Determination of Total Sulfur in Fertilizers by High Temperature Combustion

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Introduction

Sulfur is one of the essential macronutrients required for plant growth, aiding the formation of amino acids and proteins, as well as chlorophyll formation. Sulfur deficiencies can cause chlorosis in new leaf formations, as well as stunted growth and higher plant mortality rates. Initiatives to reduce sulfur emissions have led to less sulfur being deposited in soil, causing an increased use of sulfur-containing fertilizers and an increased demand for sulfur determination. The current method for sulfur determination, AOAC Method 980.02, is a labor-intensive, gravimetric technique that requires the use of hazardous materials. An alternative technique, developed in cooperation with the AOAC Fertilizer Expert Review Panel (ERP), determines sulfur content by high-temperature combustion.

Total sulfur combustion instruments utilize a high-temperature resistance furnace to achieve complete decomposition of fertilizers. Sulfates present decompose to sulfur dioxide, SO_2, while elemental sulfur, sulfides, and organic sulfur species are oxidized to form SO_2. The combustion products are swept through reagents and carried to infrared detectors, where SO_2 is measured and converted to a quantifiable concentration based upon sample mass.

This poster presentation will cover the optimization of LECO total sulfur instruments for the analysis of fertilizers. Data will be examined that was obtained from the AOAC Fertilizer ERP Round Robin sample suite, which included fertilizers containing elemental sulfur, sulfates, sulfides, and organic sulfur species.

Referenced Methods

- AOAC 980.02: Sulfur in Fertilizers – Gravimetric Method
- AOAC 969.01: Sampling of Fluid Fertilizers
- AOAC 929.01: Sampling of Solid Fertilizers

Methodology

Equipment: LECO S832DR

S832DR with Autoloader

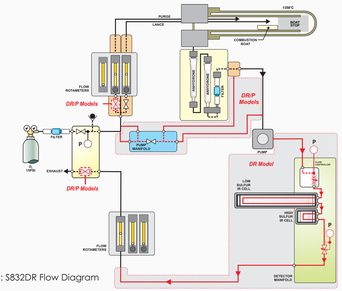

Figure 1: S832DR Flow Diagram

S832DR Theory of Operation

The S832DR series sulfur analyzer is a resistance furnace system designed for determination of sulfur content in a multitude of matrices from coals, cokes, graphitic compounds, ores, and cements to soils, plant tissues, and fertilizers.

Analysis begins as a sample is weighed into a combustion crucible and mixed with an accelerator/promotor. The sample is then introduced into the furnace, regulated at a temperature of up to 1450 °C, with a pure oxygen environment. The sample combusts, releasing sulfur, which is oxidized to form SO_2. After a preset time, additional oxygen is introduced via a ceramic lance directly above the sample to accelerate the combustion of refractory materials. The combustion gases are swept to the back of the furnace and then forward through the inner and outer furnace tubes, allowing the combustion gases to remain in the high-temperature zone of the furnace, ensuring efficient oxidation. Upon exiting the furnace, the combustion gases flow through a drying agent and on to the flow controller, setting the flow of the combustion gases through the NDIR sulfur detection cells.

Background

The goal of this study was to develop an automated method for rapid determination of sulfur content in fertilizers to replace the current, labor-intensive gravimetric method. The current AOAC method, 980.02 "Sulfur in Fertilizers", requires samples to be pretreated with hazardous materials, such as barium chloride and carbon disulfide, to determine the sulfate and elemental sulfur content of fertilizers. The method proposed in this poster utilizes high-temperature combustion for direct determination of total sulfur in fertilizers, without the need for sample pretreatment. During development of this method, an effort was made to allow for all fertilizer matrices to be successfully analyzed under the same parameters, and to reduce analysis complexity.

Required Reagents

The following reagents are required to perform sulfur determination in fertilizers by high-temperature combustion using a LECO S832DR:

- Magnesium Perchlorate (Anhydrone) – supplied by the instrument manufacturer
- Oxygen, 99.5% Pure – Compressed gas contained in a cylinder equipped with a suitable pressure regulator
- Com-Cat™ – supplied by the instrument manufacturer
- Antimony – supplied by the instrument manufacturer
- Potassium Iodide – supplied by the instrument manufacturer
- Glass Wool – supplied by the instrument manufacturer

Halogens

Chloride is an essential micronutrient for plant development and is required by all crops in small quantities. Chloride has a direct role in photosynthesis and stomatal regulation, as well as osmotic adjustments of the plant. The use of fertilizers containing chlorides, specifically potassium chloride, has become increasingly common. Combustion of chloride-containing fertilizers promotes the formation of HCl, which can cause loss of analyte and corrosion within the LECO S832DR analyzer. As such, a halogen trap, such as the one shown in Figure 2, is required for analysis of chloride-containing fertilizers.

