



Delivering the Right Results

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

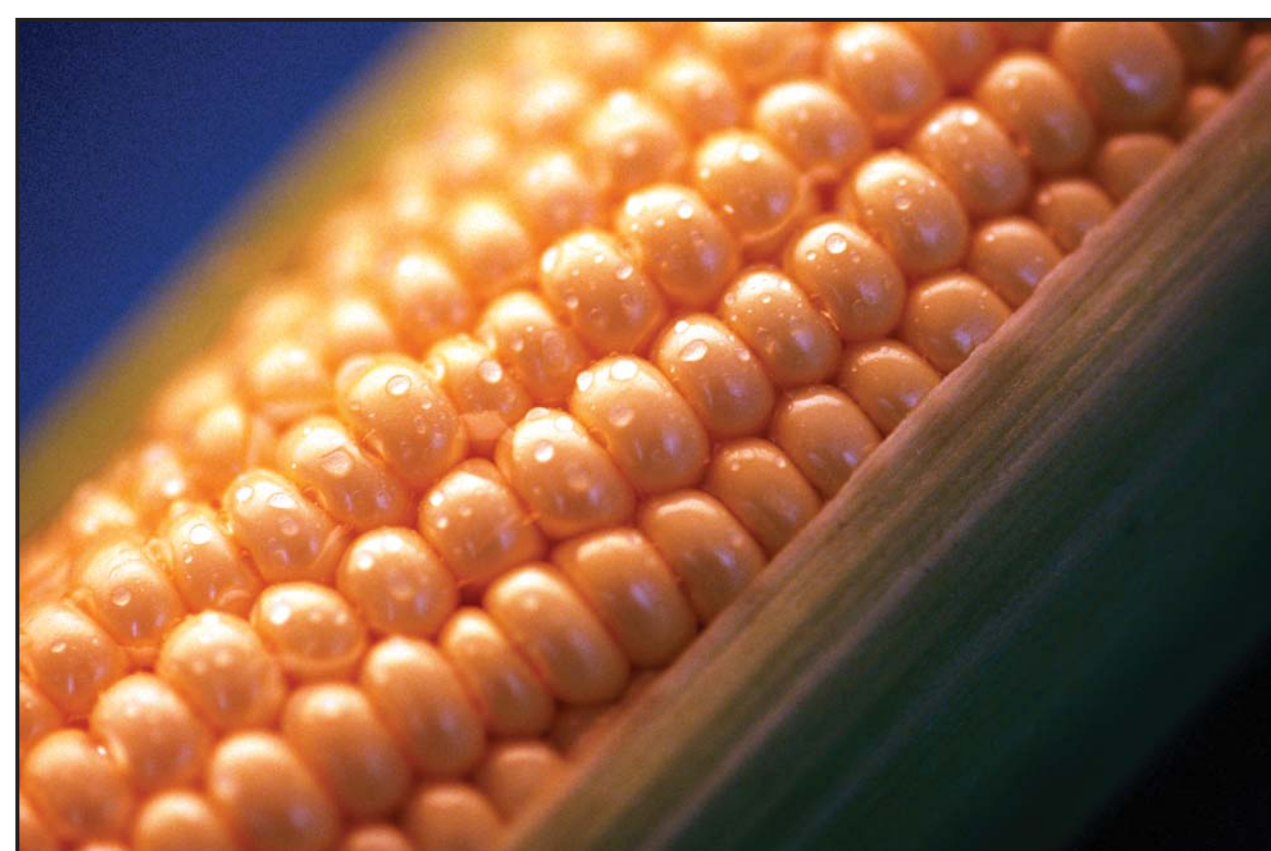
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INTRODUCTION

The recent expansion in the ethanol industry has resulted in larger amounts of corn milling co-products for animal feed. These dry distiller grains with solubles (DDGS) make good animal feed, but sulfur levels must be monitored. The sulfur content of DDGS is known to be variable and can be significantly higher than the generally recognized upper limit for cattle feed of 0.4% sulfur (dry weight) depending upon processing conditions of the corn mill. A greater level of sulfur has been linked to polioencephalomalacia (PEM) in cattle. PEM causes a disturbance of the central nervous system leading to the swelling of the brain and is usually fatal to the animal.

High-temperature tube furnace combustion with infrared absorption offers many advantages over the gravimetric and Inductively Coupled Plasma Emission Spectrometry (ICP-AES) 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.

