

SULFUR IN DISTILLATE AND RESIDUAL OILS BY X-RAY FLUORESCENCE

UOP Method 836-82

SCOPE

This non-destructive method is for determining sulfur in liquid distillate and residual oils, using non-dispersive x-ray fluorescence. The range of detection is 100 ppm up to 5 mass-%. The method has two interferences, molybdenum and lead that, when either is present at levels above 100 ppm, cause sulfur peak overlap and will negate use of this method. Higher levels of other metals can also cause interferences. The interference is not obvious and, therefore, questionable samples must be analyzed for these compounds before the determination of sulfur can be made. Suitable screening techniques include energy dispersive x-ray or atomic absorption spectroscopy.

The method is written for use with a Horiba Model SLFA-800 instrument, however, other equivalent equipment is satisfactory.

OUTLINE OF METHOD

A sample of distillate or residual oil is poured into a polypropylene cup which is then fitted with a Mylar window. The cup is introduced into the instrument and irradiated by chromium x-rays. The sulfur in the sample emits characteristic x-ray spectral lines producing a sulfur peak. This peak plus a scattered background peak are exclusively passed through filters and impinge on the detector head. The two peaks are separated, amplified and the ratio of the intensity of the sulfur peak to the background peak is obtained. The sulfur concentration is calculated using this ratio in a quadratic equation along with values obtained for sulfur standards in a similar matrix. This instrument compensates for carbon-to-hydrogen mass-percent differences that may occur between standards and unknown samples.

APPARATUS

Cup windows, Mylar, Horiba, Cat. No. 350254, or equivalent

Sample cup, XRF, polypropylene, Chemplex Industries, Inc., Cat. No. 1850, or equivalent

X-ray fluorescence instrument, Horiba, Model SLFA-800, or equivalent

IT IS THE USER'S RESPONSIBILITY TO ESTABLISH APPROPRIATE PRECAUTIONARY PRACTICES AND TO DETERMINE THE APPLICABILITY OF REGULATORY LIMITATIONS PRIOR TO USE. EFFECTIVE HEALTH AND SAFETY PRACTICES ARE TO BE FOLLOWED WHEN UTILIZING THIS PROCEDURE. FAILURE TO UTILIZE THIS PROCEDURE IN THE MANNER PRESCRIBED HEREIN CAN BE HAZARDOUS. MATERIAL SAFETY DATA SHEETS (MSDS) OR EXPERIMENTAL MATERIAL SAFETY DATA SHEETS (EMSDS) FOR ALL OF THE MATERIALS USED IN THIS PROCEDURE SHOULD BE REVIEWED FOR SELECTION OF THE APPROPRIATE PERSONAL PROTECTION EQUIPMENT (PPE).

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REAGENTS AND MATERIALS

All reagents shall conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, when such specifications are available, unless otherwise specified. References to water shall mean deionized or distilled water. Unqualified references to solutions shall mean aqueous solutions unless otherwise stated.

Butyl disulfide, BP 112/13 mm, Sargent-Welch Scientific Co., Cat. No. EK1826-100GM, or equivalent

Mineral oil, heavy, laboratory grade, Sargent-Welch Scientific Co., Cat. No. SC 13635-500ML, or equivalent

Sulfur standards. The following sulfur standards, are available from the U.S. Department of Commerce, National Bureau of Standards:

1624A, 0.141 mass-% sulfur, No. 2 Diesel

1623A, 0.240 mass-% sulfur, No. 6 Fuel Oil

1619, 0.719 mass-% sulfur, No. 6 Fuel Oil

1621B, 0.950 mass-% sulfur, No. 6 Fuel Oil

1622B, 1.982 mass-% sulfur, No. 6 Fuel Oil

1620A, 4.504 mass-% sulfur, No. 6 Fuel Oil

PREPARATION OF SAMPLE

Pour the liquid sample into a sample cup to a minimum depth of approximately 1.25 cm; a larger volume may be used but will have no effect on results. Viscous samples can be warmed on a hot plate before sampling to ensure homogeneity and ease in filling sample cups, however, the heating temperature should not exceed 60 C (140 F). Stretch a Mylar sheet over the cup opening and secure it using the ring portion of the cup. Invert the cup and label it on the bottom. Care should be exercised to ensure that the sample cup is tightly sealed and that no leakage occurs (see Note 1).

