



A Honeywell Company

Sulfur in Organic and Inorganic Materials by Combustion and IR Detection

UOP Method 864-12

Scope

This method is for determining total sulfur in organic materials, such as petroleum products, and inorganic materials, such as catalysts, by combustion using a LECO S632 Sulfur Analyzer. The range of analysis is from 100% down to a lower limit of quantitation of 0.005 mass-% sulfur. Water and halogens, such as fluoride and chloride, must be removed from the carrier stream by using a trap to prevent acids from forming and damaging the infrared cell. For liquids, the method is generally limited to samples having initial boiling points above 200°C. However, it can be applied to some wider boiling range samples, such as crude oils, where experience has shown that no losses occur during the combustion process.

Reference

UOP Method 999, "Precision Statements in UOP Methods," www.astm.org

Outline of Method

The LECO S632 Sulfur Analyzer is set to the correct temperature for the sample type and method; the halogen and moisture trap is loaded with fresh reagents; and the calibration is verified by analyzing quality assurance materials. A sample is weighed and combusted in an oxygen atmosphere where the sulfur is oxidized to SO₂. The SO₂ gas is passed through a purification system to remove halogens, moisture, and dust, and is then detected by a solid state infrared detector. The instrument software calculates the results by comparison to preprogrammed values obtained for sulfur standards.

Apparatus

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

Balance, readability 0.0001 g

Mortar, porcelain, 130-mm OD, with pestle, Fisher Scientific, Cat. Nos. 12-961C and 12-961-5C, respectively

Oven, capable of operation at 105°C, Fisher Scientific, Cat. No. 13-247-625G

Pipet, dropping, straight tip, with bulb, Fisher Scientific, Cat. No. 14-955-215

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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Scoop, measuring, large, capacity about 0.85 g, LECO, Cat. No. 503-032

Spatula, micro, Fisher Scientific, Cat. No. 21-401-15

Sulfur analyzer, Model S632, LECO, Cat. No. 200-706, including the following spare parts and accessories:

Boat stop, LECO, Cat. No. 606-308

Combustion tube, inner, LECO, Cat. No. 606-313

Combustion tube, outer, LECO, Cat. No. 606-309

Lance tube, ceramic, LECO, Cat. No. 625-401-351

Purge tube, LECO, Cat. No. 625-401-317

Regulator, oxygen, 2 stage, LECO, Cat. No. 501-291

Tongs, crucible, stainless steel, riveted, Fisher Scientific, Cat. No. 15-186

Reagents and Materials

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used. References to water mean deionized or distilled water.

Anhydrone, LECO, Cat. No. 501-171

Antimony metal, for halogen trap, LECO, Cat. No. 769-608-HAZ

Combustion boat, 250/box, LECO, Cat. No. 528-203-250

COMCAT accelerator, LECO, Cat. No. 502-321

F-Cl absorbent, for halogen trap, LECO, Cat. 769-610-HAZ

Oxygen, ultra high purity, local supply

Quartz wool, fine, LECO, Cat. No. 502-177

Standards, calibration, coal, 0.28, 1.54, 3% sulfur, LECO, Cat. Nos. 502-433, 502-436, 502-437, respectively

Standards, calibration, in paraffin oil, 0.3, 1.0, 2.0, and 4% sulfur, LECO, Cat. Nos. 764-545, 764-546, 764-547, 501-099, respectively

Standards, calibration, manganese ore concentrate, 290 mg/kg sulfur, ICRM, No. P12/2, available from Brammer Standard

Standards, calibration, sandstone rock, 860 mg/kg sulfur, CNAC, NCS DC 73304, available from Brammer Standard

Standards, calibration, soil, 0.016, 0.088 % sulfur, LECO Cat. Nos. 502-062, 502-309, respectively

Water, deionized or distilled

Procedure

The analyst is expected to be familiar with general laboratory practices, the technique of sulfur analysis by combustion-IR, and the equipment being used. Dispose of used reagents, materials, and samples in an environmentally safe manner according to local regulations.

The detailed procedure listed below is specific to the instrument listed in the *Apparatus* section. Other instruments may require different procedures.

Operating Parameters

Install the analyzer according to the instructions in the manufacturer's operating manual. The system electronics require a two-hour warm up and the furnace must be at the specified operating temperature. The conditions listed in Table 1 apply to the LECO Model S632. If other instrumentation is used, the conditions will be different.

Table 1
Operating Conditions

Furnace temperature*	1350 - 1450 °C
Oxygen carrier gas input pressure	205 kPa (30 psig)
System pressure	70 kPa (10 psig)
Gas flows (during operation)	
Purge	3.0 L/min
Lance	1.0 L/min
Analysis time	60 sec minimum
Lance delay	30 sec
Comparator level	1 - 3
Answer precision	3
Clean interval	15

***1350 °C is used for organics; 1450 °C is used for inorganics. If it is unclear what temperature to use for a particular material, consult the instrument manufacturer for recommendations.**

All voltage, sulfur cell temperature, and electronic unit temperature adjustments are to be made as described in the instruction manual.

Instrument Preparation

The instrument must be prepared daily prior to analyses by performing the following steps:

1. Check oxygen gas supply.
2. Empty the spent sample boats from the internal collection container (bucket).
3. Check halogen/moisture trap, reload if anhydronite is hard and yellowed or F-Cl absorbent is dark orange or brown. Halogen/moisture trap is loaded as follows:
 - a. Quartz wool, 2-3 cm
 - b. Antimony, 2-3 cm
 - c. Quartz wool, 2-3 cm
 - d. F-Cl absorbent, 6-8 cm
 - e. Quartz wool, 2-3 cm
 - f. Anhydronite, 8-10 cm
 - g. Quartz wool, 1-2 cm
 - The halogen/moisture trap should be monitored during the analyses. Some samples, e.g., those with high chloride or moisture, may require frequent reloading of the trap.
4. Analyze 3-5 conditioning samples using the instrument calibration program appropriate to the sample type, which will set the furnace temperature. Conditioning samples consist of approximately 0.3 g of any material with a sulfur concentration of at least 0.1% mixed with one

scoop of COMCAT accelerant. The low-level coal calibration standard may be used. These samples condition the detector prior to standard and sample analyses.