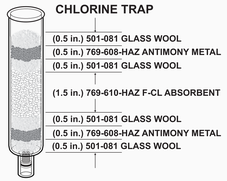

Figure 2: Halogen Trap

Analysis Parameters

The accuracy and precision of this method is directly determined by the method parameters. The method parameters listed in Table 1 were selected to deliver the optimal instrument performance for all fertilizer types. Under these method parameters, full cycle analysis time was roughly three minutes per sample.

Table 1: Optimal Method Parameters

Elemental Parameters	
Furnace Temperature	1350 °C
Use Comparator	Yes
Comparator Level	0.30%
Minimum Integration Time	120 seconds
Maximum Integration Time	360 seconds
Range Select	Auto
Range Lower Limit	975
Range Upper Limit	1000

Sample Preparation

Solid Fertilizer Samples

Solid fertilizers should be collected following the procedure outlined in AOAC Method 929.01 "Sampling of Solid Fertilizers", or other recognized procedure. The analytical sample should be prepared to pass a 0.5 mm sieve to ensure sample homogeneity. From the homogenized material, 50–100 mg of sample is accurately weighed into a pre-baked LECO 528-203 Combustion Crucible. The sample mass and identification are entered into the instrument software, and the weighed sample is mixed with ~1.0 g LECO 502-321 Com-Cat™, or other suitable combustion promoter.

Liquid Fertilizer Samples

Liquid fertilizers should be collected following the procedure outlined in AOAC Method 969.01 "Sampling of Fluid Fertilizers", or other recognized procedure. Weigh ~0.5 g LECO 502-321 Com-Cat™, or other suitable combustion promoter, into a pre-baked LECO 528-203 Combustion Crucible and form into a trough. Accurately weigh 50–100 mg of sample into the trough formed in the combustion crucible. The sample mass and identification are entered into the instrument software, and then the sample is covered with an additional ~0.5 g Com-Cat™.

Note: LECO 528-203 Combustion Crucibles should be pre-baked, prior to use, to remove any residual sulfur. It is recommended to heat the crucibles to 1000 °C for one hour and cool in a desiccator.

Sample Results

Calibration/Verification

To allow for all fertilizer types to be analyzed under the same method parameters, multiple calibration schemes were required. Determination of the appropriate calibration scheme was based upon the expected sulfur concentration of each respective sample. For the data we will examine, four separate calibration schemes were utilized to achieve the most accurate and precise results.

For fertilizers containing very low concentrations of sulfur (< 1% Sulfur), it is recommended to utilize a non-hygroscopic, pure chemical reference material for calibration, such as BBOT. This calibration is required to be linear and forced through origin to prevent any bias due to calibration within the expected range. Additionally, it was observed that samples containing 1% to 7% Sulfur were also best analyzed under a non-hygroscopic pure reference material calibration, such as BBOT. The optimum calibration for this range was a fractional mass, full regression calibration. The accuracy of these calibrations can be verified utilizing a second non-hygroscopic, pure chemical reference material.

For fertilizers containing 7% to 35% sulfur, it is recommended to utilize a sulfate-containing reference material for calibration. For the purpose of this method a fractional mass, full regression Ammonium Sulfate calibration was utilized. The accuracy of this calibration was verified utilizing Potassium Sulfate and Calcium Sulfate Dihydrate.

For fertilizers containing high concentrations of sulfur (> 35% Sulfur), it is recommended to utilize Sublimed Sulfur for calibration. For the purpose of this method a fractional mass, full regression calibration was utilized and verified with a second sublimed sulfur reference material.

For fertilizers containing an unknown concentration of sulfur, it is necessary to perform a test analysis to determine the approximate sulfur content. From the results of the test analysis, the appropriate instrument calibration can be determined.

Table 2: Recommended calibration reference materials

Expected Sulfur Conc.	Calibration Material	Calibration Type	Instrument NDIR Cell	Sample Analysis Mass (mg)
<1%	BBOT	Linear, Forced Through Origin	Low Cell	100
1-7%	BBOT	Linear, Full Regression	Low Cell	100
7-35%	Ammonium Sulfate	Linear, Full Regression	High Cell	100
>35%	Sublimed Sulfur	Linear, Full Regression	High Cell	50

Sample Suite

The sample suite for this study was selected by the AOAC Fertilizer ERP for development of AOAC proposed method "Determination of Total Sulfur in Fertilizers by High Temperature Combustion". Fertilizer samples were selected to cover a wide range of sulfur concentrations, from 0% to 94% S, consisting of both solid and liquid samples. To demonstrate the analytical performance and application capability of the instrument, fertilizers containing sulfates, organic sulfur compounds, elemental sulfur, and mixtures of each were selected. Consensus sulfur values were provided for all samples for comparison purposes.