This poster presents a simple and rapid analytical technique for the determination of total sulfur in DDGS matrix. Results for a variety of DDGS samples will be presented and associated data evaluated.



METHODOLOGY



Equipment Required

LECO TruSpec® Sulfur Module

Procedure

- Weigh ~150 mg sample (100-200 mg) 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

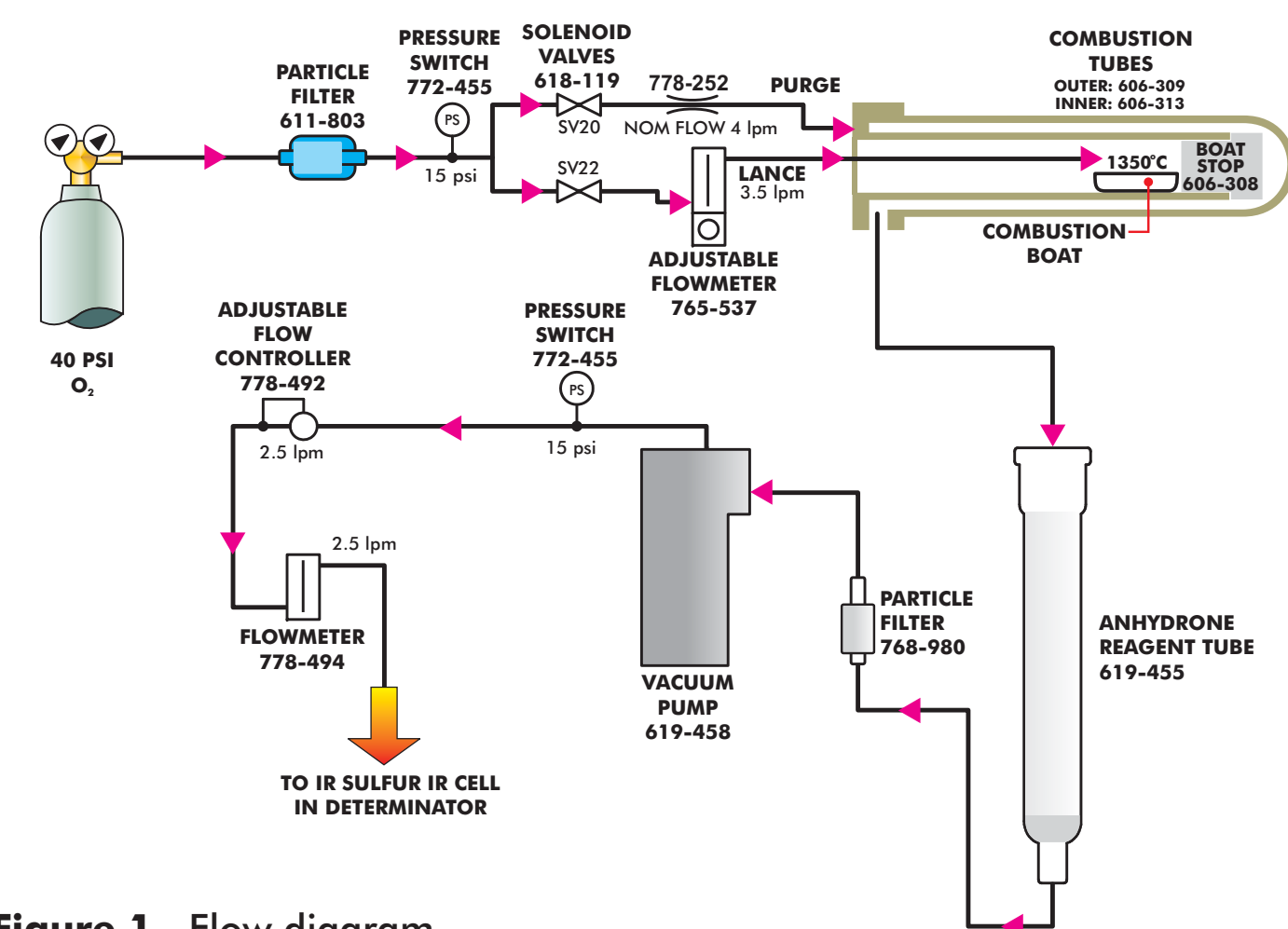


Figure 1. Flow diagram.

