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Simultaneous Analysis of Underivatized Formic Acid and Volatile Fatty Acids (C2-C5) using the Brevis GC-2050

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1. Introduction

Analysis of low molecular carboxylic acids, or Volatile Fatty Acids (VFAs), is essential in environmental samples, especially in wastewater and sludge treatment, hydraulic fracturing operations and landfills. These chemicals are metabolites formed through the biological processes that water resource recovery facilities (formerly known as wastewater treatment plants) employ to eliminate organic matter and other contaminants. But they can also occur, under favorable conditions, in other applications that involve anaerobic biological activity, such as various fermentation processes in the food industry. VFAs can be easily determined using a gas chromatograph with flame ionization detector (GC-FID) in their free form [1], except for formic acid. Normally, derivatization to methyl formate is required to detect formic acid by FID. Here we demonstrate that using an in-jet methanizer (Jetanizer™), formic acid was successfully quantified using FID, along with other short chain volatile fatty acids, in a single injection.

2. Experimental

A Shimadzu GC-2050 with split/splitless injector (SPL), flame ionization detector (FID) and an in-jet methanizer (Jetanizer™), shown in Figure 1, was used for this analysis. Analysis conditions are outlined in Table 1. LabSolutions software was used for data acquisition and processing.

Table 1: Instrument Configuration and Analysis Conditions

GC system	Shimadzu Nexis GC-2050 with SPL, FID, AOC-30i autosampler
Column	SH-wax, 30 m x 0.32 mm x 1 µm, connected to short guard column
Column Temp	80 °C, 2 min – 20 °C/min – 200 °C, 3 min
Injection	0.5 µL splitless
Carrier Gas	Helium, constant flow of 5 mL/min
FID Detector	400 °C, Air 250 mL/min, H_2 32 mL/min, N_2 makeup 24 mL/min

3. Results and Discussion

3.1. Shimadzu's GC-2050 and Jetanizer™

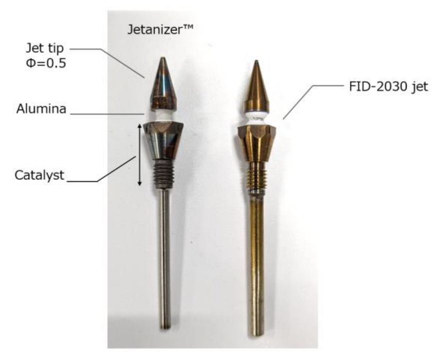

Figure 1: GC-2050 with AOC-30i autosampler and the enlarged view of Jetanizer™.

Shimadzu GC-2050 with autosampler AOC-30i was chosen for this analysis. The whole setup with the autosampler on top measures less than 14-in wide. AOC-30i can hold up to 30 samples (Figure 1), despite the compact footprint.

Conversion of carbon-containing compounds to methane (methanization) enables the detection of compounds such as CO and CO_2 by FID [2]. It also helps to equalize response factors of organic compounds traditionally problematic for FID analysis. Therefore, methanization was tested for detection of formic acid.

To achieve methanization, a special in-jet methanizer (Jetanizer™) was installed in the FID (Figure 1). Installation of Jetanizer requires no extra space or plumbing. Instead, it is a simple replacement of the normal FID jet. It uses gases already supplied to FID. In addition, it shows improved resistance to oxygen and sulfur poisoning compared to other methanizers. Taken together, Jetanizer is the perfect choice for a rugged yet compact system.

3.2. Detection of formic acid

A purchased free fatty acids test standard mix (containing acetic, propionic, iso-butyric, butyric, iso-valeric and valeric acid) was used for this assay. Formic acid was either added to the fatty acid mix standard or run individually. All compounds were diluted in water to the concentrations indicated (Table 2).

First, these short-chain VFAs (C1 to C5) were run on GC-FID without derivatization using regular a setup (FID with the normal jet). Previous research showed that formic acid does not have a significant response on FID. As expected, formic acid was not detected at 1000 ppm while other targeted compounds had great responses at 100 ppm (Figure 2).

