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). In some cases, an Inductively Coupled Plasma Emission Spectrometry (ICP-EIS) technique has been used at high temperature tube furnace combustion with infrared (IR) absorption detection methods. 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 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 in comparison to the Magruder consensus total sulfur values of AGAC 980.02a method.

METHODOLOGY

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 ~1.4% to ~23% sulfur and has a range of 0.5% to 23% for the typical sample mass range of 50 mg to 100 mg.

Calibration

Instrument Response (Peak Area)

<table>
<thead>
<tr>
<th>% Sulfur</th>
<th>Expected (%S)</th>
<th>Recovery (% Sulfur)</th>
<th>RSD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.24</td>
<td>1.23</td>
<td>1.25</td>
<td>0.06</td>
</tr>
<tr>
<td>4.53</td>
<td>4.52</td>
<td>4.54</td>
<td>0.07</td>
</tr>
<tr>
<td>99.8</td>
<td>99.2</td>
<td>99.6</td>
<td>0.28</td>
</tr>
</tbody>
</table>

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.

OBSERVATIONS AND COMMENTS

The objective of this work was to demonstrate an acceptable comparison between total sulfur results obtained by the AGAC 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 with 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 method deviates from 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 throughputs and improved efficiency.
- Little to no sample pre-treatment required
- Improved safety—no hazardous chemicals used (green chemistry technique)
- Low cost analysis (~$5-45) 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 incurring instrument capital costs.

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