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Application News

No. HPLC-024

High Performance Liquid Chromatography

Rapid Analysis of Seven Common Anions in Water Using Suppressed Conductivity IC

■ Introduction

Common inorganic anions in EPA Methods 300.0 [1] and 300.1 [2] for water analysis refer to Fluoride (F-), Chloride (Cl-), Nitrite (NO_2-), Bromide (Br-), Chloride (Cl-), Nitrate (NO_3-), Phosphate (PO_4^{3}-) and Sulfate (SO_4^{2}-). Suppressed conductivity ion chromatography (IC) is used in EPA Methods 300.0 and 300.1 to determine the concentration of the seven inorganic anions in waters. Water analysis using suppressed ion chromatography represents the most widely used application of IC. This study provides a rapid ion chromatography method using a Shimadzu electrolytically regenerated suppressor to successfully separate seven common inorganic anions in 8 minutes.

■ 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 electrodialytic suppressor starter kit
- LabSolutions chromatography software

Column

- Shodex IC SI-35 2B, 2 x 50 mm
- Guard filter IC SI-2GF

Materials

Sodium carbonate and sodium bicarbonate were obtained from Sigma-Aldrich. Standards including Fluoride (F-) 1000 ppm, Chloride (Cl-) 1000 ppm, 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. Working standards at different concentrations were prepared by diluting from the commercial stock standards using degassed deionized water with resistivity equal or greater than 18.0 MΩ-cm.

Eluent preparation

Preparation of 1 L of 0.18 M stock sodium carbonate; dissolve 19.08 g sodium carbonate (Na2CO3) in deionized water and dilute to 1 L. Preparation of 1 L of 0.17 M stock sodium bicarbonate; dissolve 14.28 g of sodium bicarbonate (NaHCO3) in deionized water and dilute to 1 L. Preparation of 1 L of eluent (0.36 mM sodium carbonate/5.1 mM sodium bicarbonate); pipet 2 mL of stock sodium carbonate and 30 mL of stock sodium bicarbonate into a 1 L volumetric flask, then dilute to the mark with deionized water.

Method Conditions

Column:	Shodex IC SI-35 2B, 2 x 50 mm
Eluent:	0.36 mM sodium carbonate/ 5.1 mM sodium bicarbonate
Flow rate:	0.4 mL/min
Oven:	40 °C
Inj. Vol.:	20 µL
System Backpressure:	~ 1450 psi
Detection:	Suppressed conductivity; 180 mA in external water mode, water flow rate is 1.0 mL/min
Background Conductance:	~ 25 µS/cm
Noise:	< 1 nS/cm peak to peak

■ Results and Discussion

In this method, external fresh water is continuously pumped through the suppressor regeneration channel at a 1 mL/min flow rate using a second pump to affect the electrolysis regeneration of the suppressor. Figure 1 shows that the seven common anions listed in EPA Method 300 can be separated in 8 minutes using this rapid analysis method. Since a short column (50 mm) with a 2 mm diameter is used, fluoride elutes on the edge of the negative system peak (also called water dip), a compromise to the greater resolution using regular analysis [3] and a high-resolution method [4]. However, the rapid analysis yields robust and reproducible results. The excellent reproducibility and linearity of the method shown later in this application note demonstrate the method can be used for high-throughput sample analysis.

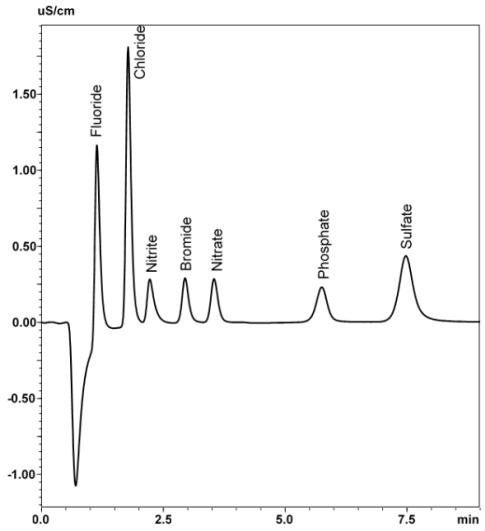

Figure 1: Separation of seven common anions using the Shodex IC SI-35 2B column.

