



Delivering the Right Results

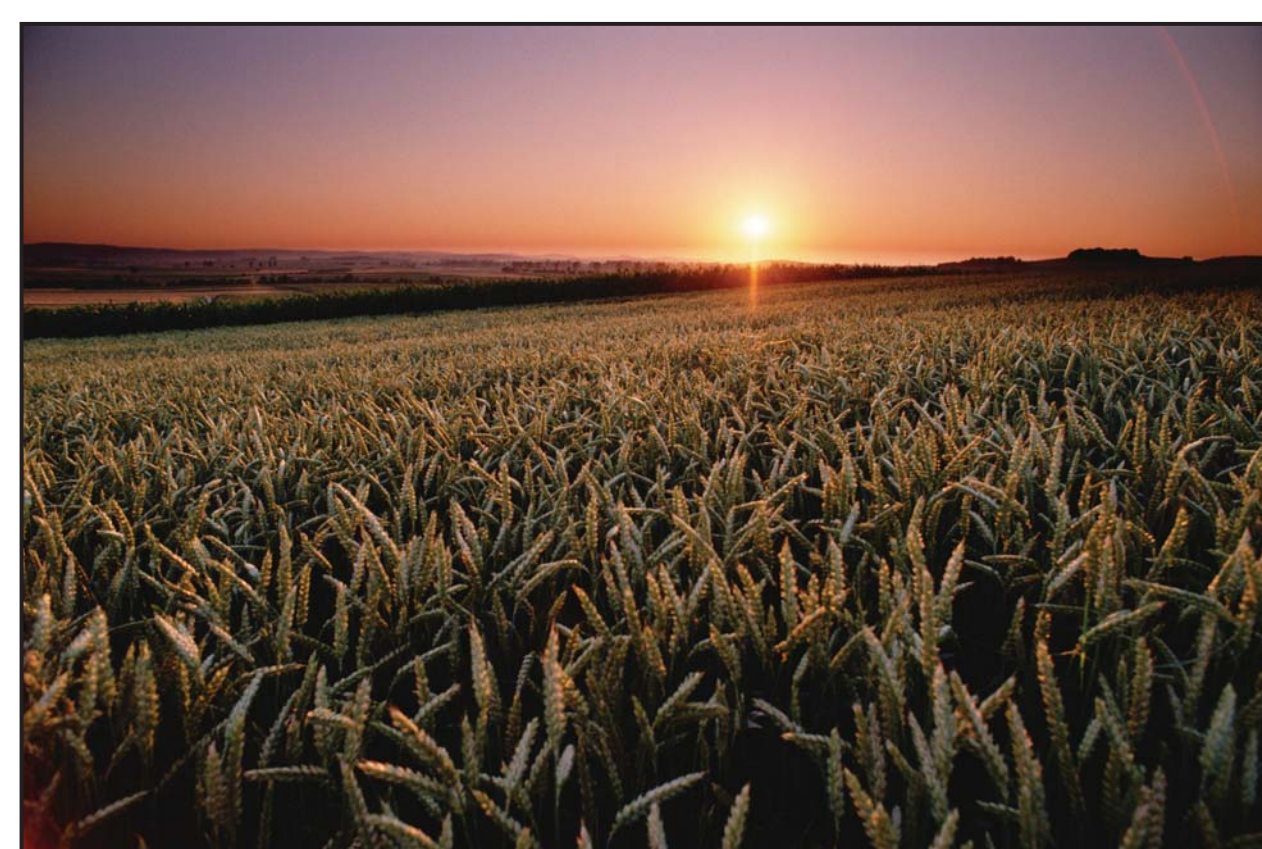
Determination of Total Sulfur in Dry Fertilizers Using High-Temperature Tube Furnace Combustion with Infrared Absorption Detection

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INTRODUCTION

Sulfur is an important element in plant nutrition playing a vital role in plant physiology. Sulfur deficiency in plants can cause light green plant appearance, cupped leaves, stunting, and poor seed development. An overall reduction in atmospheric sulfur deposition linked to global implementation of Clean Air legislation restricting sulfur dioxide emission has resulted in areas of arable sulfur deficiency worldwide. These arable sulfur deficiencies have raised the interest and need for fertilizers containing guaranteed levels of total sulfur. Sulfur has been historically measured within the fertilizer industry using a classical wet chemical gravimetric method (AOAC 980.02a), or in some cases an Inductively Coupled Plasma Emission spectrometry (ICP-AES) technique. The high-temperature tube furnace combustion with infrared (IR) absorption technique offers many advantages over the gravimetric and ICP-OES techniques for sulfur determination that require labor intensive, wet chemical digestion of the samples. The high-temperature combustion technique offers users a rapid analysis time (typically ~2 min) and little to no sample pre-treatment, as well as precision and accuracy over a wide analytical range.