Table 3: Sample Suite summary and expected constituent concentration

#	Sample ID	Source of Material	Primary Sulfur Source	Expected Sulfur (%)
1	160511	Magruder	N/A	0
2	2011-05	Magruder	Poultry Litter Combustion Ash	1.55
3	2011-08	Magruder	Potassium Sulfate	6.42
4	2011-07	Magruder	Ammonium Sulfate/Elemental Sulfur	9.84
5	2016-0276	OISC	Potassium Sulfate/Magnesium Sulfate	22.10
6	2016-0667	OISC	Ammonium Sulfate	24.14
7	Wil-Dry	Wilbur-Ellis	Copper Sulfate/Elemental Sulfur	24.21
8	2016-0753	OISC	Liquid Ammonium Thiosulfate	26.12
9	Sulfur DF	Wilbur-Ellis	Elemental Sulfur	80.02
10	Micronized Sulfur	Wilbur-Ellis	Elemental Sulfur	96.24

For all samples listed in Table 3, a test analysis was performed to confirm the expected sulfur content. Following completion of the test analyses, the sample suite was separated based upon sulfur content and analyzed under the applicable calibration from Table 2.

Table 4: Fertilizer Results < 1% Sulfur

Sample	Expected Sulfur (%)	Mass (g)	S832DR Sulfur (%)
160511 Magruder	0	0.1025 0.1023 0.1037	0.006 0.006 0.006
		Average Standard Deviation	**0.006 0.0004**

Table 5: Fertilizer Results 1% to 7% Sulfur

Sample	Expected Sulfur (%)	Mass (g)	S832DR Sulfur (%)
2011-05 Magruder	1.55	0.1004 0.1007 0.1023	1.62 1.59 1.60
		Average Standard Deviation	**1.60 0.01**
2011-08 Magruder	6.42	0.1000 0.1007 0.1036	6.31 6.28 6.20
		Average Standard Deviation	**6.27 0.06**

The total sulfur results displayed in Tables 4 and Table 5 demonstrate the analytical capability of the S832DR's low sulfur NDIR cell. Determined sulfur values were consistent with the consensus values provided by the AOAC Fertilizer ERP.

Table 6: Fertilizer Results 7% to 35% Sulfur

Sample	Expected Sulfur (%)	Mass (g)	S832DR Sulfur (%)
2011-07 Magruder	9.84	0.1016 0.1010 0.1010	10.01 10.12 10.07
		Average Standard Deviation	**10.06 0.06**
2016-0276 OISC	22.10	0.1012 0.1023 0.1016	21.93 22.00 21.95
		Average Standard Deviation	**21.96 0.03**
2016-0667 OISC	24.14	0.1005 0.1039 0.1011	23.90 24.01 23.93
		Average Standard Deviation	**23.95 0.06**
Wil-Dry Wilbur-Ellis	24.21	0.1055 0.1024 0.1025	24.72 24.22 25.30
		Average Standard Deviation	**24.75 0.06**
2016-0753 OISC	26.12	0.1108 0.1034 0.1113	25.96 25.91 26.00
		Average Standard Deviation	**25.96 0.04**

Table 7: Fertilizer Results > 35% Sulfur

Sample	Expected Sulfur (%)	Mass (g)	S832DR Sulfur (%)
Sulfur DF Wilbur-Ellis	80.02	0.0530 0.0532 0.0507	82.83 82.87 82.99
		Average Standard Deviation	**82.90 0.08**
Micronized Sulfur Wilbur-Ellis	96.24	0.0503 0.0502 0.0518	96.20 96.23 96.41
		Average Standard Deviation	**96.28 0.12**

The total sulfur results displayed in Tables 6 and Table 7 demonstrate the analytical capability of the S832DR's high sulfur NDIR cell. Determined sulfur values were consistent with the expected sulfur values for nine of the ten samples analyzed, with the outlier being Sample #9 "Sulfur DF Wilbur-Ellis". Consensus sulfur values for this sample were obtained following the CS2 procedure outlined in AOAC 980.02, which determines only elemental sulfur content. Following analysis of the sample suite, it was indicated that Sulfur DF Wilbur-Ellis may contain gypsum and lignosulfonates as filler materials, likely causing the observed bias.

Conclusion

The primary objective of this work was to demonstrate the analytical performance and application capability of an S832DR instrument that has been optimized for the analysis of sulfur in fertilizers. The method parameters selected allowed for all fertilizer matrices to be analyzed under the same method. In order to facilitate the most accurate and precise results, multiple calibration schemes were required, with the appropriate scheme being determined by the samples expected sulfur concentration. For samples with unknown sulfur concentrations, a test analysis is required to determine the appropriate calibration scheme.

To demonstrate the robustness of the developed method, a suite of ten fertilizer samples of varying composition were analyzed. Results obtained for the sample suite were consistent with the expected sulfur concentrations for nine of the ten samples, with the outlier most likely due to an error in determination of the consensus value.

This method was developed in cooperation with the AOAC Fertilizer ERP to replace the labor-intensive and timely gravimetric sulfur determination method. Development of this method is ongoing with a vote on AOAC First Action status pending.

Delivering the Right Results