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Application News

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Liquid Chromatography Mass Spectrometry

# Analysis of Sulfamic Acid in Fertilizers Using LC/MS (LCMS-2020)

Sulfamic acid, due to its plant growth inhibiting effects, is subject to maximum limits in fertilizers as specified in the official standard[1] for ordinary fertilizers according to the Japanese Fertilizers Regulation Act. According to the Testing Methods for Fertilizers[2] supervised by Japan's Food and Agricultural Materials Inspection Center (FAMIC), the ion chromatography (IC) method is specified as the test method for sulfamic acid in ammonium sulfate. It has been reported, however, that when applying this IC method with byproduct compound fertilizer (fertilizer produced by concentrating and drying liquid byproducts obtained from fermentation plants involved in amino acid production, etc.) samples that contain large amounts of organic matter, it is difficult to separate the sulfamic acid peaks from contaminant peaks generated from sample matrix.[3]

In this application, we investigated the analytical conditions for LC/MS that would permit acquisition of mass information and provide high selectivity in order to eliminate the effects of contaminating components. The LCMS-2020 single quadrupole mass spectrometer was used for the analysis.

Good quantitative results were obtained, confirming the applicability of this method using byproduct compound fertilizer as the actual sample.

## Analysis of Standard Solution

Table 1 shows the analytical conditions, and Fig. 1 shows chromatogram obtained using a standard solution (0.1 mg/L aqueous solution) of sulfamic acid.

As retention of a zwitterionic compound such as sulfamic acid is difficult using reversed phase conditions, we adopted conditions using a HILIC column. Isocratic analysis was conducted using a mobile phase consisting of acetonitrile / ammonium formate + formic acid (pH 3.2).

Applying the LC/MS method (ESI-Negative), we conducted selected ion monitoring (SIM) analysis using the deprotonated molecule at *m/z* 95.9. Fig. 2 shows the calibration curve. Excellent linearity was obtained over the entire concentration range of 0.001 to 0.1 mg/L, with a correlation coefficient greater than 0.999.

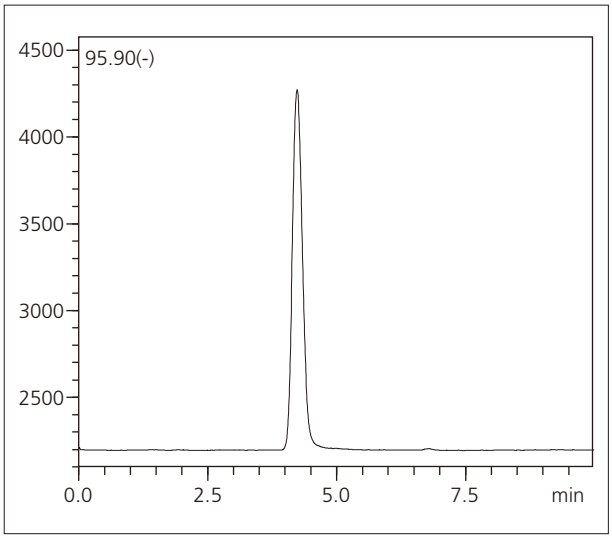


**Fig. 1 Mass Chromatogram (SIM) of Sulfamic Acid (0.1 mg/L)**

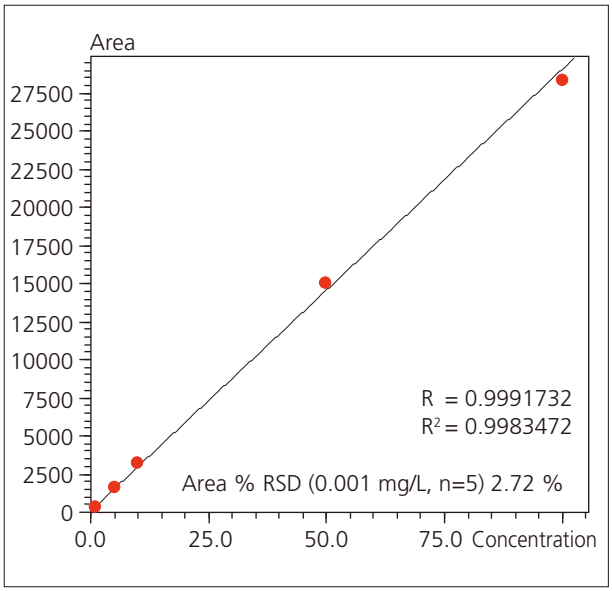


**Fig. 2 Calibration Curve (0.001 – 0.1 mg/L)**

**Table 1 Analytical Conditions**

| | |
|---|---|
| Column | : Phenomenex Luna HILIC 20A (100 mm L. × 2.0 mm I.D., 5 µm) |
| Mobile Phases | : Acetonitrile/100 mmol/L Ammonium Formate+ Formic Acid (pH 3.2) = 90:10, v/v |
| Flowrate | : 0.2 mL/min |
| Column Temperature | : 40 ˚C |
| Injection Volume | : 1 µL |
| Probe Voltage | : -3.5 kV (ESI-negative mode) |
| DL Temperature | : 250 ˚C |
| Block Heater Temperature | : 400 ˚C |
| Nebulizing Gas Flow | : 1.5 L/min |
| Drying Gas Flow | : 15 L/min |
| Monitoring Ion (SIM) | : *m/z* 95.9 |

## Analysis of Sulfamic Acid in Fertilizers

We verified the applicability of the LC/MS method using a byproduct compound fertilizer as an actual sample. The permissible content level of sulfamic acid is set based on the total amount of the principal component in each type of fertilizer. Here, taking the lower limit of quantitation of sulfamic acid in fertilizer as 1/5 the value of the minimum concentration permissible (sulfamic acid concentration 0.005 % per principal component 1 %), we conducted spike and recovery testing using a spike quantity equivalent to the lower limit of quantitation.