The work described here utilizes the high-temperature combustion methodology for total sulfur determination in the dry fertilizer matrix. Results for a range of dry fertilizer samples from the Magruder Fertilizer Check Sample Program are presented and data evaluated with comparison to the Magruder consensus total sulfur values of AOAC 980.02a method.



METHODOLOGY



Equipment Required

LECO TruSpec® Sulfur Module

Procedure

- Weigh 50-150 mg sample into ceramic combustion boat
- Cover sample with ~1 g combustion accelerant (LECO COM-CAT PN #502-321)
- Mix the COM-CAT and sample with weighing spatula
- Place the sample into the High-Temperature Tube Furnace

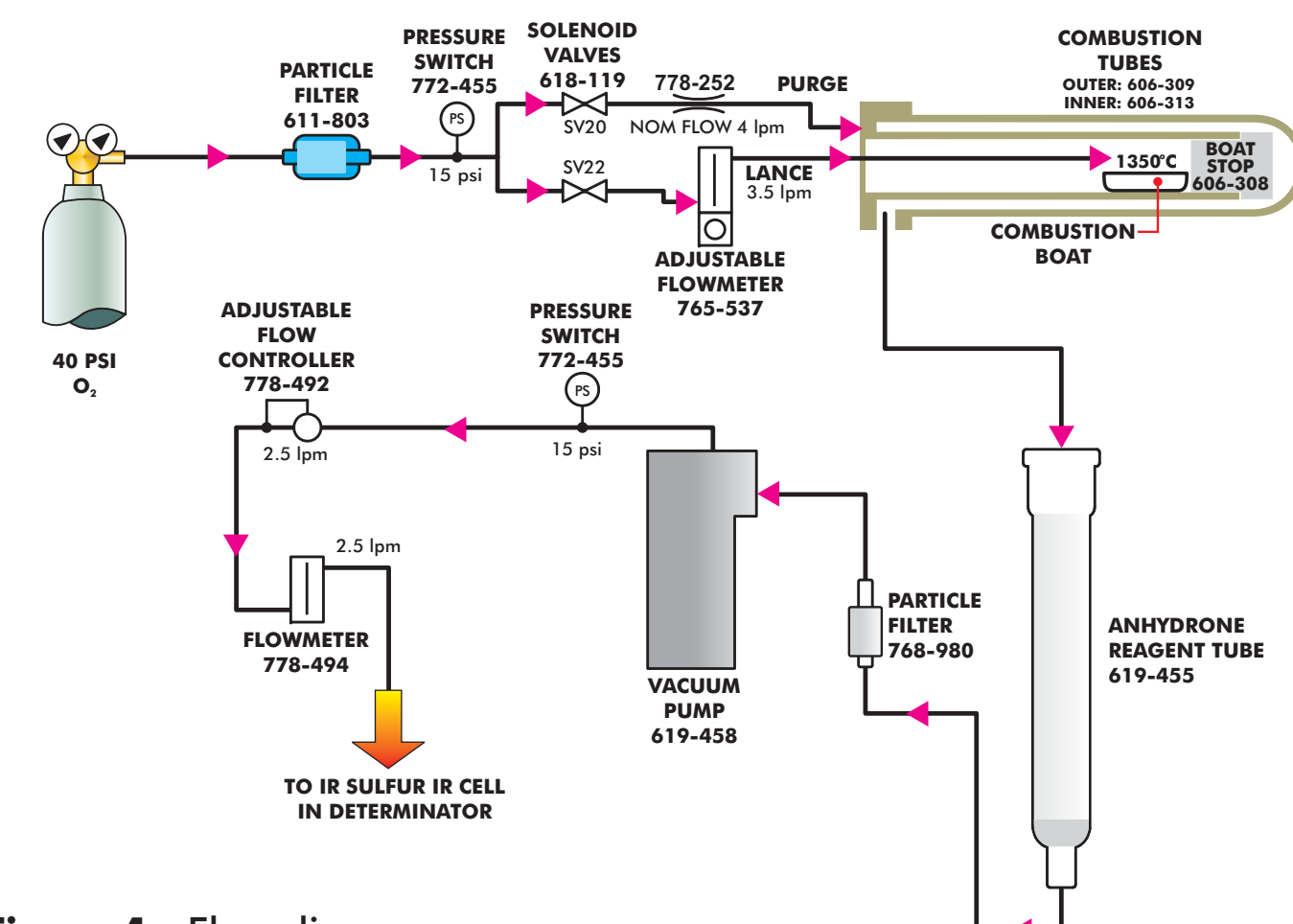


Figure 1. Flow diagram.

The sample is combusted in the furnace at 1350°C with pure oxygen causing all sulfur to be oxidized to SO₂. Combustion gases pass through anhydrous, removing moisture, and on to the Infrared Detection cell.

CALIBRATION

The TruSpec Sulfur Module was calibrated using NIST SRM 886 (Gold Ore Refractory), Sulfamethazine (pure chemical LECO PN 502-209), and Fly Ash Reference Material (LECO PN 502-096) using the masses listed in the table below. A multipoint Linear