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Application News

No. M296

Gas Chromatography Mass Spectrometry

Analysis of Reaction Products (Formic Acid, Formaldehyde) in Artificial Photosynthesis by GCMS™

Various analysis techniques are used in measurements of reaction products in the field of artificial photosynthesis. Examples of analysis by GC and GCMS have already been introduced.* This article introduces an example of a GCMS analysis of formaldehyde and formic acid, which are important compounds in the field of artificial photosynthesis, using the phosphoric acid-treated insert.

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* Examples of GC and GCMS analysis of reaction products in artificial photosynthesis field
- GC: Application News No. G279A, G280C
- GCMS: Application Data Sheet No. 81

Phosphoric Acid Treatment of Insert

In measurements of formaldehyde and formic acid at low concentrations by GC and GCMS, care is necessary to avoid adsorption on various component parts. Therefore, in order to prevent adsorption on the injection-related parts, phosphoric acid treatment of the glass insert of the sample vaporization chamber was carried out. The wool-filled glass insert (Restek Topaz Liner, P/N: 23319) was immersed in a 0.3 % phosphoric acid/acetone solution for 1 min, removed and dried. After this procedure, the glass insert was used in the analysis.

For the detailed treatment method, please refer to Application News No. G279A.

Adjust the wool position of the wool-filled insert so its upper edge is 25 mm from the top of the insert.
↓
Prepare the 0.3 % phosphoric acid/acetone solution.
↓
Immerse the wool-filled insert in the 0.3 % phosphoric acid/acetone solution for 1 min.
↓
Remove, and then dry with an air or nitrogen stream.

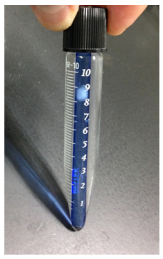

Fig. 1 Glass Insert Phosphoric Acid Treatment Procedure

Sample Preparation

Formic acid was adjusted to a concentration of 0.1 % with a 20 % methanol aqueous solution. Next, 100 µL of the prepared formic acid and 100 µL of a 0.1 % formaldehyde standard solution (FUJIFILM Wako Pure Chemical Corporation, product code: 066-06561) were mixed and diluted to 10 mL in a measuring flask using a 20 % methanol aqueous solution. Samples were then prepared by serial dilution of this solution to obtain formic acid and formaldehyde concentrations of 1 ppm, 0.5 ppm, and 0.1 ppm.

Analysis Conditions

Table 1 shows the GCMS instrument composition and analysis conditions.

When analyzing hydrous samples, repeatability and separation are sometimes improved by reducing the sample injection volume in comparison with normal analyses. Therefore, in this experiment, the injection volume was set at 0.5 µL.

On the other hand, repeatability may be worse due to heavy plunger operation during use if the analysis is conducted with a standard AOC syringe. To avoid this problem, an AOC elastic syringe (P/N: 221-49548) with a titanium plunger was used to enable stable sample injection.

Table 1 GCMS Instrument Composition and Analysis Conditions

Model	: GCMS-QP™2020 NX
Autosampler (AOC-20i)	
Syringe	: Elastic syringe
Injection volume	: 0.5 µL
GC	
Injection	: SPL
Injection temp.	: 240 °C
Injection mode	: Split
Split ratio	: 1:10
Carrier gas	: He
Carrier gas control	: Constant linear velocity (45 cm/s)
Column	: SH-Rtx™-1 (60 m × 0.32 mm, 5.0 µm)
Column temp.	: 40 °C (2 min)- 20 °C /min - 150 °C - 40 °C /min - 200 °C - 25 °C /min - 220 °C (10 min)
Purge flow	: 3 mL/min
MS (EI method)	
Ion source temp.	: 200 °C
Interface temp.	: 200 °C
Ionization mode	: EI
Measurement mode	: SIM
Event time	: 0.3 s
Monitor ion (*m/z*)	: 30, 29 (2.00 min - 4.33 min) 46, 45 (4.33 min - 8.00 min)

Effect of Phosphoric Acid-Treated Insert

Figs. 2 and 3 show the SIM chromatograms when the 1 ppm standard solution was analyzed using inserts with/without phosphoric acid treatment. Detection of the respective peaks was possible when the phosphoric acid-treated insert was used.

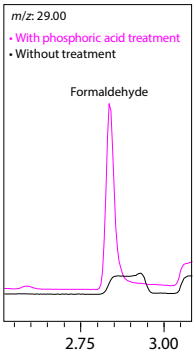

Fig. 2 SIM Chromatograms of Formaldehyde With/ Without Insert Treatment

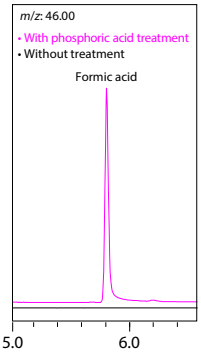

Fig. 3 SIM Chromatograms of Formic Acid With/ Without Insert Treatment

Analysis Results

Figs. 4 and 5 show the SIM chromatograms for analysis of the 0.1 ppm standard solution, and Figs. 6 and 7 show the calibration curves. Table 2 shows the repeatability of repeated analyses (n=3) in the analysis of the 0.1 ppm standard solution. Satisfactory results were obtained for sensitivity, linearity, and repeatability.

