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Application News

No.G280C

Gas Chromatography

High-Sensitivity Analysis of Formic Acid Using GC-BID in Artificial Photosynthesis Research

Artificial photosynthesis refers to a technique of creating high-energy materials using photocatalysis and solar energy, and is expected to play a role in the development of next-generation renewable energy. In the photochemical carbon dioxide reduction reaction, which is currently a research theme, there are instances in which formic acid is the main reaction product. Analysis of formic acid is typically conducted by liquid chromatography, ion chromatography or capillary electrophoresis, etc. However, since analysis of the formic acid dissolved in the organic solvent requires at least a ten-fold dilution of the solvent using water or mobile phase, such a low-concentration analysis can sometimes be difficult. On the other hand, since a gas chromatograph (GC) can directly measure organic solvents as is without dilution, use of the BID-2010 Plus for high-sensitivity detection of formic acid permits analysis at the ppm level.

This Application News introduces an example in which the GC-BID is used for analysis of formic acid in an actual sample consisting of the solvent *N*,*N*-dimethylacetamide, used in the research of artificial photosynthesis. Also, regarding analysis of formic acid at low concentrations, additional cautionary notes can be found in Application News G279.

■Analysis of Actual Sample Obtained from Artificial Photosynthesis Reaction

The sample solution consisted of the solvent *N*,*N*-dimethylacetamide as the carbon dioxide reduction reagent, in which 0.1 M tetraethylammonium tetrafluoroborate (NEt_4BF_4) was dissolved[1]. The analytical conditions used are shown in Table 1. The sample solution was spiked with formic acid at 10 ppm (v/v), and ten repeat measurements were then conducted. The formic acid peak areas showed a gradual decline, as can be seen in Fig. 1.

[1] This sample was provided by Professor Osamu Ishitani of the University of Tokyo Institute of Technology Graduate School of Science and Engineering.

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.

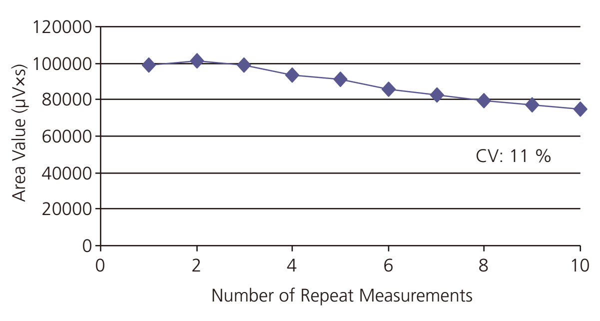
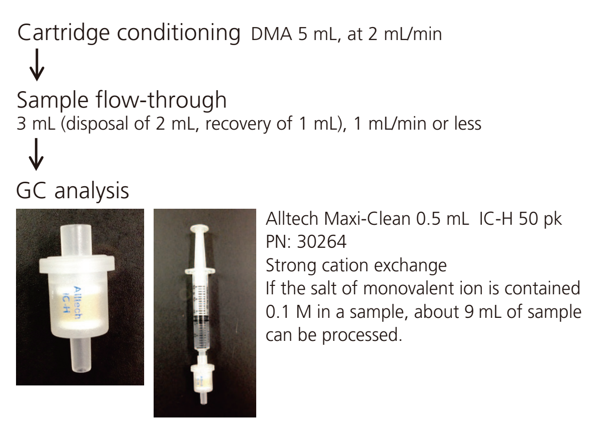


Fig. 1 Changes in Formic Acid Peak Area Before Pretreatment

Since it was presumed that the adsorption of formic acid in the GC injection unit was due to accumulation of the electrolyte NEt_4BF_4 which coexists with the sample in the injection unit, the NEt_4BF_4 was removed prior to GC measurement using a cation exchange cartridge (Alltech Maxi-Clean 0.5 mL IC-H 50 pk, P/N 30264). The NEt_4BF_4 removal procedure is shown in Fig. 2. We then conducted ten repeat measurements of the sample after eliminating the NEt_4BF_4, and verified results with good repeatability (Fig. 3). It is believed that the influence of salt was removed by replacing the cation (Net_4^+) with H^+ using a cation exchange cartridge.


Cartridge conditioning DMA 5 mL, at 2 mL/min
↓
Sample flow-through
3 mL (disposal of 2 mL, recovery of 1 mL), 1 mL/min or less
↓
GC analysis

Alltech Maxi-Clean 0.5 mL IC-H 50 pk
PN: 30264
Strong cation exchange
If the salt of monovalent ion is contained 0.1 M in a sample, about 9 mL of sample can be processed.

