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Application News

Gas Chromatograph Nexis™ GC-2030/FID (Jetanizer™)

High-Sensitivity Analysis of Formic Acid in Methanol Solution Using Jetanizer™

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User Benefits

- Using Jetanizer as a GC-FID nozzle makes it possible to accurately analyze formic acid in methanol solution.
- The Jetanizer simply replaces the conventional GC-FID nozzle, making it easy to install and inexpensive.

■ Introduction

Green Transformation (GX) initiatives aim to transition from fossil fuels to green energy and balance greenhouse gas emissions reduction with economic growth. These initiatives are expected to use innovative technologies such as artificial photosynthesis, which utilizes sunlight to produce hydrogen and organic compounds from water and carbon dioxide.

Research on such artificial photosynthesis, along with the analysis of impurities in chemical products and raw materials, highlights the demand for high-sensitivity analysis of formic acid. A simple method for analyzing formic acid is gas chromatography (GC), where a TCD detector is used for high-concentration samples, and a BID detector is used for low-concentration samples. Unfortunately, the FID detector, a general-purpose detector, lacks sensitivity to formic acid. However, by replacing the FID detector with a Jetanizer (In-Jet type methanizer) that contains a catalyst in the FID nozzle and adjusting the analysis conditions, high-sensitivity measurement of formic acid at the ppm level becomes possible.

This Application News presents an example of the high-sensitivity analysis of formic acid contained in a methanol solvent using Jetanizer as the GC-FID nozzle.

■ Features of the Jetanizer

The Jetanizer is a compact FID-Jet type methanizer that contains a catalyst filled inside (Fig. 1). As a result, it enables the detection of CO and CO_2, which cannot be detected by a standard FID, by reducing them and converting them into methane. Additionally, the heating elements, sensors, and extra hydrogen gas supply lines previously required for methanizers are no longer necessary, allowing for direct installation and use just like a standard FID.

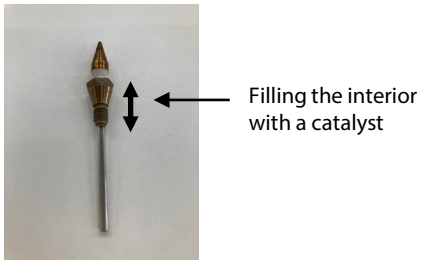

Fig. 1 Jetanizer™

■ Phosphoric Acid Treatment of the Insert and Column

It is known that formic acid adsorbs onto the inlet and column, making it difficult to achieve good peak detection. To obtain a formic acid peak, phosphoric acid treatment on the glass insert and column must be performed prior to measurement. The procedure for phosphoric acid treatment of the glass insert is shown in Fig. 2, and the procedure for phosphoric acid treatment of the column is shown in Fig. 3.

(1) Prepare the split insert (P/N 227-35007-01).
↓
(2) Prepare a 0.3 % phosphoric acid in acetone solution.
↓
(3) Immerse (1) in (2) for 1 minute.
↓
(4) Dry at 50 °C for 1 hour.

Fig. 2 Acid Treatment Procedure for Glass Inserts

(1) Prepare a 100 ppm phosphoric acid methanol solution.
↓
(2) Measure four times under the analytical conditions shown in Table 1.
↓
(3) Measure methanol ten times at 150 °C for the column (with other conditions as in Table 1 except column temp.) to stabilize the inside of the column.

Fig. 3 Procedure Manual for Phosphoric Acid Treatment of the Column

■ Analysis Conditions

The analytical conditions are shown in Table 1.

Table 1 Analysis Conditions

GC Analysis Conditions	
Model:	Nexis GC-2030
Detector:	Flame Ionization Detector FID (Jetanizer)
Column:	SH-PolarWax (0.32 mm I.D. × 30 m, d.f. = 1.0 µm) P/N 227-36252-01
Column Temp.:	80 °C – 5 °C/min – 130 °C – 15 °C/min. – 230 °C (Total 19.67 min)
Purge:	3 mL/min.
Injection Mode:	Split 1 : 2
Carrier Gas Controller:	Constant Linear Velocity (He)
Linear Velocity:	35 cm/sec
Detector Temp.:	400 °C (Detector Insertion Length: 45 mm)
FID H_2 Flowrate:	32 mL/min.
FID Make Up Flowrate:	24 mL/min. (N_2)
FID Air Flowrate:	250 mL/min.
Injection Volume:	1µL

■ Measurement of Formic Acid in Methanol

The chromatograms of formic acid at various concentrations in methanol (1, 5, 10, 50, 100, 500, and 1000 ppm) and an enlarged view of the low concentration range are shown in Fig. 4. The calibration curve for N = 5 is presented in Fig. 5. Additionally, the overlaid chromatograms for continuous measurement at 10 ppm are shown in Fig. 6, and the RSD% of the area values for N = 5 at each concentration is provided in Table 2. Good reproducibility of the area was confirmed at each concentration.