Fig. 3 shows the sample pretreatment procedure. The extraction method conforms to the Testing Methods for Fertilizers (2013) supervised by FAMIC. After weighing out 1 g of byproduct compound fertilizer, extraction was conducted using 100 mL of water, and after further diluting this 100 to 1 with water, the mixture was filtered to complete preparation of the fertilizer measurement solution.

As the total quantity of the principal component represented 5 % of the fertilizer content, the concentration of sulfamic acid corresponding to the lower limit of quantitation is calculated as 50 mg/kg of fertilizer. In the spike and recovery test, 0.5 mL of 100 mg/L standard sample was added to the fertilizer, and after letting the mixture stand for 30 minutes, a measurement solution was prepared using the same procedure. The concentration of sulfamic acid in the measurement solution is therefore 0.005 mg/L.

Representative chromatograms are shown in Fig. 4 including chromatograms of the standard sample (0.005 mg/L), the sample spiked with sulfamic acid, and the byproduct compound fertilizer measurement solution. Table 2 shows the analytical results. Sulfamic acid was not detected in the byproduct compound fertilizer, nor were there any noticeable peaks associated with contaminant components.

In the spike and recovery test, excellent results were obtained in continuous analysis (n=5), with an average recovery rate of 101 %. The LC/MS method investigated here in the analysis of highly contaminated byproduct compound fertilizer was demonstrated to permit quantitation by simply adding a dilution step following extraction, as opposed to the IC method which requires tedious processing to address the issue of high-contaminant content.

**Table 2 Repeatability of Peak Area and Retention Time in Spike and Recovery Test**

| | R.t (min) | Peak Area | Recovery (%) |
|---|---|---|---|
| 1st | 4.217 | 1564 | 103 |
| 2nd | 4.252 | 1561 | 102 |
| 3rd | 4.229 | 1508 | 99 |
| 4th | 4.224 | 1511 | 99 |
| 5th | 4.219 | 1534 | 100 |
| Ave | 4.228 | 1535 | 101 |
| %RSD | 0.336 | 1.735 | |

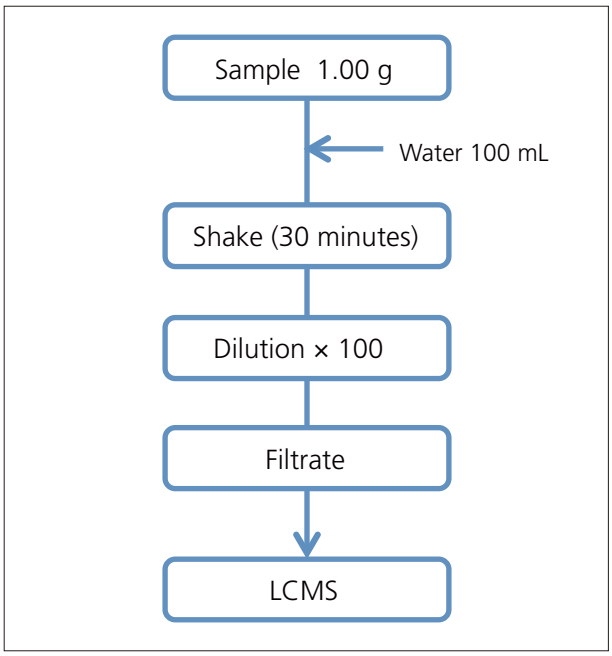


**Fig. 3 Preparation Flow**

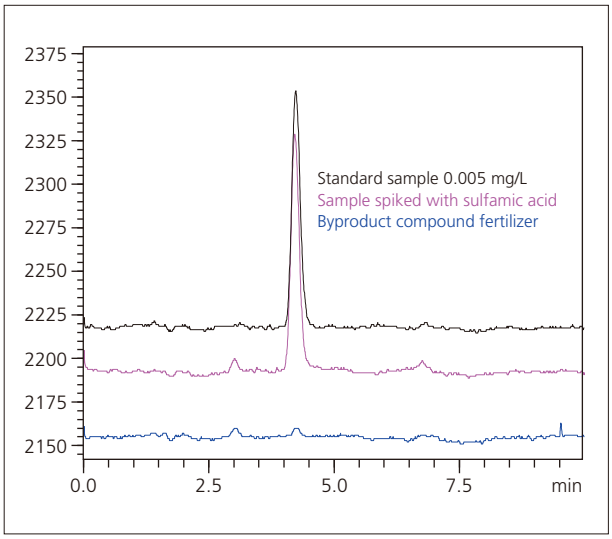


**Fig. 4 SIM Chromatograms of STD and Fertilizer Sample**

[References]
1) Notification Regarding Determination of the Official Standard for Ordinary Fertilizer Based on the Fertilizers Regulation Act, February 22, 1986, the Japan's Ministry of Agriculture, Forestry and Fisheries Notification No. 284, Final Revision
December 5, 2013 the Ministry of Agriculture, Forestry and Fisheries Notification No. 2939 (2013)
2) Food and Agricultural Materials Inspection Center (FAMIC): Testing Methods for Fertilizers
< http://www.famic.go.jp/ffis/fert/sub9.html >
3) Hiroi T., Shirai Y.: Simultaneous Determination of Sulfamic Acid and Ammonium Thiocyanate in Ammonium Sulfate by Nonsuppressed Ion Chromatography, Research Report of Fertilizer, 5, 1 – 12 (2012)

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