



Chapter Q

Total sulfur by combustion

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Principle

Total sulfur in geologic materials is determined using an automated sulfur analyzer (Jackson and others, 1985, 1987). Approximately 0.25 g sample is weighed and mixed with 1 g vanadium pentoxide flux. The sample is combusted in an oxygen atmosphere at 1350°C where the sulfur oxidizes to sulfur dioxide. Moisture and dust are removed and the sulfur dioxide gas is then measured by a solid state infrared detector.

Interferences

Possible interfering elements are fluorine and molybdenum, both of which can coat the cell walls and the detector. Samples suspected to contain greater than 0.2 percent F or 1 percent Mo should be analyzed by using a reduced sample weight. Also, a halogen trap must be installed in the flow system when higher concentrations of fluorine are present in the samples. A problem may be encountered due to abnormally rapid combustion of organic-rich materials. This problem can usually be corrected by the addition of a retardant (COM-AID) to the sample. It may be necessary to cover some samples completely with vanadium pentoxide to assure complete conversion of the sulfur to the dioxide.

Scope

The reporting range for total sulfur is from 0.05 percent to about 35 percent. Approximately 40 samples can be analyzed in a day.

Apparatus

- Sulfur analyzer, Leco Model SC-432
- Ceramic combustion sample boats
- Tank of high purity oxygen, with regulator

Reagents

- COM-AID, combustion retardant
- Vanadium pentoxide, V_2O_5
- Conditioner, ground coal (approximately 0.50% Sulfur)
- Anhydron, magnesium perchlorate, $Mg(ClO_4)_2$
- Distributing organization and reference material samples are:
 - LECO Corporation coal: 0.40, 0.56, 1.05, 1.78, 2.10, 2.98, 3.32, 5.13 percent sulfur
 - U.S. Geological Survey: SDO-1, GXR-4
 - National Institute of Standards and Technology (NIST): SRM 1633b, SRM 2710, SRM-113A
 - Canadian Certified Reference Materials Project (CCRMP): STSD-4, SO-2, SO-4, SU-1a

Safety precautions

The major potential danger in this procedure is thermal burns to the operator from contact with the very hot sample boats when removed from the furnace. Care must be exercised in removing the boats with tongs. Avoid contact of the hot boats with combustible materials. A lab coat, safety glasses and protective shoes should be worn while operating the instrument. Toxic gases may be produced upon sample combustion, therefore, the instrument should be used under a working exhaust hood, or vented to one. See the *CHP* and *MSDS* for further information.

Procedure

(Additional details are in the manual provided by the LECO Corporation.)

1. Replace the left anhydron tube with the right anhydron tube. Replace the right side with a fresh anhydron tube. This procedure must be followed daily when using the instrument.
2. Begin by pressing on the monitor anywhere, now press the “MAINTENANCE” key on the monitor, and then the “AMBIENT MONITOR” key. This will provide a list showing the current status of the various systems parameters. The furnace temperature will gradually rise to 1350°C. Turn on the necessary fume hoods.
3. Open valve on oxygen cylinder and set second stage regulator to 40 psi.
4. Turn on the printer.
5. Calibrate the balance.
6. Conditioning the instrument for analyses:
 - a. First run 3 to 4 blanks. (Use spent boats for this purpose.)
 - b. Go to “FRONT PANEL” by pressing “ESC” twice. Press “ANALYZE”.
 - c. Press “Select ID Code”, select the blank code. Press “ESC”. Press “Manual Weight”, enter 0.3500g, press “Enter” 3 times, then press “Manual Weight” again.
 - d. To begin, place the boat next to the viewing window, press the “ANALYZE” key.
 - e. Wait until the message center displays “Load Sample Now” and then slide the boat into the furnace until it touches the boat stop.
 - f. Close the viewing window and immediately press “Start integration”.
 - g. After analysis is complete, remove the combustion boat from the furnace CAREFULLY.
 - h. Complete the other blanks.
 - i. Now run 3 conditioning coal samples (approximately 0.50 %) and then 3 to 5 conditioning samples by randomly picking samples from the jobs to be analyzed to determine the concentration range for the samples. (Use spent boats for this purpose.)
 - j. Press “Select ID Code”, select the appropriate code to identify the sample. Press “ESC”.
 - k. Weigh approximately 0.2 g of the sample material. If the sulfur concentration is low, (less than 0.40%), take approximately 0.3 g of the material. Make sure you are using the low Detector Range. (Select “Method”, then select the standard that you are using, press “View Method”, go to page 3.)
 - l. After weighing the samples, press “print” on balance, then spread the sample evenly by gently rocking the boat back and forth. Then add 2 scoops of vanadium pentoxide (approximately 1g) to cover geologic materials only. This will help to assure complete conversion of the sulfur to the dioxide. Do not use vanadium pentoxide on coals.
 - m. To begin analysis, place the boat next to the viewing window, press the “ANALYZE” key.
 - n. Wait until the message center displays “Load Sample Now” and then slide the boat into the furnace until it touches the boat stop.
 - o. Close the viewing window and immediately press “Start integration”.
 - p. After analysis is complete, the sulfur content will be displayed and printed.
 - q. Remove the combustion boat from the furnace CAREFULLY.
 - r. Continue with the steps above until all samples are complete.