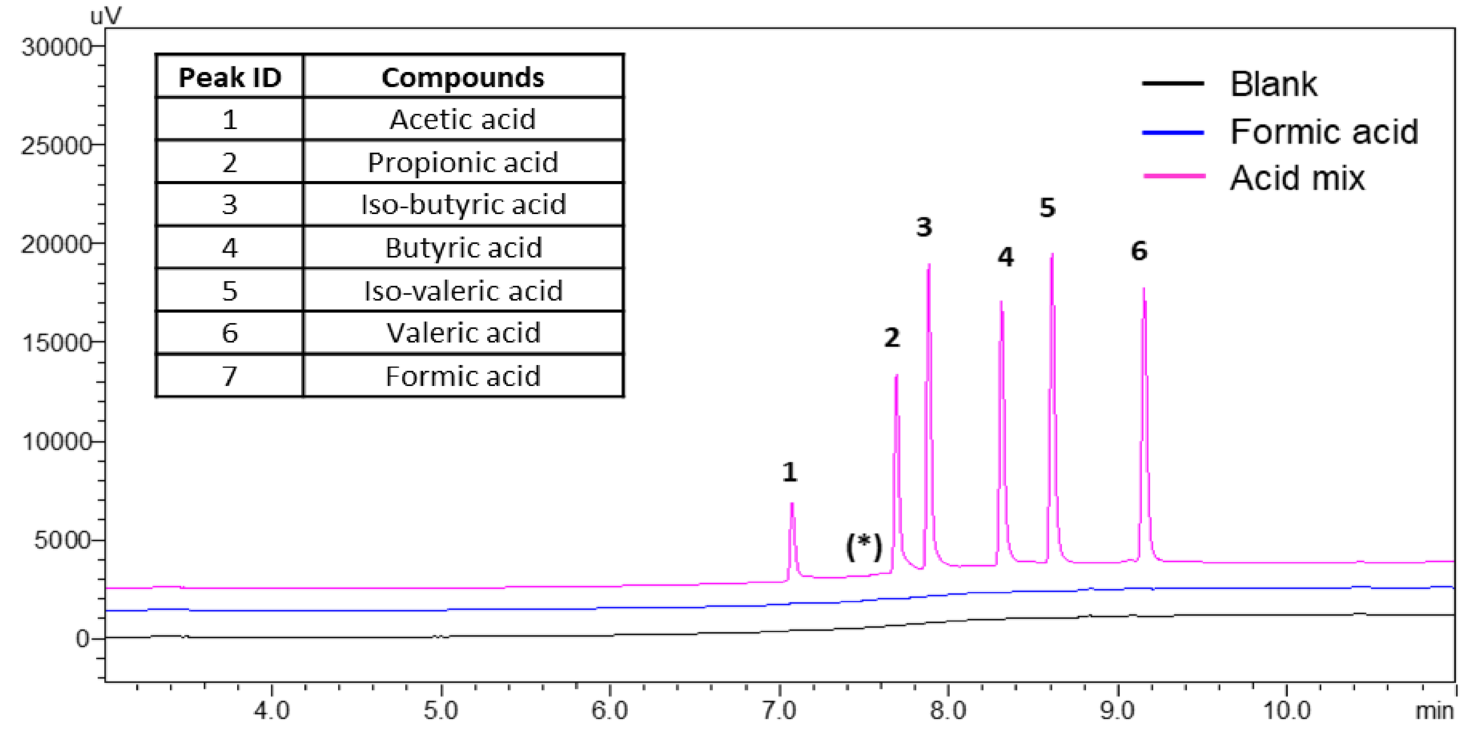

Figure 2. Chromatograms of blank (water), formic acid in 1000 ppm standard (blue) and a mix of fatty acids in 100 ppm standard (pink) using regular FID jet. (*) Expected retention time for formic acid.

Table 2. Targeted compounds, calibration range and correlation coefficient.

Peak ID	Compounds	RT (min)	Conc. range (ppm)	r^2
1	Acetic acid	5.917	75-500	0.994
2	Propionic acid	6.494	75-500	0.997
3	Iso-butyric acid	6.673	75-500	0.998
4	Butyric acid	7.070	75-500	0.997
5	Iso-valeric acid	7.321	75-500	0.998
6	Valeric acid	7.737	75-500	0.997
7	Formic acid	6.369	200-1000	0.996

The mixture of acids was then analyzed with Jetanizer™ installed, All targeted compounds, including formic acid, were detected (Figure 3).