Linearity

A series of five calibration standards across the concentration range of 0.2 to 10 ppm for chloride, phosphate and sulfate, and 0.1 to 5 ppm for fluoride, nitrite, nitrate and bromide, respectively, were used for a linearity study. As shown in Fig. 2 and Table 1, excellent linear response with coefficient of determination greater than 0.9999 was obtained for all seven anions.

Table 1: Linearity obtained using Shimadzu rapid IC analysis

Anions	Calibration range (ppm)	Linearity (r^2)
Fluoride (F^-)	0.1-5	0.9999
Chloride (Cl^-)	0.2-10	0.9999
Nitrite (NO_2^-)	0.1-5	0.9999
Bromide (Br^-)	0.1-5	0.9999
Nitrate(NO_3^-)	0.1-5	0.9999
Phosphate(PO_4^{3-})	0.2-10	0.9999
Sulfate (SO_4^{2-})	0.2-10	0.9999

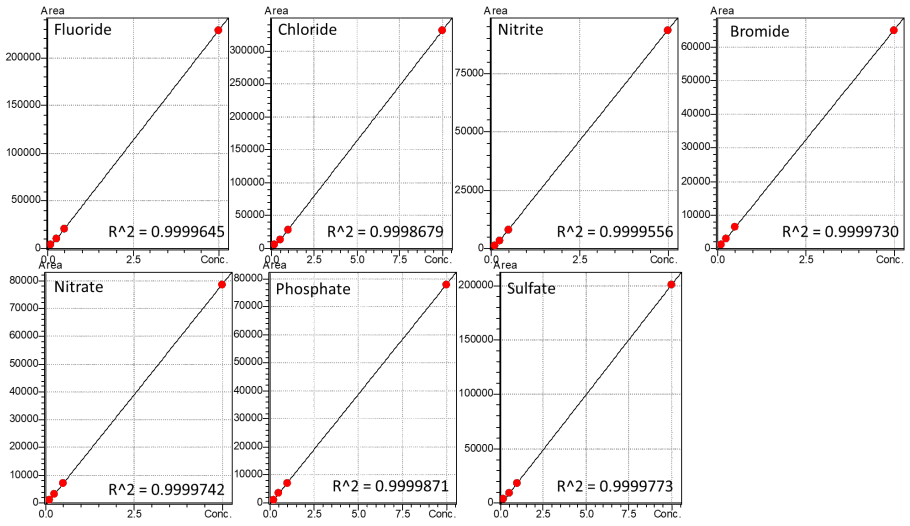

Figure 2: Calibration curves for seven anions listed in EPA Method 300.

Reproducibility
Method precision was performed using a mixed standard with a concentration of 0.5 ppm for fluoride, nitrite, nitrate and bromide, and a concentration of 1 ppm for chloride, phosphate and sulfate, respectively. Table 2 shows retention time precision and peak area precision of seven anions from 8 injections of the mixed standard. As shown in the table, excellent reproducibility was achieved for both retention time and peak area. Retention time RSDs of seven anions are from 0.02% to 0.08% and peak area RSDs are from 0.23 to 0.37% for all inorganic anions.

Table 2: Retention time and peak area reproducibility

Anions	T_r precision (RSD)	Area precision (RSD)
Fluoride (F^-)	0.03%	0.3%
Chloride (Cl^-)	0.02%	0.25%
Nitrite (NO_2^-)	0.04%	0.36%
Bromide (Br^-)	0.07%	0.32%
Nitrate(NO_3^-)	0.08%	0.3%
Phosphate(PO_4^{3-})	0.04%	0.37%
Sulfate (SO_4^{2-})	0.03%	0.23%

■ Conclusion

This study demonstrates that seven common inorganic anions listed in EPA Method 300 can be reliably separated in 8 minutes using the Shimadzu IC system with electrolytically regenerated suppression. The rapid analysis method may be used for high-throughput analysis.

■ References

1. EPA Method 300.0 Determination of inorganic anions by ion chromatography.
2. EPA Method 300.1 Determination of inorganic anions in drinking water by ion chromatography Revision 1.0.
3. Shimadzu Application Note HPLC-021, The determination of EPA method 300 anions using a Shimadzu ion chromatography system.
4. Shimadzu Application Note HPLC-022, The determination of 10 anions in EPA Method 300.1 using Shimadzu high-resolution ion chromatography.

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