7. Calibration procedure:
 - a. A wide variety of standards are used depending upon the concentration range of the unknown samples used for conditioning the instrument and the type of material being analyzed.
 - b. Press the "Select ID Code" to select the appropriate standard. Press "ESC".
 - c. Weigh out 5 aliquots of the calibration standard. Use new boats for this purpose.
 - d. Continue as described above (steps k. through r.).
 - e. After the 5 standards are analyzed, press "ESC", then "Calibrate", and then "Standard Calibrate". Chose the 5 analyzed standards for the calibration curve. Press "ESC", press "Yes" for the calibration curve. Press "ESC". The calibration information will be printed.
 - f. Go to "Front Panel". Press "Method", select the appropriate calibration standard. This information will be printed. Press "ESC".
8. Sample analysis: (Reference standards and samples)
 - a. Analyze one or two reference standards using new boats. The reference standard is a check for the calibration curve. Continue as described above in Conditioning the instrument for analyses: (steps j. through r.)
 - b. Analyze all the samples using new boats and continue as described above in Conditioning the instrument for analyses: (steps j. through r.). If the sulfur % is higher than the calibration standard, take a smaller weight and repeat analysis or use a higher calibration curve just for the samples with higher sulfur contents.
 - c. Run one duplicate sample for each job at the end of the day.

Calculation

Calculations are performed by the instrument's microprocessor, and the percent sulfur is reported for each sample.

Assignment of uncertainty

Table 1 is the analytical results for total sulfur of selected reference materials, duplicate samples, and method blanks by combustion.

Table 1.—Analytical performance summary for total sulfur (percent)

[A=National Bureau of Standards (NBS), 1985; B=NBS, 1982; remaining *pv* from Potts and others, 1992]

| <i>Reference</i> | <i>Description</i> | <i>n</i> | <i>Mean</i> | <i>s</i> | <i>pv</i> | <i>% RSD</i> | <i>% R</i> |
|------------------|--------------------|----------|-------------|----------|--------------------------|--------------|------------|
| SO-4 | CCRMP | 16 | 0.0434 | 0.0033 | 0.050 | 7.6 | 87 |
| STSD-4 | CCRMP | 10 | 0.0941 | 0.0037 | 0.090 | 4.0 | 105 |
| SRM 1633b | coal fly-ash | 18 | 0.201 | 0.007 | 0.2075 A | 3 | 97 |
| MAG-1 | marine mud | 10 | 0.36 | 0.005 | 0.39 | 1 | 92 |
| SRM 1572 | citrus leaves | 10 | 0.406 | 0.005 | 0.407 B <i>cv</i> | 1 | 100 |
| SRM 1646 | estuarine sediment | 10 | 0.98 | 0.01 | 0.96 | 1 | 102 |
| SDO-1 | shale | 10 | 5.44 | 0.01 | 5.35 | 0.2 | 102 |

Table 1.—Continued—Duplicate samples results

| <i>Duplicate samples</i> | <i>k</i> | <i>n</i> | <i>Mean</i> | <i>s</i> | <i>% RSD</i> | <i>Concentration range</i> | <i>No. of < (total)</i> | <i>No. of < (pairs)</i> |
|--------------------------|----------|----------|-------------|----------|--------------|----------------------------|--------------------------------|--------------------------------|
| | 52 | 2 | 1.82 | 0.06 | 3 | 0.05 to 32 | 7 | 2 |

Table 1.—Continued--Method blank results 3s values are considered the lower limit of detection (LOD), and 5s values are considered the lower limit of determination (LLD)

| <i>Method blank</i> | <i>n</i> | <i>Mean</i> | <i>s</i> | <i>3s</i> | <i>5s</i> |
|---------------------|----------|-------------|----------|-----------|-----------|
| | 32 | 0.0001 | 0.0001 | 0.0004 | 0.0007 |

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