CALIBRATION OF INSTRUMENT

Calibration of the instrument is required with standard blends. Such blends may either be purchased or prepared by weighing to the nearest 0.01 g butyl disulfide into mineral oil. Preferably, the standards should be similar in composition to the unknown samples although the instrument will automatically compensate for differences in carbon/hydrogen ratio.

The instrument is capable of holding one calibration in memory, developed from the analysis of three calibration standards, which should cover or closely bracket the expected sulfur contents of the samples. In practice, when samples of unknown sulfur content are to be analyzed, an initial calibration is carried out by running 3 blends in the 2 to 5% range. All samples are analyzed and values that fall within this range are accepted. Samples containing more than 5% sulfur can be brought within this range of analysis by quantitatively diluting them with mineral oil. When calculating the sulfur content, the extent of dilution must be considered. Recalibration is then carried out in the 0.2 to 2% range and/or 0.01 to 0.2% range for determining lower sulfur contents.

After an initial 30 minute warm-up period calibration can commence. Manually set the correct time, date, test number, number of repeats and low, medium and high standard concentrations on the instrument front panel switches. Place each standard in the instrument and analyze for five minutes. After the values for the standards have been acquired and stored in memory, a calibration curve is developed by the instrument using the least squares fitting technique. Calibrations should be checked on a daily basis or whenever a series of samples is analyzed.

PROCEDURE

Place the sample cup into the sample chamber, close the lid, push the sample drawer back into the instrument, enter parameters and push the measure button. The acquiring time may be preset to 30, 100 or 300 seconds. A 30-second time with 3 repeats has been found satisfactory. When the 3 repetitions are completed, the instrument will calculate the average counts and print out the average sulfur mass-%. If more than 8 repetitions are determined, the estimated standard deviation is calculated and printed out. After the measurement is completed, remove and disassemble the sample cup. Place the disposable cup and the oil in appropriate waste containers.

CALCULATIONS

The mass-% sulfur calculation is carried out automatically by the Horiba Model SLFA-800 instrument according to the following equation:

$$\text{Sulfur, mass-\%} = A_2X^2 + A_1X + A_0$$

where:

A_2, A_1, A_0 = regression coefficients derived from sulfur standards

$$X = \frac{\text{Intensity of sulfur peak}}{\text{Intensity of scattered peak}}$$

NOTES AND PRECAUTIONS

1. After filling the sample cup, it should be left on a paper towel for a period of time to be certain it is not leaking. The nature of the covering material is such that any sharp abrasion or slight flaw may rupture the film. Extensive damage to the instrument can result if sample material contacts the detector window or x-ray generator.

2. The Horiba Model SLFA-800 instrument has a feature to automatically correct for differences in carbon mass-% / hydrogen mass-%. This C/H error will be negligible if unknown samples are similar to standards. However, there can be a sulfur concentration error if there is a wide disparity between unknowns and the standards used.

3. If the sample contains sediment, it must be filtered before measurement since deposition on the cell window will give an erroneous result. In cases where the sediment is considered to be part of the sample, an accurate determination cannot be made by this technique.

4. Samples containing volatile components may cause the cup window to bulge during analysis, thereby producing erroneous results. To prevent this, poke a small vent hole in the bottom of the cup (which becomes the top when the cup is inverted for analysis).

PRECISION

Based on 10 replicate determinations at each of 4 sulfur levels, the estimated standard deviation (esd) was calculated and is listed in the following table. Duplicate results by the same operator should not differ by more than the allowable difference shown (95% probability).

Sulfur Concentration, mass-%	esd, mass-%	Allowable Difference, mass-%
0.22	0.004	0.013
0.94	0.004	0.013
1.96	0.012	0.040
4.51	0.025	0.081

TIME FOR ANALYSIS

The elapsed time and the labor requirement for a single analysis are identical, 0.11 hour.

SUGGESTED SUPPLIERS

Chemplex Industries, Inc., 140 Marbledale Rd., Eastchester, NY 10707

Horiba Instruments, Inc., 1021 Duryea Ave., Irvine, CA 92714

Sargent-Welch Scientific Co., 7300 N. Linder Ave., Skokie, IL 60077

U.S. Department of Commerce, National Bureau of Standards, Office of Standard Reference Materials,
Washington, D.C. 20234