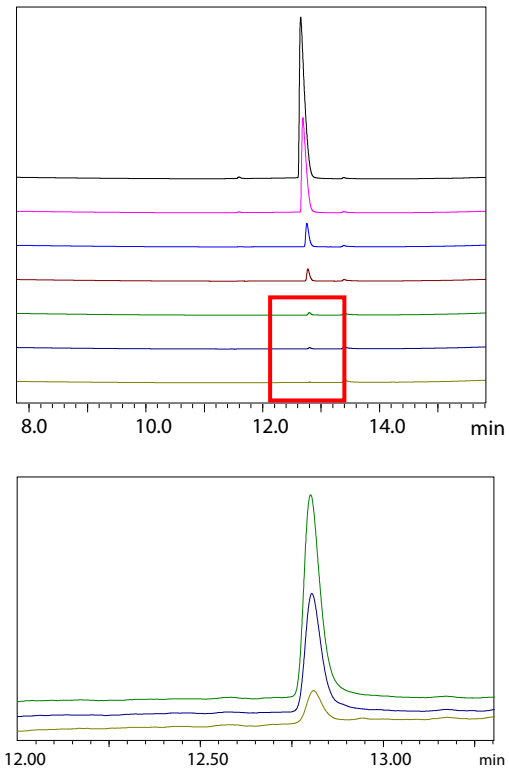

Fig. 4 Top: Chromatograms of Formic Acid at Various Concentrations
Bottom: Enlarged View of 1 to 10 ppm

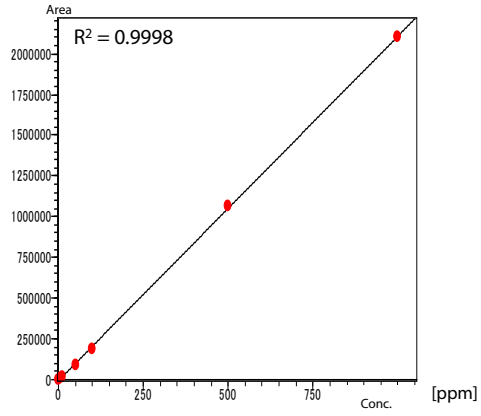

Fig. 5 Calibration Curves of Formic Acid (1 to 1000 ppm)
(Carrier Gas: He)

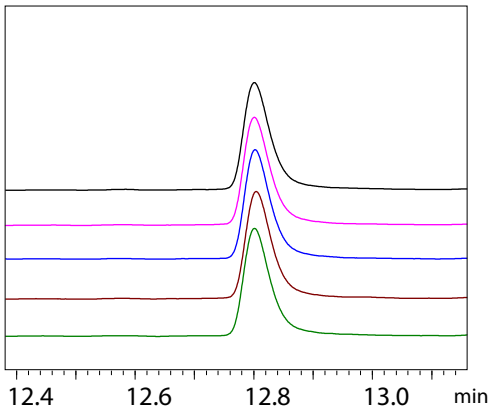

Fig. 6 Chromatogram of 10 ppm Formic Acid (Carrier Gas: He)
Continuous Analysis for 5 runs

Table 2 Reproducibility of Area Values for Various Concentrations of Formic Acid (Carrier Gas: He)

Conc. (ppm)	Area RSD% (n = 5)
1	2.27 %
5	2.15 %
10	0.62 %
50	1.97 %
100	1.14 %
500	1.29 %
1000	1.16 %

■ Conclusion

High-sensitivity analysis of formic acid is essential for the impurity analysis of chemical products and raw materials, including GX. When analyzing formic acid using GC, it is necessary to select the appropriate detector based on the measurement concentration range. The method introduced here allows for the convenient analysis of formic acid by performing phosphoric acid treatment on the insert and column and utilizing a Jetanizer.

<Related Applications>

1. Assessment of Jetanizer™ and Quantitative Analysis of CO_2 and CH_4 in the Atmosphere
   Application News No. 01-00599-en
2. Analysis of Trace Carbon Monoxide (CO) in Hydrogen Fuel Using Jetanizer™
   Application News No. 01-00638-en

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