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Application News

No.G279A

Gas Chromatography

Improvement of Sensitivity and Repeatability in Analysis of Formic Acid

– Artificial Photosynthesis Research and Impurity Analysis of Chemical Raw Material –

In the study of artificial photosynthesis and impurity analysis of raw materials and chemical products, high-sensitivity analysis of formic acid has become an important requirement. When conducting analysis of formic acid by gas chromatography (GC), detection is typically conducted using either a thermal conductivity detector (TCD) or a combination of methanizer + FID detector. As the TCD is appropriate for relatively low-sensitivity detection, it is mainly used for analysis of high-concentration samples, while the methanizer + FID combination is used in analysis of low-concentration samples. Because the FID alone exhibits little or no response to formic acid as is, it must first be reduced to methane using a methanizer, which then permits detection by FID.
A methanizer can be a useful tool, but it does have its disadvantages under certain conditions, including deactivation of the catalyst if the oxygen concentration in the sample is greater than 100 ppm, or if the sample environment is high in carbon dioxide. Furthermore, if excessive water enters the system, it can take considerable time to restore the system. These disadvantages require the use of a valve system to eliminate oxygen or carbon dioxide. On the other hand, a barrier discharge ionization detector (BID) is a detector that is capable of detecting formic acid at ppm-order concentrations, thereby permitting high-sensitivity measurement, as long as coexisting components such as oxygen can be separated by the column.
In this Application News, we introduce an example of high-sensitivity analysis of formic acid included in various organic solvents using a GC-BID system.

Validation of Phosphoric Acid Treatment

When conducting GC measurement of formic acid at low concentrations, care must be taken to prevent adsorption to the various component surfaces. To prevent adsorption at the injection port, phosphoric acid treatment of the glass insert is essential. Here, after immersing the wool-filled glass insert (Restek Sky Inlet Liner, P/N: 23319.1) in 0.3 % phosphoric acid / acetone solution for one minute, it was removed, dried and then used for the analysis. Fig. 1 shows the pretreatment procedure flow used for the glass insert, and Fig. 2 shows the effectiveness of this pretreatment in low-concentration analysis. When measurement of a 10-ppm (v/v) formic acid solution (solvent: acetone) was conducted using the analytical conditions shown in Table 1, peak detection was not achieved using an untreated glass insert, while detection with good sensitivity was achieved using a glass insert that had been pretreated with phosphoric acid. The following analyses were conducted using the analytical conditions shown in Table 1.

Position of wool packing is adjusted so that its upper edge is 25 mm from top of insert.
↓
Prepare 0.3 % phosphoric acid / acetone solution.
↓
Immerse wool-packed insert in 0.3 % phosphoric acid / acetone solution for 1 minute.
↓
Remove, and then dry with air or nitrogen gas streams.

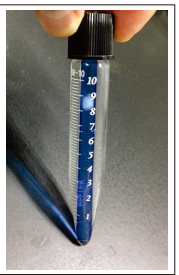

Fig. 1 Glass Insert Phosphoric Acid Treatment Procedure

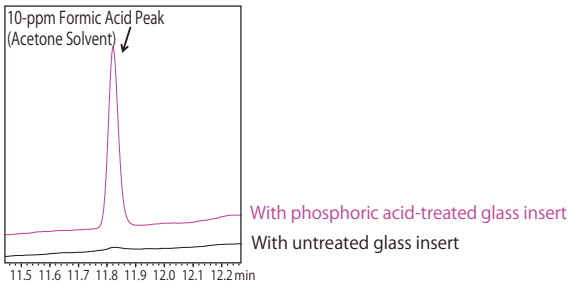

Fig. 2 Effectiveness of Glass Insert Phosphoric Acid Treatment in Low-Concentration Formic Acid Analysis

Table 1 Analytical Conditions

Model	: Tracera (GC-2010 Plus + BID 2010 Plus)
Inj. Mode	: Split 1:2
Inj. Temp	: 240 ˚C
Carrier Gas	: He 50 cm/sec. (Constant Linear Velocity Mode)
Column	: RESTEK Rtx-WAX (60 m × 0.53 mm I.D., df = 1.0 µm)
Column Temp.	: 80 ˚C - 5 ˚C/min - 130 ˚C - 15 ˚C/min - 230 ˚C (3 min)
Det. Temp.	: 240 ˚C
Discharge Gas	: 50 mL/min (He)
Glass Insert	: RESTEK Sky Inlet Liner P/N 23319.1
Inj. Volume	: 1 µL

＊Stabilwax-DA column is not suitable for this analysis.