regression calibration was utilized. This calibration approach covers ~1.6 orders of magnitude for sulfur (~0.72 to 11.52 mg of sulfur). When using a nominal sample mass of 50 mg the calibration covers ~1.4% to ~23% sulfur and has a range of 0.5% to 23% for the typical sample mass range of 50 mg to 100 mg.

Reference Material	Mass (g)	Certificate Conc. (%S)	Calibration Calculated (%S)	Error (%)	mg Sulfur	Instrument Response (Peak Area)
Sulfamethazine	0.1010	11.52	11.49	-0.29	11.60	1.4479
Sulfamethazine	0.1025	11.52	11.50	-0.20	11.78	1.4706
Sulfamethazine	0.1022	11.52	11.49	-0.28	11.74	1.4651
Sulfamethazine	0.1039	11.52	11.51	-0.07	11.96	1.4925
Sulfamethazine	0.1018	11.52	11.56	0.36	11.77	1.4688
Nist 886	0.1041	1.466	1.46	-0.39	1.52	0.1971
Nist 886	0.1027	1.466	1.48	1.23	1.52	0.19761
Nist 886	0.1055	1.466	1.51	2.72	1.59	0.20562
Nist 886	0.1046	1.466	1.49	1.37	1.55	0.20137
Nist 886	0.1034	1.466	1.48	1.16	1.53	0.19876
LECO Fly Ash (502-096)	0.2005	0.36	0.35	-2.37	0.70	0.095934
LECO Fly Ash (502-096)	0.201	0.36	0.35	-2.26	0.71	0.096258
LECO Fly Ash (502-096)	0.2026	0.36	0.36	-0.61	0.72	0.098447
LECO Fly Ash (502-096)	0.2023	0.36	0.36	-0.38	0.73	0.098518

Table 1. Sulfur Calibration Data.

