

Application News

No. AD-0070

Nexera X2, SPD-M30A, HS capillary flow cell

Analysis of Trace Level of Acetic Acid in Wastewater Sample by HPLC with High Sensitivity Photodiode Array Detector

Introduction

Acetic acid is one of organic pollutants found in wastewater produced from domestic households, industrial and agricultural practices. It is also a most abundant carboxylic acid pollutant monitored in the atmosphere. The quantitative analysis of trace level of acetic acid in various types of samples were carried out by GC/MS or Ion chromatography (IC). For example, claimed best detection limit of IC method with conductivity detection for acetic acid was reported to be around 0.012–0.6 ppm [1-2]. However, HPLC with UV detection was not used for trace acetic acid due to the limited sensitivity for its low wavelength ($\lambda_{max} = 205 \text{ nm}$) and weak absorption. The new generation Nexera X2 UHPLC system with a high sensitivity PDA detector SPD-M30A and especially a HS capillary flow cell with an extra long (85mm) optical path offers excellent sensitivity [3], allowing extended applications that requires enhanced UV detection sensitivity. Here we report the analysis of residual acetic acid of low ppm levels in wastewater samples from an industrial facility.

Experimental

Separation of organic acids in HPLC can be accomplished by ion exclusion chromatography according to their pK_a . In this work, a Shim-pack SCR-102H ion exclusion column was used for acetic acid analysis using acidic aqueous mobile phase (Table 1). A Nexera X2 system with SPD-M30A was employed. Featured as new generation UHPLC, the system is also compatible to conventional HPLC columns and analytical conditions. A HS capillary flow cell designed for SPD-M30A detector was used, which is known to increase the sensitivity for about 5 times due to its long optical pass (85 mm).

Table 1: Nexera X2 system & analytical conditions

System	Nexera X2 UHPLC
Mobile Phase	4 mM perchloric acid in water
Column	Shim-pack SCR-102H, 300mmL x 8.0 mmID
LC Mode	Isocratic mode
Flow Rate	0.8 mL/min
Detector	PDA, SPD-M30A
Flow cell	HS capillary cell, 85mm
Wavelength	205 nm
Slit width	1 nm
Column temperature	60 °C
Injection Volume	50 μL

Results and Discussion

A HPLC method was set up for acetic acid analysis using Shim-pack SCR-102H ion exclusion column. Acetic acid eluted at 12 min as a sharp peak detected with 205 nm wavelength (Fig. 1). A linear calibration curve of six levels was established using acetic acid standard samples: 0.5, 1, 2, 5, 10 and 20 $\mu\text{g/mL}$ (ppm).

The sensitivity of acetic acid in pure water was estimated from the results of lower concentrations, to be LOD at 0.3ppm and LOQ at 1.0 ppm under the conditions (Table 2).

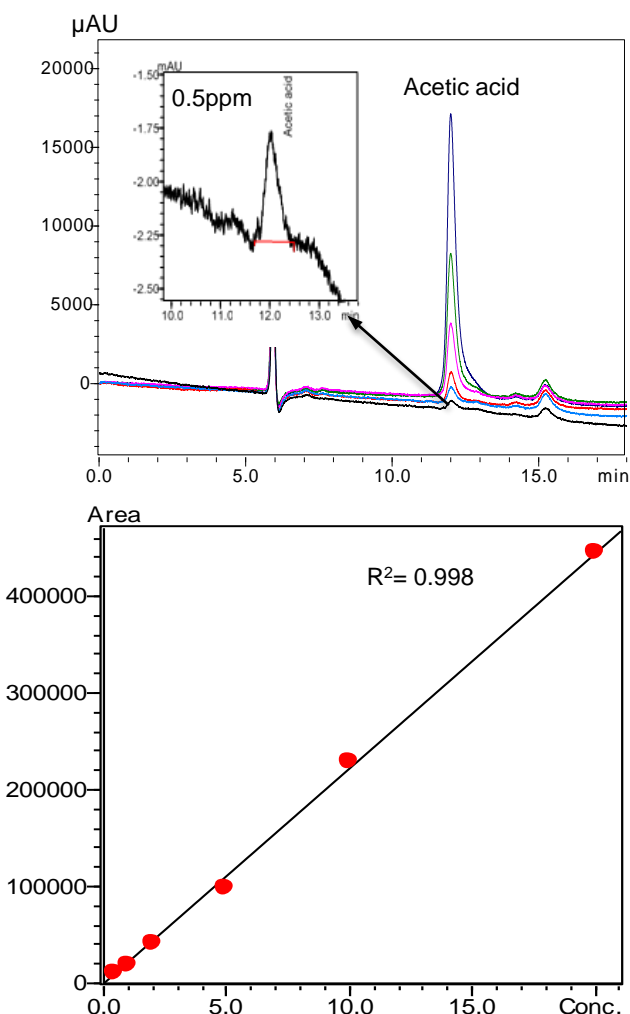


Fig 1: Overlay chromatograms of 205nm wavelength (top) and a calibration curve (bottom) of acetic acid in water. Conc.: 0.5, 1, 2, 5, 10, 20 ppm ($\mu\text{g/mL}$).

