

SULFUR IN ORGANIC AND INORGANIC MATERIALS BY COMBUSTION AND IR DETECTION

UOP Method 864-89

SCOPE

This method is for determining total sulfur in petroleum products and other organic/inorganic materials, such as catalysts, using a LECO Sulfur Analyzer. The detection range is from 100% down to a lower limit of 0.01 mass-% sulfur. Nitrogen and halogens do not interfere unless they are present in concentrations ten times higher than that of the sulfur. 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.

OUTLINE OF METHOD

The LECO Sulfur Analyzer consists of a microprocessor controlled balance, furnace and detector. 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 moisture and dust, and is then detected by a solid state infrared detector. The microprocessor 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.

Sulfur analyzer, LECO Model SC-132, LECO, Cat. No. 781-400, including the following spare parts and accessories:

Boat stop, Cat. No. 529-012

Combustion collection tube assembly, Cat. No. 773-932

Delivery tube assembly, Cat. No. 773-928

Heat insulator, Cat. No. 773-861

Lance support bracket, Cat. No. 773-944

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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UOP Methods are available through ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken PA 19428-2959, United States. The Methods may be obtained through the ASTM website, www.astm.org, or by contacting Customer Service at service@astm.org, 610.832.9555 FAX, or 610.832.9585 PHONE.

Lance tube, ceramic, Cat. No. 772-402

Liner, Cat. No. 529-011

Purge tube kit, Cat. No. 775-784

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

Scoop, measuring, large, capacity about 0.85 g, Cat. No. 762-936

Glass wool, borosilicate, Fisher Scientific, Cat. No. 11-388

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

Pipet, dropping, straight tip, with bulb, Fisher Scientific, Cat. No. 13-701

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

Weight, one-gram, LECO, Cat. No. 764-078

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 mean deionized or distilled water.

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Absorbent, halogen, LECO, Cat. No. 769-608

Anhydron, LECO, Cat. No. 501-171

Combustion Boat, 1000/box, LECO, Cat. No. 528-203

Oxygen, extra dry, Matheson Gas Products

Printer paper, roll, LECO, Cat. No. 770-764

Standard, calibration, sulfur in lube oil, 0.05% sulfur, Brammer Standard, Cat. No. MG 109 L

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. These standards are used for oil and catalyst samples. Other standards may be required for other sample types.

Vanadium pentoxide accelerator, LECO, Cat. No. 501-636

PROCEDURE

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 SC-132. If other instrumentation is used, the conditions will be different.

Table 1**Operating Conditions**

Furnace temperature	1375 C
Oxygen carrier gas input pressure	205 kPa (30 psig)
System pressure	70 kPa (10 psig)
Gas flows (during operation)	
Purge	4.0 L/min
Lance	1.0 L/min
Analysis time	60 sec minimum
Lance delay	30 sec
Comparator level	3
Answer precision	3
Clean interval	15

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

Balance Calibration

Calibrate the balance on a daily basis according to the following procedure:

- 1) Depress the system UPDATE key on the control console.
- 2) Depress the NO key until the message center displays “Calibrate Balance - yes/no”.
- 3) Depress the YES key to begin actual calibration of the balance.
- 4) Put an empty combustion boat on the balance and press the TARE key.
- 5) Place a one-gram standard weight in the combustion boat and the message center will display “Auto-Calibration Wt. = 1.000”.
- 6) When the system has automatically calibrated the balance, it will return to the operate mode.
- 7) Remove the combustion boat and weight from the balance.

Instrument Calibration and Sample Analysis

Calibrate the instrument on a daily basis and analyze samples according to the following procedure.

- 1) Depress the CLEAR key on the microprocessor until the message center displays “Empty”. This operation clears any previous weights.
- 2) The instrument allows up to 4 separate calibrations to be made and stored in memory. This permits calibration data at several sulfur concentrations or in different matrices to be stored simultaneously. The data are stored in “modes” that can be randomly used for calibration as needed. Depress the SELECT key to obtain the desired calibration mode.
- 3) Add one scoop of vanadium pentoxide accelerator to a combustion boat. Tap gently to provide an even layer across the bottom of the boat.

