

The determination of organic acids using suppressed conductivity ion chromatography

No. HPLC-025

■ Introduction

Short-chain, low molecular mass carboxylic acids (organic acids) abound in aqueous media ranging from surface water to beverages and physiological fluids. Organic acids can be vital intermediates and metabolites in biological processes. Ion Chromatography (IC) is one of the most widely used methods for organic acid analysis. The disadvantage of the method is that high concentrations of inorganic anions existing in environmental samples may interfere with the analyte of interest. The negative system peak in IC, also called the water dip, is another potential interference since the pKa values of some organic acids are relatively low, resulting in weak binding to IC columns and, therefore, early elution. However, these interferences can be minimized by adjusting the eluent concentration and flow rate in IC analysis.

This application note describes a high-resolution IC method to separate four organic acids: formic, acetic, propionic and oxalic, with seven common inorganic anions using a Shimadzu modular IC system coupled with a new Shimadzu electrolytically regenerated suppressor.

■ Experimental

Equipment

Experiments were performed using a modular Shimadzu LC system, consisting of:

- CBM-40 lite system controller
- DGU-403 degassing unit
- LC-20Ai pump with automatic rinsing kit
- SIL-20AC autosampler with inert kit
- CTO-40S column oven
- Suppressor installation kit for CTO-40S
- CDD-10Avp conductivity detector
- ICDS-40A electrochemical suppressor starter kit
- LabSolutions chromatography software

Columns

- Shodex IC SI-52 4E, 4 x 250 mm (Part number: 220-91524-04)
- Guard column, Shodex SI-90G, 4.6 x 10 mm (Part number: 220-91524-05)

Materials

Sodium carbonate and sodium bicarbonate were obtained from Sigma-Aldrich. Standards including acetate ($C_2H_3O_2^-$) 1000 ppm, formate (CHO_2^-) 1000 ppm, propionate ($C_3H_5O_2^-$) 1000 ppm and oxalate ($C_2O_4^{2-}$) 1000 were purchased from Inorganic Ventures Inc. Fluoride (F^-) 1000 ppm, chloride (Cl^-) 1000 ppm, and nitrite (NO_2^-) 1000 ppm were obtained from RICCA Chemical Company. Bromide (Br^-) 1000 ppm, nitrate (NO_3^-) 1000 ppm, phosphate (PO_4^{3-}) 1000 ppm and sulfate (SO_4^{2-}) 1000 ppm were purchased from Sigma. Standards of different concentrations were prepared by diluting from the commercial stock standards using degassed deionized water with resistivity equal or greater than 18.0 M Ω -cm.

Eluent preparation

Preparation of 1 L of 0.18 M stock sodium carbonate; dissolve 19.08 g sodium carbonate (Na_2CO_3) in deionized water and dilute to 1 L. Preparation of 1 L of eluent (5.4 mM sodium carbonate); pipet 30 mL of stock sodium carbonate then dilute to the mark with deionized water.

Method Conditions

Column: Shodex IC SI-52 4E, 4 x 250 mm (220-91524-04)
 Eluent: 5.4 mM sodium carbonate
 Flow rate: 0.8 mL/min
 Oven: 45 °C
 Inj. Vol.: 20 µL
 System
 Backpressure: ~ 1450 psi
 Detection: Suppressed conductivity; 60 mA in recycle mode
 Background
 Conductance: ~ 29 µS/cm
 Noise: < 3 nS/cm peak to peak

Results and Discussion

Figure 1 shows separation results of four organic acids and seven common anions using the Shimadzu high-resolution ion chromatography method.

As shown in the figure, acetate, formate and propionate can be fully separated using this IC method and eluted from the IC column faster than other common anions. The organic acids are also fully resolved from the water dip and fluoride peak.

Reproducibility and Accuracy

Method precision was performed using a mixed standard with a concentration of 2 ppm for acetate, formate, propionate and oxalate, 0.5 ppm for fluoride, nitrite, nitrate and bromide, and 1 ppm for chloride, phosphate and sulfate, respectively. Table 1 shows retention time precision and peak area precision of 11 anions from 8 injections of the mixed standard. Figure 2 shows the overlay chromatogram from these 8 injections. As shown in the table and figure 2, excellent reproducibility was achieved for both retention time and peak area.

Table 1: Retention time and peak area reproducibility

Anions	T _r precision (RSD)	Area precision (RSD)
Fluoride (F ⁻)	0.04%	0.19%
Acetate (C ₂ H ₃ O ₂ ⁻)	0.04%	0.33%
Formate (CHO ₂ ⁻)	0.05%	0.77%
Propionate (C ₃ H ₅ O ₂ ⁻)	0.04%	0.75%
Chloride (Cl ⁻)	0.04%	0.11%
Nitrite (NO ₂ ⁻)	0.05%	0.55%
Bromide (Br ⁻)	0.06%	0.93%
Nitrate (NO ₃ ⁻)	0.07%	0.67%
Phosphate (PO ₄ ³⁻)	0.06%	1.22%
Sulfate (SO ₄ ²⁻)	0.03%	0.34%
Oxalate (C ₂ O ₄ ²⁻)	0.03%	0.38%