5. Analyze five blank samples, consisting of a sample boat with one scoop of COMCAT. Use the sulfur concentrations of the last 2-3 of these to set the BLANK for the calibration. Analyzing blanks is not necessary for sulfur calibrations of 1% or greater.

Instrument Calibration and Sample Analysis

Certain calibration materials, such as the coal standards, must be heated in an oven for one hour at 105°C before use. Refer to the certificate of analysis included with the standard for any required pretreatment steps.

Calibrate the instrument, according to the manufacturer's operating manual, using certified standards to establish a linear calibration of at least five data points. This can be done with various weights of a single standard, or using multiple standards. The calibration is verified prior to each set of analyses by analyzing a reference material, which can be a certified material not used in the calibration. If the result of the analysis of the reference material is not within the repeatability allowable difference listed in *Precision*, Table 2, recalibrate. Recalibration must also be performed after instrument maintenance such as changing the combustion tube. The standards listed in *Reagents and Materials* are used for oil and catalyst samples. Other standards may be required for other sample types.

Standards, reference materials, and samples are analyzed according to the following steps:

1. Add one scoop of COMCAT accelerator to a combustion boat. Tap gently to provide an even layer across the bottom of the boat.
2. Add 0.20 ± 0.05 g of the appropriate standard (or sample) to the combustion boat (see *Note 1*). Calibration standards for each method are to be determined based on sulfur concentration and matrixes; see manufacturer's operating manual. For solid samples, stir with a spatula to mix.
 - Reference materials should be run periodically, depending upon sample type, to confirm proper operation of the instrument.
3. Enter the standard (or sample) identification and sample weight into the S632 program, and select the instrument program appropriate to the material type. Method parameters are determined based on sulfur concentrations and matrixes; see manufacturer's operating manual.
4. If using an automatic sample loader, ensure the sample boat is placed in the proper location. (If not using an automatic sample loader, follow manufacturer's instructions for performing manual sample analyses.)
5. Analyze standards and establish the linear calibration using at least five data points. SAVE the calibration.
 - The linearity of the calibration curve can be determined by ensuring the data points intersect with the line and the RMS is below 0.002.
6. Select a suitable reference material and analyze it whenever samples are run. From these results, establish control limits for the analysis.
7. Analyze reference material and ensure the sulfur value is within the control limits.
8. Analyze the samples. Inspect each intensity curve for anomalies such as not returning to baseline. Repeat suspect analyses.

Calculations

All calculations are performed by the instrument software. For sulfur concentrations at or above 0.01 mass-%, report results to the nearest 0.01 mass-%. For sulfur concentrations below 0.01 mass-%, report results to the nearest 0.001 mass-%. For sulfur concentrations below 0.005 mass-%, report as <0.005 mass-%.

Notes

1. If a sample result is obtained with a 0.2-g sample that is less than 0.005 mass-% sulfur, reanalyze the sample using a 0.5-g sample. If a value is then obtained that is below 0.005 mass-%, report the result as “less than 0.005 mass-%”.
2. It is recommended that samples below 0.1-% sulfur be analyzed in duplicate

Precision

Precision statements were determined using UOP Method 999, “Precision Statements in UOP Methods.”

Repeatability and Site Precision

A nested design was carried out for determining sulfur by two analysts, with each analyst performing analyses on three separate days, performing three analyses each day for a total of 18 analyses. Using a stepwise analysis of variance procedure, the within-day estimated standard deviations (esd) were calculated at the concentration means listed in Table 2. Two analyses performed in one laboratory by the same analyst on the same day should not differ by more than the repeatability allowable differences shown in Table 2 with 95% confidence. Two analyses performed in one laboratory by different analysts on different days should not differ by more than the site precision allowable differences shown in Table 2 with 95% confidence.

The data in Table 2 represent short-term estimates of the repeatability of the method. When the test is run routinely, use of a control standard and a control chart is recommended to generate an estimate of long-term repeatability.

Table 2
Repeatability and Site Precision, Sulfur, mass-%

<u>Sample</u>	<u>Mean</u>	<u>Repeatability</u>		<u>Site Precision</u>	
		<u>Within-Day esd</u>	<u>Allowable Difference</u>	<u>Within-Lab esd</u>	<u>Allowable Difference</u>
Catalyst	0.015	0.0004	0.001	0.0006	0.002
Oil	0.29	0.006	0.02	0.006	0.02
Coal	0.78	0.019	0.09	0.023	0.09
Catalyst	7.07	0.049	0.15	0.062	0.21

Reproducibility

There is insufficient data to calculate the reproducibility of the test at this time.

Time for Analysis

The elapsed time and labor requirement are identical, 0.3 hour, averaged to include conditioning and calibration.

Suggested Suppliers

Brammer Standard Company, Inc., 14603 Benfer Rd., Houston, TX 77069, USA (281-440-9396)
www.brammerstandard.com

Fisher Scientific, 711 Forbes Ave., Pittsburgh, PA 15219-4785, USA (412-490-8300)
www.fishersci.com

LECO Corporation, 3000 Lakeview Ave., St. Joseph, MI 49085, USA (269-985-5496)
www.leco.com