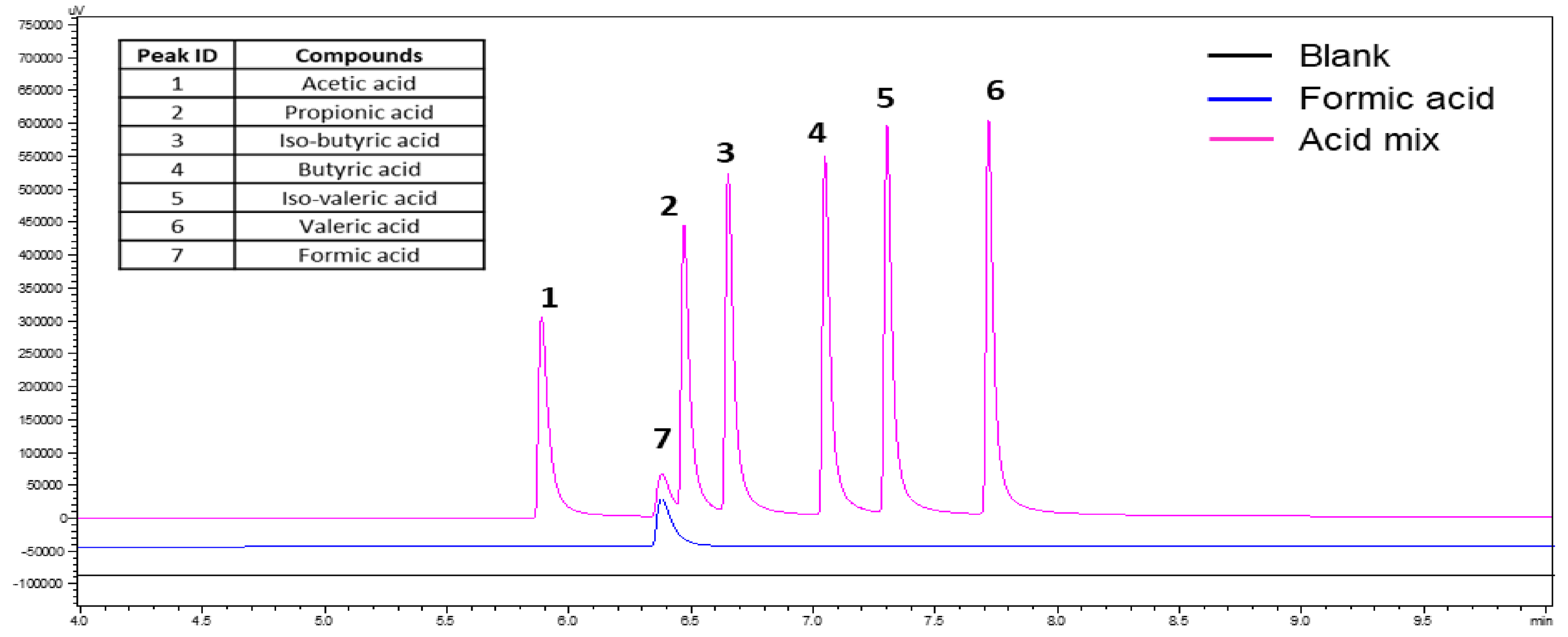

Figure 3. Chromatograms of blank (water), formic acid only (blue) and a mix of fatty acids (pink) using Jetanizer. All VFAs are 500 ppm each.

3.3. Calibration curve

A five-point calibration curve for each VFA targeted was analyzed, from 75 to 500 ppm, except for formic acid (four-point calibration curve from 200 to 1000 ppm). The curves were fitted to linear regression and all compounds showed r^2 > 0.994. Individual results are shown in Table 2.

4. Conclusion

In this study, underivatized formic acid was analyzed simultaneously with VFAs, from C2 to C5, on the GC-2050 with Jetanizer™ for FID detection. Calibration was linear for all target compounds. This method overcomes the drawbacks from sample derivatization (time consuming and prone to error) and provides a good alternative for the analysis of formic acid and other VFAs using a common instrument in environmental labs. With a width less than 14 inches, this system provides a compact solution too.

5. Reference

1. *Henderson, M.H.; Steedman, T.A. Analysis of C2–C6 monocarboxylic acids in aqueous solution using gas chromatography. Journal of chromatography A, 244(1982), 337–346.*
2. *Analysis of and Characterization of ARC's In-jet Methanizer for Permanent Gases, Carbon Dioxide, and Light Hydrocarbons, Shimadzu Scientific Instruments Application News No. GC-2103.*