

Total Sulfur by Combustion using the Leco Analyzer

1. Scope:

This document provides a procedure for the analysis of total sulfur in fertilizer by combustion using the Leco sulfur analyzer.

2. Principle:

Samples are prepared as described in RA-SP-SMPL-PREP. Samples are combusted at high temperature with high-purity oxygen to convert sulfur to SO₂ gas. An infrared detector quantitates the amount of SO₂.

3. Safety:

- 3.1. The Leco S632 is a high temperature combustion analyzer that operates from a 230-volt power source. Refer to the instruction manual for specific safety warnings.
- 3.2. Read the SDS for all materials before performing this method.
- 3.3. Wear appropriate personal protective equipment such as gloves, goggles, and lab coat when performing this analysis.
- 3.4. Com-Cat accelerator and sulfamethazine can cause acute irritation to eyes, skin, and respiratory systems. Avoid all contact and inhalation of this material.
- 3.5. Nickel boat liners can cause mild irritation to skin. Avoid contact with this material.
- 3.6. Compressed gas cylinders present a variety of hazards. Mandatory training is required before cylinders are transported, connected, or dispensed by any staff member. Perform leak test after connecting the oxygen tank to the instrument.

4. Equipment (equivalents are acceptable):

- 4.1. Sulfur combustion analyzer (Leco S632)
- 4.2. Analytical balance capable of weighing to 0.01g

5. Reagents and Supplies (equivalents are acceptable):

- 5.1. Coal reference material (Leco 502-671)
- 5.2. Unglazed ceramic boats (Leco 528-203-250)
- 5.3. Com-Cat accelerator (Leco 502-321)
- 5.4. Nickel boat liner (Leco 502-343)
- 5.5. Sulfamethazine (Leco 502-298)
- 5.6. Oxygen minimum 99.99% purity

6. Instrument Calibration:

- 6.1. Verify the instrument furnace temperature is 800°C. Allow the temperature to increase to 1350°C (this may take several hours). The furnace may be kept at 1350°C overnight.
- 6.2. Verify the outlet pressure for the oxygen is 35 psi and set the instrument in Gas Standby mode.
- 6.3. Perform a system check. If everything passes, print to save the report. Refer to the manual for any systems that did not pass.
- 6.4. Run at least 5 coal samples (~250mg) to equilibrate the system. To run the coal, weigh ~250mg in a tared ceramic boat and press the icon next to the "F" to add the sample weight to the instrument software then place on the sample carousel.
- 6.5. Run blanks to reset the sulfur blank for the method. Use mass – 1.0000g, repetitions – 10, method 10-1-20. The sample blank is ~1g Com-Cat in a ceramic boat with a nickel liner.
- 6.6. After the Com-Cat samples are analyzed select at least 5 blanks, choose Configuration | Blank | OK to reset the sulfur blank for the 10-1-20 method.
- 6.7. Run at minimum 3 calibration standards (sulfamethazine) to drift correct the 10-1-20 method. To run the standards, weigh ~0.5g Com-Cat in a tared ceramic boat with a nickel liner. Re-tare then add 30-40mg sulfamethazine. Press the icon to the right of the "F" to add the weight to the instrument software. Add an additional ~0.5g Com-Cat on top of the sulfamethazine and place on the sample carousel.
- 6.8. Analyze a check sample to check the drift correction (a Magruder sample run in triplicate is used as the check sample). To run the check samples, add ~0.5 Com-Cat to a tared ceramic boat with a nickel liner. Re-tare and add 0.05-0.07g of the Magruder sample. Enter the sample weight then add ~0.5g Com-Cat on top. Place samples on carousel.

7. Analysis:

- 7.1. For solid samples, thoroughly mix samples before weighing by rotating the jar. Tare a ceramic boat with a nickel boat liner and add ~0.5g Com-Cat. Re-tare, add sample based on the chart below, and add an additional ~0.5g Com-Cat.
- 7.2. For liquid samples, thoroughly mix the sample by shaking the bottle. Tare a ceramic boat with a nickel liner and add ~1.0g Com-Cat. Re-tare and add sample based on the chart below.

Guarantee	Mass of Sample
<1%	0.10 - 0.13g
1 - 10%	0.05 - 0.10g
10 - 20%	0.05 - 0.07g
>20%	0.020g

- 7.3. For both liquids and solids, send the weight to the computer and place the sample in the carousel.
- 7.4. A Magruder check sample run 3 times then the calibration standards are the last samples to be analyzed.
- 7.5. When the analysis is complete, reduce the gas flow to the instrument by choosing "F8 Gas Conservation" and closing the valve to the oxygen tank.
- 7.6. Reduce the furnace temperature to 800°C.

8. QA/QC:

- 8.1. Sulfamethazine is used for drift correction and calibration. It should be run before any samples and again at the end of the run. It must be within 2 standard deviations of the theoretical value.
- 8.2. A Magruder check sample shall be run 3 times before the samples and 3 times at the end of the run (it should be the last sample analyzed). The results of the check samples shall be within 2 standard deviations of the theoretical value. If the check sample result is greater than 2 standard deviations, recalibrate the instrument and run another check standard. The calibration standard shall be $\pm 1\%$ of the theoretical value (for example, if the theoretical value is 11% the acceptable range is 10% - 12%).
- 8.3. Any samples that are bracketed by an acceptable check sample or calibration standard are considered valid and may be reported.
- 8.4. The reporting limit is 0.1%.

9. Calculations:

The %sulfur for all samples and standards is calculated by the instrument. The drift correction is calculated by dividing the certified value of sulfamethazine by the average of the uncorrected values of the 6 sulfamethazine in the run. The %sulfur results are multiplied by the drift correction to obtain the corrected %sulfur results.

10. Preventative Maintenance:

Perform preventative maintenance at the intervals listed below.

Maintenance Activity	Interval
Replace anhydrous reagent	Every ~500 analyses
Clean furnace outlet	Every ~500 analyses
Inspect grippers (repair if needed)	Every ~500 analyses
Empty bucket	Every ~75 analyses
Inspect gas tubing (repair if crimped or leaking)	Every ~150 days
Inspect pre-pump filter and replace if dirty or damaged	Every ~160 days
Replace lance	Every ~5000 analyses (excluding blanks)

11. References:

- 11.1. Refer to the instrument manual for troubleshooting and maintenance information.
- 11.2. Association of Official Analytical Chemists, Official Methods of Analysis of AOAC International, Method 993.13, Nitrogen (Total) in Fertilizers – Combustion Method, (Chapter 2.4.02), 19th Edition, 2012

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