision History

- 10.1 Revision 2.0 Effective Date: July 23, 2014.
 - 10.1.1 Significant Changes:
 - 10.1.1.1 Remove the certified reference material paragraph from Section 4 – This paragraph is identical to section 5.2.1.
 - 10.1.1.2 Change in Section 5.2.1 – Changed the calibration range to better determine the new lower level of fuel sulfur requirement in ocean-going vessels within California waters.
 - 10.1.1.3 Addition of Section 8.2.2 – Added the repeatability calculation equations.

11. References

- 11.1 California Code of Registration, Title 17, Section 93118.2. Airborne Toxic Control Measure for Fuel Sulfur and Other Operational Requirements for Ocean-going Vessels within California Waters and 24 Nautical Miles of the California Baseline.
- 11.2 California Code of Registration, Title 13 Section 2299.2. Fuel Sulfur and Other Operational Requirements for Ocean-going Vessels within California Waters and 24 Nautical Miles of the California Baseline.
- 11.3 ISO 8754:2003 (E), Petroleum Products- Determination of Sulfur Content- Energy-dispersive X-Ray Fluorescence Spectrometry.