Fig. 2 Pretreatment Procedure Using Cation-Exchange Cartridge

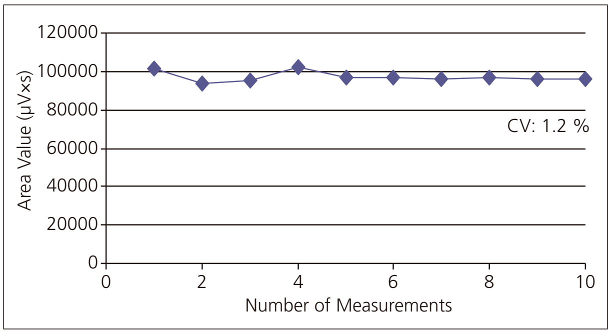


Fig. 3 Changes in Formic Acid Peak Area After Pretreatment

Table 2 Results of Recovery Test

	Quantitation Value ppm (n=3 mean)
Spiked at 1 ppm	0.97
Spiked at 10 ppm	9.5
Spiked at 50 ppm	50

Table 3 Results of Pretreatment Repeatability Test

	First	Second	Third	Fourth	Fifth	Mean	SD	RSD%
Formic acid peak area	97159	94176	91712	92819	91562	93485.6	2305.47	2.47

To verify the rate of recovery, sample solutions spiked with formic acid at 1, 10 and 50 ppm (v/v), respectively, were subjected to pretreatment according to the procedure of Fig. 2, and then measured by GC. The results are shown in Table 2. The rates of recovery were nearly 100 %. Further, to check the repeatability of the pretreatment procedure, a sample solution spiked with 10 ppm (v/v) formic acid was subjected to pretreatment and measurement five times, once each per sample. The chromatogram is shown in Fig. 4, and the formic acid peak area repeatability values are shown in Table 3.

The pretreatment procedure shown in Fig. 2 that was used for the samples in this investigation was effective, but in cases where the samples contain salt at higher concentrations, it might not be sufficiently effective, requiring repeat processing of the cartridge. If the salt, solvent type or concentration varies depending on the sample, verification must be conducted for each sample separately. In addition, please note that if treatment is conducted on samples containing sulfate or hydrochloride using a cation exchange cartridge, corrosion of the column, etc. may occur due to the strong acidity that may develop.

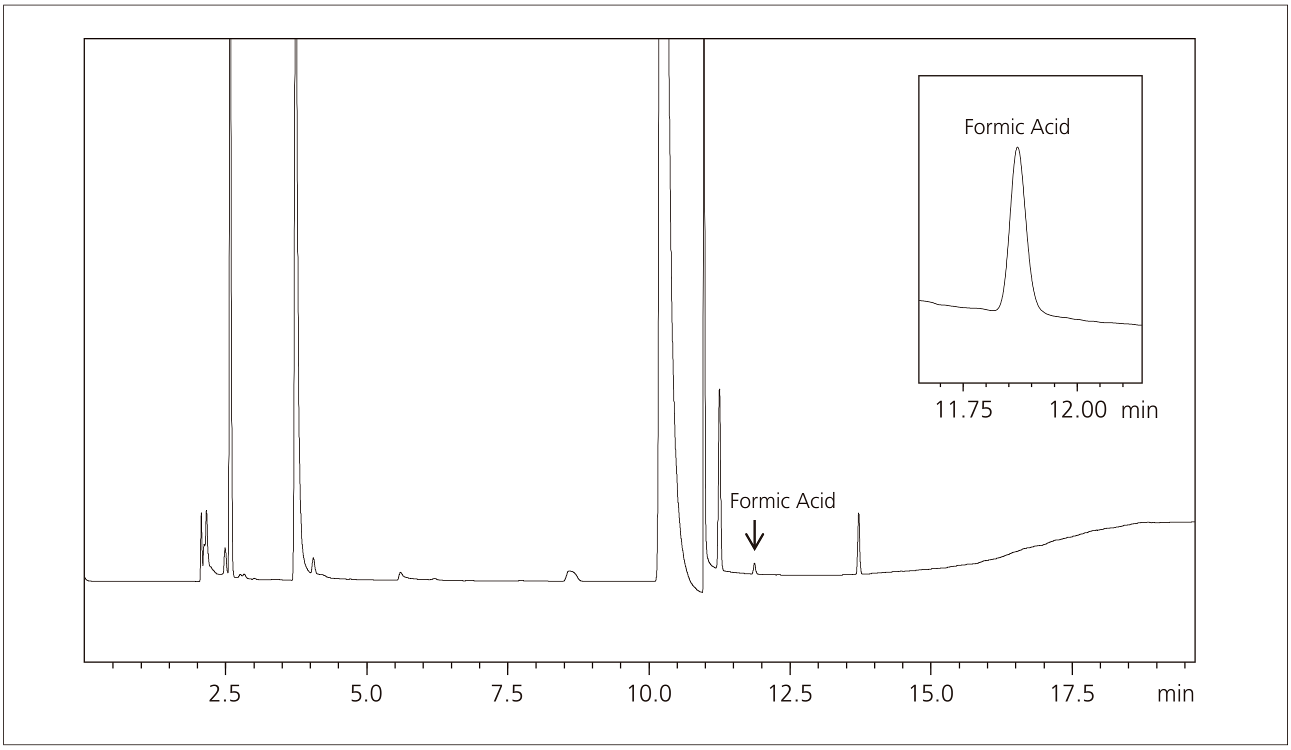


Fig. 4 Chromatogram from Analysis of 10 ppm Pretreated Formic Acid in Actual Sample Solution

4th Edition : Sep. 2018
First Edition : Jul. 2014

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