A Novel Method for Total Sulfur Determination for Garlic-derived Sulfide Compounds

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Abstract

Garlic-derived sulfide compounds are well known natural nematicides, especially after European Union approved the use of ECOspray. As sulfur is a component element of these compounds, and elemental sulfur is typically used in the synthesis and ремита in the final products, accurate sulfur content determination becomes critical in product purity evaluation. Although sulfur determination on ICP-OES has been challenging, an efficient approach has been developed and successfully utilized at EPL for agricultural products. However, the garlic-derived sulfides pose a new challenge as they are insoluble in water. When tested on the ICP with the assistance of a hydrotrope, inconsistent and erratic signals were observed. In addition, when an average recovery of 98% was obtained for sulfides, and a recovery of 96% for widely used organic sulfur standard MSA (methanesulfonic acid), it was evident that the signal distortion became so detrimental that it invalidated all the preliminary test results. To improve the method, an optimized oxidation reaction was performed to transform the sulfides. After the transformation, the samples were dissolved in aqueous dimethylformamide (DMF) solution. The ICP conditions were also modified with several critical changes in order to minimize the signal enhancement of the sulfate, the signal suppression of the MSA, and to eliminate sample carry-over. Using the standard diallyl sulfide as a representative of the garlic derived sulfides we demonstrated the efficiency of this method in both accuracy (98 and 102 % recovery) and precision (<3% CV).

Objective

- Develop and validate an analytical method for the determination of total sulfur for garlic-derived sulfides.
- Materials and Methods
  - Chemicals and Reagents
  - Samples
  - Instruments
  - Sample Preparation
  - IC-PES Analysis
  - Results & Discussion
  - Challenges in Sample Preparation and ICP Analysis
  - Final Test Results

Materials and Methods

- Chemicals and Reagents
- Sulfur as methane sulfonic acid (MSA) standard
- Dimethylformamide (DMF)
- Peracetic acid (or hydrogen peroxide and acetic acid)
- DI water

Sample Preparation

- Wash approximately 0.0500 g (0.04050-0.0550 g) of sample into a leached crystallization dish.
- Add 5 mL peracetic acid solution.
- Add 5 mL water.
- Stir for 3 hours at 40°C (37-41°C) in a water bath.
- Allow the mixture to cool for about 1-1.5 hours at ambient temperature.
- Rinse with 10 mL of 3% peracetic acid and rinse with water.
- Fortification: multiple samples were spiked with 0.2 mL of MSA or 0.05 mL of diallyl sulfide.

ICP-OES Analysis

- Analysis: Sulfur (S) at 181.980 nm
- Calibration Parameters: Linear, Minimum Correlation Coefficient 0.99
- Calibration standards 10 - 200 ug/mL of sulfur
- Internal standards: Yttrium (Y) at 371.029 nm

Table 1. ICP-OES parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Setting</th>
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<tbody>
<tr>
<td>Slit (nm)</td>
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<tr>
<td>Power (W)</td>
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<tr>
<td>Discharge current (A)</td>
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<tr>
<td>Gas flow (L/min)</td>
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<tr>
<td>Nebulizer Flow</td>
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<tr>
<td>View distance (mm)</td>
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<tr>
<td>View angle</td>
<td>105</td>
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<td>Sample Introduction</td>
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</table>

Table 2. Preliminary Test Results.

<table>
<thead>
<tr>
<th>Spike Level</th>
<th>Spike Recovery</th>
<th>Average Recovery</th>
<th>%CV</th>
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<tbody>
<tr>
<td>1X</td>
<td>98%</td>
<td>98%</td>
<td>1.55%</td>
</tr>
<tr>
<td>2X</td>
<td>100%</td>
<td>100%</td>
<td>1.55%</td>
</tr>
<tr>
<td>3X</td>
<td>102%</td>
<td>102%</td>
<td>1.55%</td>
</tr>
</tbody>
</table>

Results & Discussion

- Preliminary Test Results
- Total sulfur recovery tests of both organic sulfur standards (Table 2)
  - MSA: a common organic sulfur standard
  - Diallyl sulfide: a representative sulfide component of garlic origin
- Both spiked into samples of garlic derived sulfide mixture
- Both standards: spiked at 1x level with respect to the sample concentrations
- Both standards: inconsistent recoveries obtained among the three spikes
- Diallyl sulfide: severe signal enhancement observed
- MSA: severe signal suppression observed

- Calibration Curve of Sulfur.

- Figure 2.

Challenges in Sample Preparation and ICP Analysis

- Hydroxide Options
- Role of peroxide and organic solvents
- MSA: a common organic sulfur standard
- Diallyl sulfide: a representative sulfide component of garlic origin
- Both standards: spiked at 1x level with respect to the sample concentrations
- Both standards: inconsistent recoveries obtained among the three spikes
- Diallyl sulfide: severe signal enhancement observed
- MSA: severe signal suppression observed

- Figure 3.

Final Test Results

- Total sulfur tests of samples of garlic derived sulfides (Table 3)
- Spike levels were prepared and tested on three different days
- All samples achieved good precision (<3% CV) and accuracy (98 and 102% in average recoveries)
- MSA recovery improved to 97.8% with good precision (2.49% CV)
- Diallyl sulfide improved to 102% in recovery with good precision (1.55% CV)

Table 3. Final Test Results

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- References

Conclusion

- An analytical method for the determination of sulfur in garlic-derived sulfide compounds was developed and validated with satisfactory accuracy and precision.