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 2691 (Coal Fly Ash, 0.83%S) and NIST SRM 2690 (Coal Fly Ash, 0.15%S) with the masses listed in Table 1 below. A multipoint Linear regressed calibration was utilized. When using a nominal sample mass of 150 mg the calibration covers ~0.25% to ~1.4% sulfur and has a range of ~0.2% to ~2.0% for the typical sample mass range of 100 mg to 200 mg.

Reference Material	Mass (g)	Certificate Conc. (%S)	Calibration Calculated (%S)	Error (%)	mg Sulfur	Instrument Response (Peak Area)
NIST 2691	0.2508	0.83	0.820	-1.18	2.06	0.24193
NIST 2691	0.2551	0.83	0.842	1.42	2.15	0.25043
NIST 2691	0.2523	0.83	0.845	1.76	2.13	0.24383
NIST 2691	0.2029	0.83	0.846	1.87	1.72	0.19856
NIST 2691	0.2058	0.83	0.834	0.53	1.72	0.20320
NIST 2691	0.2018	0.83	0.839	1.11	1.69	0.19900
NIST 2691	0.2004	0.83	0.835	0.66	1.67	0.19427
NIST 2691	0.1547	0.83	0.820	-1.21	1.27	0.15343
NIST 2691	0.152	0.83	0.834	0.53	1.27	0.15146
NIST 2691	0.1532	0.83	0.836	0.68	1.28	0.15177
NIST 2691	0.1031	0.83	0.828	-0.24	0.85	0.10443
NIST 2691	0.1033	0.83	0.820	-1.21	0.85	0.10451
NIST 2691	0.1007	0.83	0.833	0.38	0.84	0.10163
NIST 2691	0.1045	0.83	0.818	-1.41	0.86	0.10272
NIST 2690	0.2512	0.15	0.148	-1.41	0.37	0.046169
NIST 2690	0.2549	0.15	0.148	-1.59	0.38	0.046726
NIST 2690	0.2517	0.15	0.149	-0.68	0.37	0.046577

Table 1. Sulfur Calibration Data.