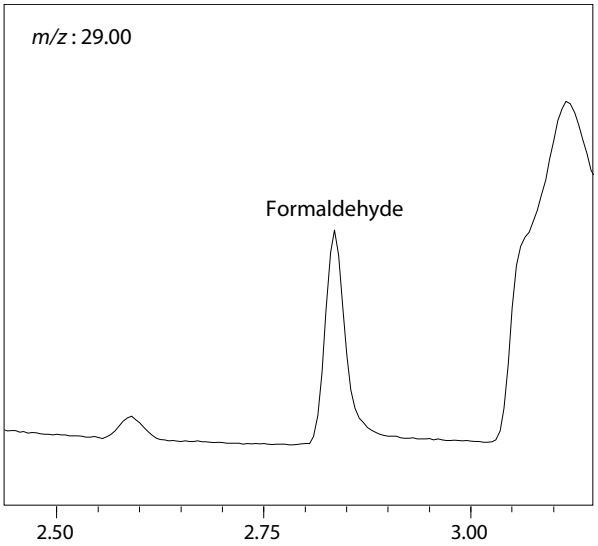

Fig. 4 SIM Chromatogram of 0.1 ppm Formaldehyde Standard Solution

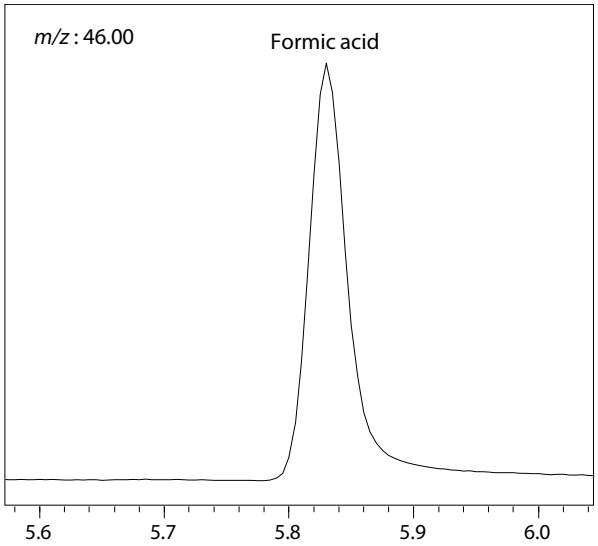

Fig. 5 SIM Chromatogram of 0.1 ppm Formic Acid Standard Solution

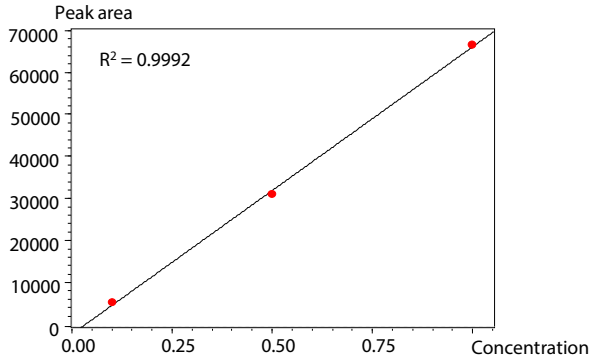

Fig. 6 Calibration Curve of Formaldehyde

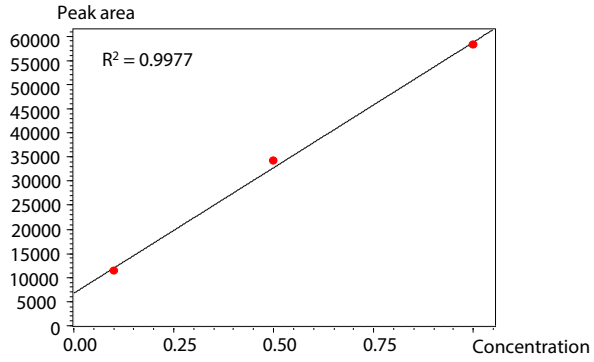

Fig. 7 Calibration Curve of Formic Acid

Table 2 Repeatability of Repeated Analyses

Compound	Data 1	Data 2	Data 3	Peak area average	%RSD
Formaldehyde	7148	7192	7322	7221	1.3
Formic acid	13635	15303	15372	14770	6.7

Conclusion

An analysis of formaldehyde and formic acid, which are important components in the field of artificial photosynthesis, was conducted to the 0.1 ppm level using GCMS. Satisfactory results were obtained for both linearity and repeatability.

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