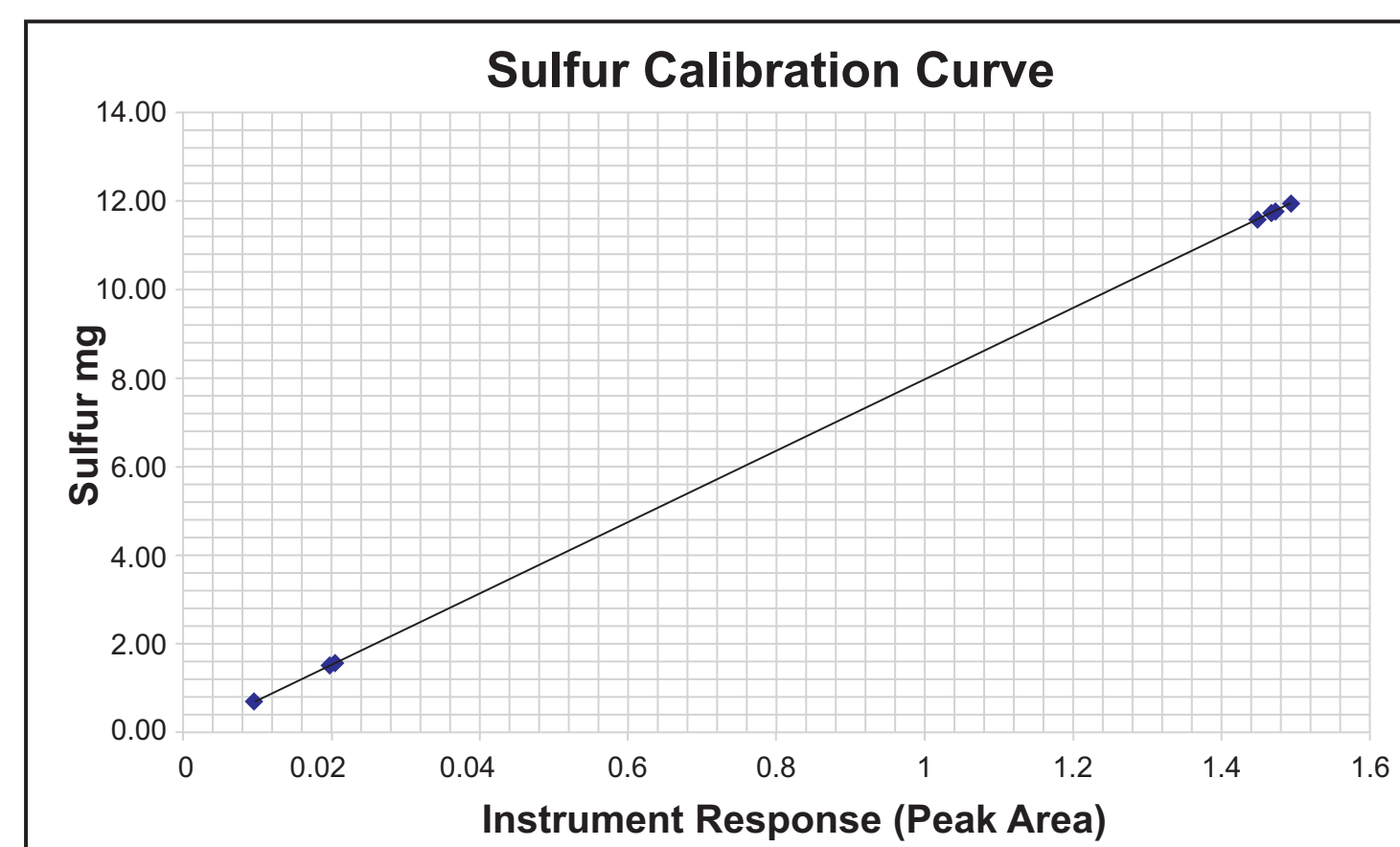


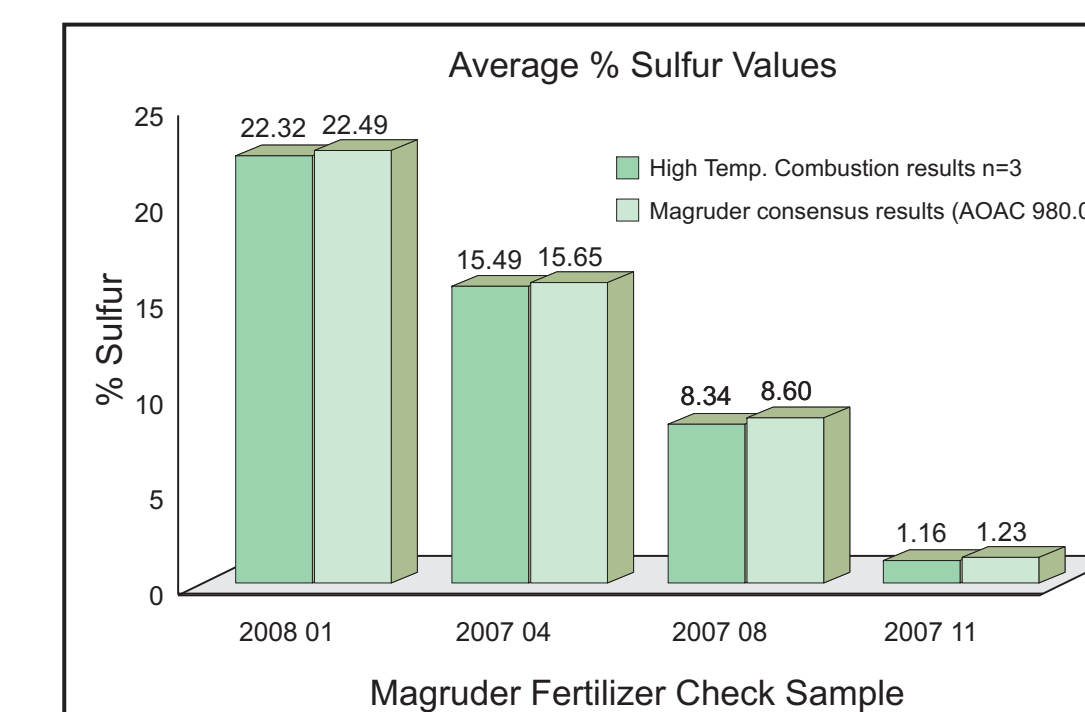
Figure 2. Sulfur calibration curve.