The Rtx-WAX column (Restek Co.) was used for the analysis. Peak tailing was evident when measurement of a 10-ppm (v/v) formic acid aqueous solution (Solvent: Acetone) was conducted using an unused column directly after aging treatment. We then applied the same phosphoric acid treatment that was used for the glass insert to the column as well. The column phosphoric acid treatment procedure is shown in Fig. 3. A 100-ppm (v/v) phosphoric acid / methanol solution was measured four times, and this was followed by ten repeat measurements methanol alone using a constant column temperature of 150 °C (the other conditions were the same as those shown in Table 1). Then, we conducted repeat measurements of 10-ppm (v/v) formic acid solution (Solvent: Acetone), and we checked the stability of the peak shape and retention time. A comparison of the peak shapes of formic acid before and after the column phosphoric acid treatment is shown in Fig. 4. The comparative results confirmed that the peak shape was sharper following phosphoric acid treatment of the column.

Prepare 100-ppm phosphoric acid / methanol solution.
↓
Conduct four repeat measurements using conditions of Table 1.
↓
Stabilize column using ten repeat measurements of methanol with column at 150 ˚C (other conditions the same as shown in Table 1).
↓
Check repeatability of peak shape and retention time by repeat measurement of 10-ppm formic acid / acetone solution.

Fig. 3 Procedure for Column Phosphoric Acid Treatment

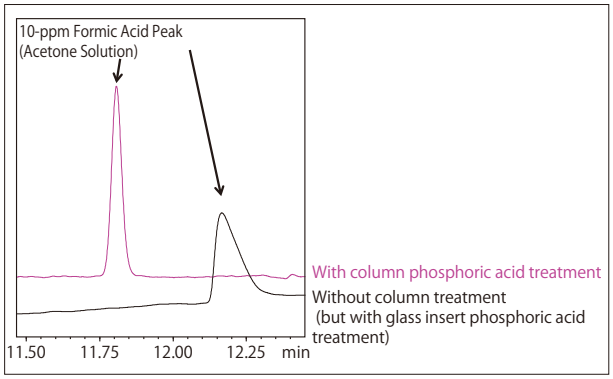

Fig. 4 Comparison of Formic Acid Peak Shapes Before and After Column Phosphoric Acid Treatment

To check the stability obtained with the glass insert and column phosphoric acid treatment, 100 repeat measurements of a 10-ppm (v/v) formic acid solution (Solvent: Acetone) were conducted. The area repeatability obtained was CV 1.6 %, and considering that the septum replacement guideline is based on 100 analyses, this confirms the effectiveness of the phosphoric acid treatment (Fig. 5).
Although the Rtx-WAX column was used in this study, we have not yet evaluated whether or not the same results would be obtained with other WAX columns. Further, since a column subjected to the same phosphoric acid treatment may have an adverse effect when used to conduct a different analysis, it is advisable to use the column specifically for formic acid analysis.

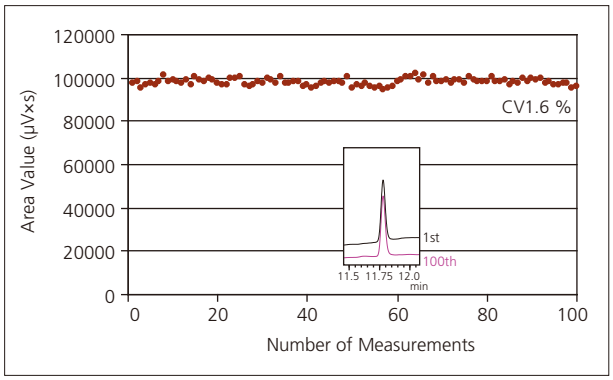

Fig. 5 Repeatability of Peak Area with 10-ppm Formic Acid / Acetone Solution at the Hundredth Analysis

Analysis of Low-Concentration Formic Acid in Various Organic Solvents

We checked the linearity of results using various concentrations of formic acid (1, 10, 50 ppm (v/v)) in different solvents, including acetone, *N*,*N*-dimethylacetamide, acetonitrile, and methanol.The linearity and chromatograms obtained in analysis of the acetone, *N*,*N*-dimethylacetamide, acetonitrile, and methanol solvent samples are shown in Figs. 6 to 9, respectively.