Table 2: Sensitivity evaluation of acetic acid with standard sample (UV 205 nm)

Acetic Acid	Intensity (μAU)	S/N	LOD (ppm)	LOQ (ppm)
0.5 ppm	487	5.58	0.27	0.9
1.0 ppm	937	8.96	0.33	1.1
Average			0.3	1.0

A wastewater sample collected from industrial facility was suspected to contain trace acetic acid. However, the analysis result by above method showed that acetic acid was not detected in the sample (the bottom chromatogram in Figure 2). The sensitivity of the method established with acetic acid in pure water could not reflect the sensitivity in the wastewater sample due to high baseline and interferences. As shown in Figure 3, the wastewater has very strong UV absorption at low wavelength (195~220nm), which could not be eliminated from the UV absorption of acetic acid.

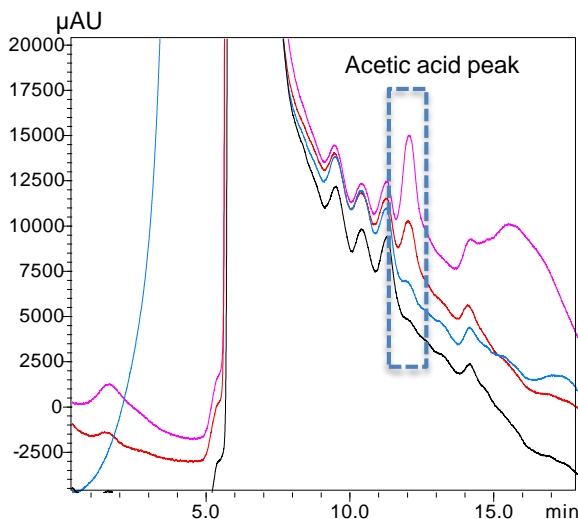


Fig 2: Chromatograms of wastewater sample (bottom) and the same sample spiked with acetic acid of 1, 5, 10 ppm (second low to top).

To confirm this result and estimate the detection limit in actual sample, acetic acid was spiked into the wastewater sample at 1.0, 5.0 and 10.0 ppm. As shown in Table 3, the recoveries of the spiked acetic acid in the wastewater were 33~79%. Thus, it could be concluded that the wastewater sample either does not contain acetic acid or its concentration below 1 ppm. The LOD of the method for acetic acid in the wastewater sample is 1 ppm.

References

1. A. Krata, V. Kontozova-Deutsch, L. Bencs, F. Deutsch, R. VanGrieken, *Single-run chromatographic separation of inorganic and low-molecular-mass organic anions under isocratic elution: Application to environmental samples*, Talanta, 2009, 79, 16-21.
2. Robyn E. Hodgkins, Cecily M. Grzywacz, Robin L. Garrell, *An Improved Ion Chromatography Method for Analysis of Acetic Acid and Formic Acid Vapour*, e-Preservation Science, 8, 74-80 (2011)
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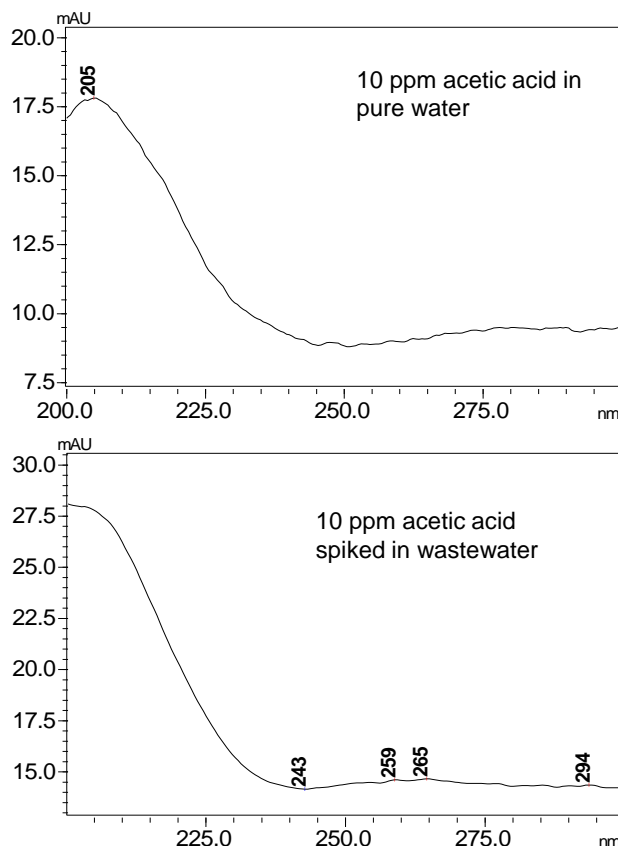


Fig 3: UV spectra of 10 ppm acetic acid in pure water and in wastewater by SPD-M30A with HS cell, RT=12.0 min.

Table 3: Recovery results of acetic acid spiked samples

Sample	AA Spiked (ppm)	RT (min)	Area	Conc. (ppm)	Recovery (%)
Wastewater	0	Not Det.	0	0	N.A.
Wastewater spiked with acetic acid (AA)	1	11.9	7344	0.33	33.0
	5	12.0	61134	2.75	55.0
	10	12.1	175259	7.88	78.8

Conclusions

With a SPD-M30A high sensitivity PDA detector and 85 mm capillary HS flow cell, the HPLC-UV method established enables to detect 0.3 ppm level of acetic acid in pure water and 1 ppm in wastewater sample. This sensitivity is comparable with the conventional ion chromatography method.