- 4) Place the boat on the balance and it will automatically tare.
- 5) Add approximately $0.2\text{g} \pm 50\text{ mg}$ of the appropriate standard (or sample) to the combustion boat (see *NOTE*).
- 6) Wait until the balance stabilizes and then depress the ENTER key.
- 7) Remove the boat and cover the standard with two scoops of vanadium pentoxide.
- 8) Depress the ANALYZE key.
- 9) When the message display center displays "LOAD FURNACE", slide the combustion boat into the furnace until it touches the stop at the back end of the furnace. Depress the ANALYZE key for materials containing less than 0.05%.
- 10) The analysis will continue to completion in approximately 60 seconds, and the percent sulfur will be printed out on the display.
- 11) Remove and discard the expended boat.
- 12) Repeat Steps 3 through 11 until five values per standard have been obtained.
- 13) Depress the system UPDATE key.
- 14) Depress the NO key until the display indicates "CALIBRATION BY STACK YES/NO", and depress YES.
- 15) "CALIBRATION SELECT" will be displayed, and the previously chosen calibration "mode" (see Step No. 2) is entered.
- 16) "SULFUR STANDARD %" will be displayed, and the concentration of the standard being used in that mode is entered.
- 17) The message center will now display each analysis of the standard analyzed individually with "YES/NO" displayed. Depress YES or NO for the analyses to be included or excluded from the calibration.
- 18) The calibration factor will automatically be calculated and entered into the system's memory.
- 19) Run another standard of the same concentration to confirm that the system is now calibrated by starting at Step No. 3 and continuing through Step 12. If the system produces a value that is within 5% of the calibrated value, the system is properly calibrated.
- 20) Repeat the above procedure for other calibration levels if the concentrations of sulfur in the samples are expected to vary more than 1/2 or twice the standard value of the first calibration.
- 21) Analyze samples by following Steps 3 through 11 but grind catalyst samples to a fine powder before starting Step 3.

CALCULATIONS

All calculations are performed by the microprocessor and printed out automatically. Report data to the nearest 0.01 mass-%.

NOTE

If a sample result is obtained with a 0.2-g sample that is less than 100 ppm, reanalyze the sample using a 0.5-g sample. If a value is then obtained that is below 100 ppm, report the result as “less than 100 ppm”.

PRECISION

Repeatability

Based on two tests performed by each of two analysts on each of two different days (8 tests per lab), and using data collected from three laboratories for the catalyst and from one laboratory for the oils, the within-laboratory estimated standard deviations (esd) were calculated for sulfur at the concentrations listed in Table 2. Two tests performed in one laboratory by different analysts on different days should not differ by more than the allowable difference shown in Table 2 at the concentrations listed (95% probability).

Reproducibility

Two tests performed in different laboratories by different analysts, on different days, should not differ by more than the allowable difference shown in Table 2 at the concentration listed (95% probability).

Table 2

Sample Type	Sulfur Concentration, mass-%	Repeatability		Reproducibility	
		Within-Lab esd, mass-%	Allowable Difference, mass-%	Between-Lab esd, mass-%	Allowable Difference, mass-%
Catalyst	0.01	0.0009	0.003	0.0009	0.006
Heavy Oil	0.06	0.0043	0.017	*	*
Heavy Oil	0.30	0.0067	0.023	*	*

*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, 0.1 hour.

SUGGESTED SUPPLIERS

Brammer Standard Co., Inc., 14603 Benfer Rd., Houston, TX 77069
 Fisher Scientific, 1600 W. Glenlake Ave., Itasca, IL 60143
 LECO Corporation, 3000 Lakeview Ave., St. Joseph, MI 49085-2396
 Matheson Co., P.O. Box 96, Joliet, IL 60434