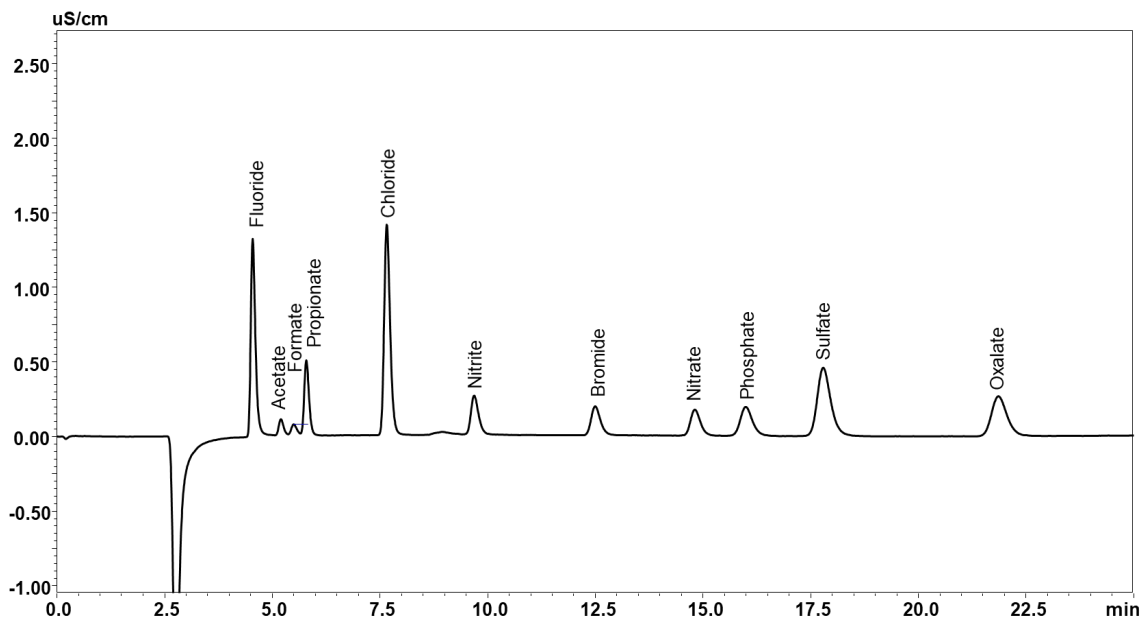


Figure 1: Separation of 4 organic acids and 7 common anions using the Shodex IC SI-52 4E column.

Peaks: 1. Fluoride (0.5 ppm), 2. Acetate (2 ppm), 3. Formate (2 ppm), 4. Propionate (2 ppm), 5. Chloride (1 ppm), 6. Nitrite (0.5 ppm), 7. Bromide (0.5 ppm), 8. Nitrate (0.5 ppm), 9. Phosphate (1 ppm), 10. Sulfate (1 ppm), 11. Oxalate (2 ppm)

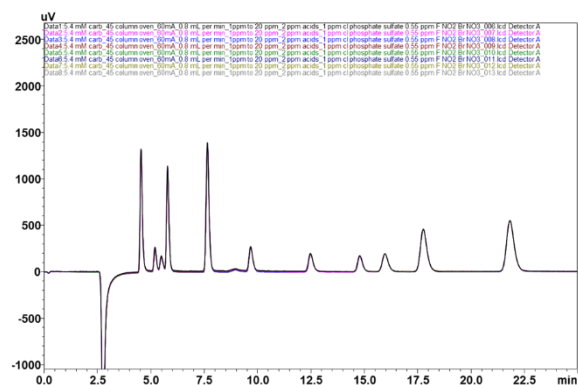


Figure 2: Reproducibility test for 4 organic acids and 7 common anions using the Shodex IC SI-52 4E column.

The performance and accuracy of the methods were investigated by spiking organic acid standards with 2 ppm concentration for each acid into lake water and tap water samples. Table 2 shows excellent recoveries from 91.8% to 102.8% obtained for four organic acids in both lake water and tap water.

Table 2: Recoveries in different waters.

Organic Acids	Added concentration (ppm)	Lake water Recovery (%)	Tap water Recovery (%)
Acetate	2	100	91.8
Formate	2	99	96.9
Propionate	2	99.1	93.2
Oxalate	2	102	102.8

Linearity

Figure 3 shows the linearity plots for the four organic acids. As shown in the figure, great linearity was obtained from the range of 1 ppm to 10 ppm for all of them.

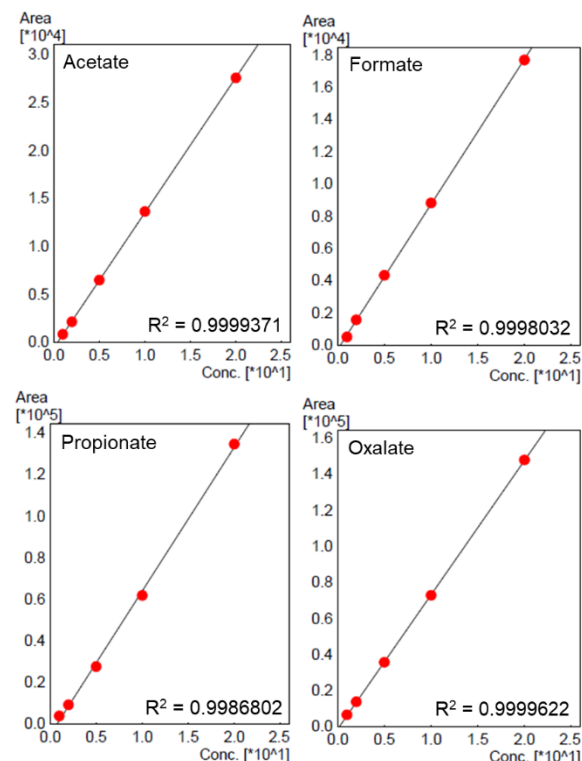


Figure 3: Linearity of acetate, formate, propionate and oxalate

Conclusion

This study demonstrates that robust and reliable performance of the Shimadzu high-resolution IC system with electrolytically regenerated suppression for the determination of organic acids including acetate, formate, propionate and oxalate.

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