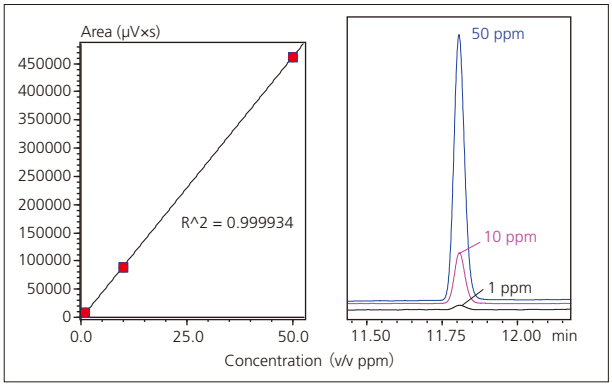

Fig. 6 Linearity of Formic Acid in Acetone (1, 10, 50 ppm)

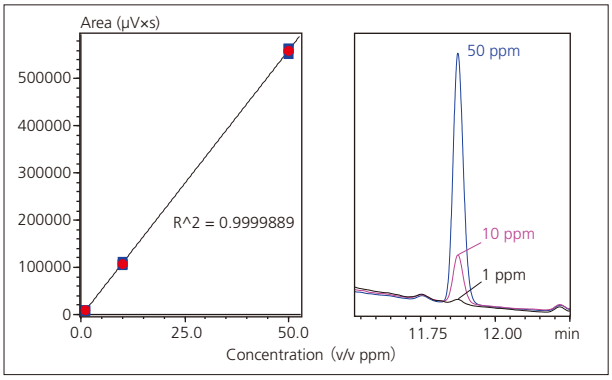

Fig. 7 Linearity of Formic Acid in *N*,*N*-Dimethylacetamide (1, 10, 50 ppm)

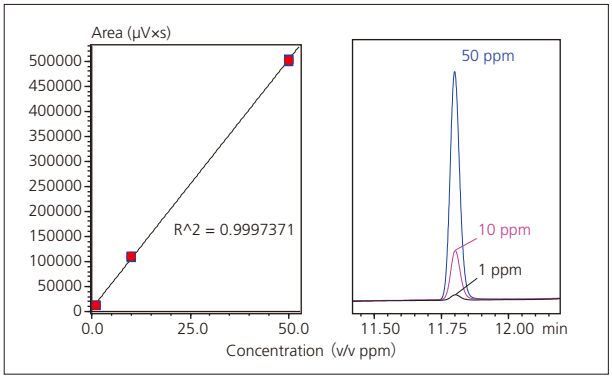

Fig. 8 Linearity of Formic Acid in Acetonitrile (1, 10, 50 ppm)

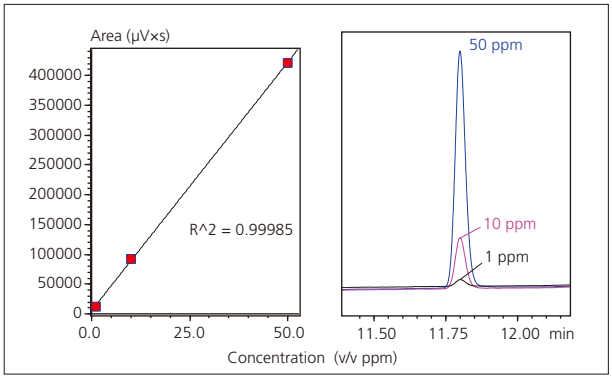

Fig. 9 Linearity of Formic Acid in Methanol (1, 10, 50 ppm)

Second Edition: Sep. 2018
First Edition: Jul. 2014

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