RESULTS

Four dry inorganic Magruder fertilizer check samples were chosen representing the range of sulfur concentrations for typical dry fertilizers to show the performance of the instrument for the total sulfur in fertilizer application. Magruder fertilizer check samples were utilized for comparison of the total sulfur obtained via the high temperature combustion method versus the published consensus AOAC 980.02a gravimetric data. The total sulfur concentration range for sulfur, using the Magruder consensus sulfur values (AOAC 980.02a method), was 1.23% to 22.49% sulfur.

Magruder Fertilizer Check Sample	High Temp. Combustion results n=3			Magruder consensus results (AOAC 980.02a)		Difference
	Sample Mass (g)	%S	Std Dev	% S	Std Dev	
2008 01	~0.050	22.32	0.08	22.49	0.46	0.17
2007 04	~0.050	15.49	0.06	15.65	0.2	0.16
2007 08	~0.100	8.34	0.05	8.60	0.14	0.26
2007 11	~0.100	1.16	0.00	1.23	0.1	0.07

Table 2. Sulfur Results for Magruder Dry Fertilizers Check Samples.



During this work, both Sulfamethazine (#502-209) and Ore Tailing (#502-319) reference materials were run as check samples interspersed with the Magruder Dry Fertilizer Check Samples. The results obtained on these checks verify that the instrument and its calibration remained stable.

Reference Material	Sulfamethazine (#502-209)	Ore Tailing (#502-319)
Average (%S)	11.5	1.24
Standard Deviation	0.15	0.06
RSD (%)	1.3	4.53
Expected (%S)	11.52	1.25
Recovery (%)	99.8	99.2
# of Runs	9	8

Table 3. Sulfur Check Sample Data.

OBSERVATIONS AND COMMENTS

The objective of this work was to demonstrate an acceptable comparison between total sulfur results obtained by the AOAC 980.02a classical wet chemistry method versus the high-temperature combustion with IR absorption detection method. The high-temperature combustion method data generally compared well to the Magruder AOAC 980.02a consensus values. With the exception of one sample (2007 08), all of the high-temperature combustion method results fell within one standard deviation of consensus AOAC 980.02a results. The result of the high-temperature combustion for the 2007 08 sample was more than one standard deviation lower than the AOAC 980.02a consensus data, but the result was within two standard deviations of the 980.02a consensus average.

The high-temperature combustion with IR absorption method offers laboratories many benefits compared to the classical wet chemical or alternative techniques requiring acid digestion.

- Simple and fast (2 min analysis time) method
- Instrument automation (50-position autoloader) coupled with the fast analysis time results in both high throughput and improved efficiency
- Little to no sample pre-treatment required
- Improved Safety—no hazardous chemicals used (green chemistry technique)
- Low cost/analysis (~\$0.45) compared to chemical and disposal costs

For fertilizer laboratories that already own a TruSpec N for nitrogen analysis, a Sulfur Add-on Module provides sulfur determination capabilities to an existing TruSpec N instrument, eliminating the need to purchase a dedicated sulfur instrument and lowering instrument capital costs.

Acknowledgement – Data employed to compare the high-temperature combustion method to AOAC 980.02a consensus values was taken from the Magruder Fertilizer Check Sample Program operated by the Magruder Check Sample Committee.