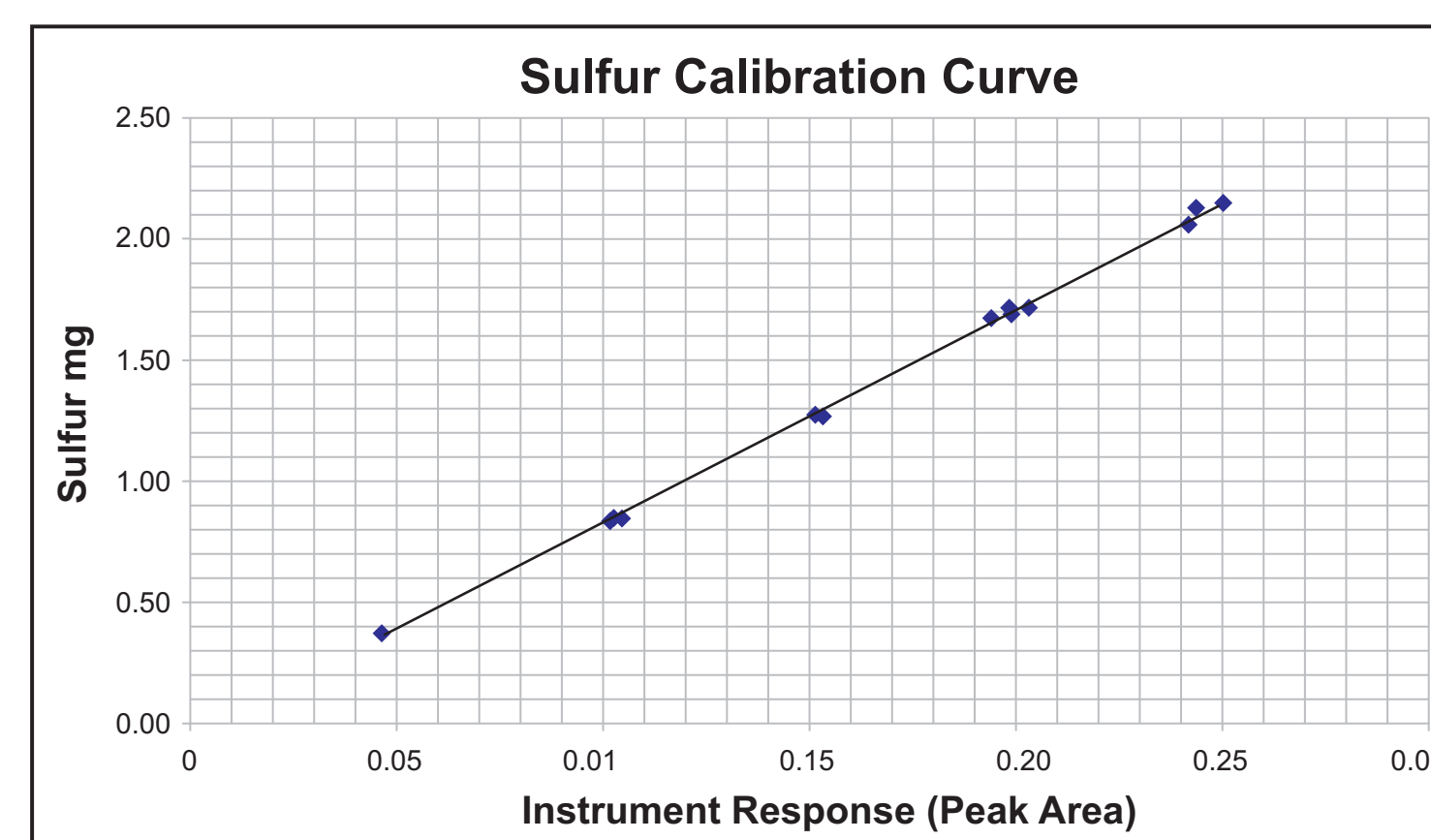


Figure 2. Sulfur calibration curve.

RESULTS

Five DDGS samples were chosen from different ethanol dry corn milling facilities operated within the United States to demonstrate the performance of the instrument for the total sulfur determination in DDGS sample matrix.

Sample	Mass (g)	%S
1	0.1548	0.5142
	0.1505	0.5090
	0.1533	0.5148
	0.1534	0.5140
	0.1512	0.5140
Average		0.5135
Std Dev		0.0025
RSD (%)		0.50
2	0.1524	0.5618
	0.1536	0.5704
	0.152	0.5607
	0.1527	0.5664
	0.1555	0.5757
Average		0.5670
Std Dev		0.0062
RSD (%)		1.09
3	0.1508	0.3723
	0.1531	0.3758
	0.154	0.3759
	0.1546	0.3709
	0.1537	0.3794
Average		0.3749
Std Dev		0.0033
RSD (%)		0.89
4	0.1519	0.7255
	0.1508	0.7458
	0.1538	0.7491
	0.1511	0.7483
	0.1531	0.7434
Average		0.7424
Std Dev		0.0097
RSD (%)		1.31
5	0.1518	0.7938
	0.1543	0.7983
	0.1503	0.7878
	0.1528	0.7934
	0.1506	0.7923
Average		0.7911
Std Dev		0.0056
RSD (%)		0.70

Table 2. DDGS Sample Sulfur Data.

During this work, both NIST 2690 (Coal Fly Ash) and Tobacco Leaves Reference Material (LECO #502-319) were run as check samples interspersed within the DDGS samples. The results obtained on these checks verify that the instrument and its calibration remained stable.

Reference Material	NIST SRM 2690	Tobacco Leaves Reference Material (#502-082)
Average (%S)	0.148	0.600
Standard Deviation	0.001	0.002
RSD (%)	0.68	0.33
Expected (%S)	0.15	0.60
Recovery (%)	98.7	100.0
# of Runs	3	3

Table 3. Sulfur Check Sample Data.

CONCLUSIONS

The objective of this work was to demonstrate the acceptable quantitative sulfur recovery and precision in the DDGS matrix when using the high-temperature combustion with IR absorption detection method. The high-temperature combustion instrument demonstrated the technique's matrix independence by using inorganic matrix SRM (Coal Fly Ash 2691 & 2690) for calibration, and verifying and checking the instrument's calibration using an organic reference material (tobacco leaves – LECO #502-082). The high-temperature combustion method had excellent precision with all of the sample's RSD being less than 1.5% and all of the data was within the expected sulfur ranges for the DDGS samples.

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 feed laboratories that already own a TruSpec N for protein 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.