

The Determination of EPA Method 300 Anions Using a Shimadzu Ion Chromatography System

■ Introduction

Suppressed conductivity ion chromatography (IC) is commonly used to determine the concentration of inorganic ions, particularly for environmental waters and drinking waters. U.S. National Primary Drinking Water and National Secondary Drinking Water regulations specify the maximum contaminant level (MCL) for a number of common inorganic anions, including fluoride, chloride, nitrate, nitrite and sulfate, to minimize potential health effects from environmental waters and drinking waters. U.S. EPA Methods 300.0 and 300.1 provide details for the determination of inorganic anions in waters by ion chromatography.

Since the baseline conductivity of typical mobile phases for ion chromatography is quite high, the detection limits for common anions can be poor (low ppm). Background suppression is used to effectively reduce the conductivity of the mobile phase, thus reducing the detection limits for the analytes by several orders of magnitude (low ppb). Electrolytic suppression has been a popular approach for reasons of convenience. In this study, a new Shimadzu electrolytic suppressor was used as part of a Shimadzu modular IC system to determine seven common inorganic anions in various water samples as noted in EPA Method 300: Fluoride (F⁻), Chloride (Cl⁻), Nitrite (NO₂⁻), Bromide (Br⁻), Nitrate (NO₃⁻), Phosphate (PO₄³⁻) and Sulfate (SO₄²⁻).

Mechanism of background suppression: As post-column eluent passes through the suppressor, hydronium ions generated from water electrolysis at the anode exchange with co-cations (sodium or potassium). Eluent anions are converted to their weak-acid form with a lower conductivity. Consequently, background conductivity from the eluent is suppressed relative to the conductivity of the analytes. The analyte signal-to-background ratio is thus enhanced.

■ 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-90 4E, 4 x 250 mm (part number: 220-91524-15)
- 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 Fluoride (F⁻) 1000 ppm, Chloride (Cl⁻) 1000 ppm, Nitrite (NO₂⁻) 1000 ppm, were obtained from RICCA Chemical Company. Bromide (Br⁻) 1000 ppm, Nitrate (NO₃⁻) 1000 ppm, Phosphate (PO₄³⁻) 1000 ppm and Sulfate (SO₄²⁻) 1000 ppm, were purchased from Sigma. Working standards at different concentrations were prepared by diluting from the commercial stock standards with 18.0 MΩ-cm or better resistivity degassed deionized water.

Method Conditions

Column: Shodex IC SI-90 4E
4 x 250 mm (220-91524-15)
Eluent: 1.8 mM sodium carbonate
1.7 mM sodium bicarbonate
Flow rate: 1 mL/min
Oven: 40 °C
Inj. Vol.: 50 µL
System
Backpressure: ~ 1020 psi
Detection: Suppressed conductivity;
60 mA in recycle mode
Background
Conductance: ~ 20 µS/cm
Noise: < 5 nS/cm peak to peak

Eluent Preparation

Preparation of 1 L of 0.18 M stock sodium carbonate; dissolve 19.08 g sodium carbonate (Na₂CO₃) in 18.0 MΩ-cm resistivity degassed 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 DI water and dilute to 1 L. Preparation of 1 L of eluent (1.8 mM sodium carbonate/1.7 mM sodium bicarbonate); pipet 10mL of stock sodium carbonate and 10 mL of stock sodium bicarbonate into a 1 L volumetric flask, then dilute to the mark with DI water.

Sample Preparation

All samples were filtered through 0.45 µm PES syringe filters, discarding the first approx. 1 mL of the effluent.

■ **Results and Discussion**

In this study, the anions were detected by suppressed conductivity. The electrolytically regenerated suppressor used in the system provides

improved baseline stability and less than 5 nS baseline noise at 60 mA current. The system backpressure remained constant at approx. 1020 psi over 1000 injections at 1 mL/min flow rate. All seven anions were separated in 15 minutes. Figure 1 shows the separation result of seven anions.

Linearity and Method Detection Limit

In order to evaluate the method and overall system performance, linearity, method detection limits (MDL), recovery and reproducibility were also determined. Method detection limit (MDL) investigation was performed following the procedure described in EPA Method 300 by making seven replicate injections of MDL standards. MDL standards were prepared by fortifying the blank with anion standards to a concentration 3 to 5 times that of the instrument detection limit.

MDL was calculated as $(t) \times (S)$, where t is student's t value for 99% confidence level ($t=3.14$ for seven replicates) and S is standard deviation from seven injections. The linear calibration range, linearity (or coefficient of determination), MDL standard concentration and calculated MDL are shown in table 1. Figure 2 shows the calibration curves for all anions.

Table 1: Linear calibration range, linearity (coefficient of determination), MDL standards and MDL

Anions	Calibration range (ppm)	Linearity (r ²)	MDL Standard (ppb)	Calculated MDL (ppb)
Fluoride (F ⁻)	0.05-20	0.9999	10	3.31
Chloride (Cl ⁻)	0.1-100	0.9992	5	2.05
Nitrite (NO ₂ ⁻)	0.05-20	0.9995	20	1.49
Bromide (Br ⁻)	0.05-20	0.9989	20	3.3
Nitrate (NO ₃ ⁻)	0.05-20	0.9991	20	2.69
Phosphate (PO ₄ ³⁻)	0.05-20	0.9995	50	14.38
Sulfate (SO ₄ ²⁻)	0.05-20	0.9992	20	3.63

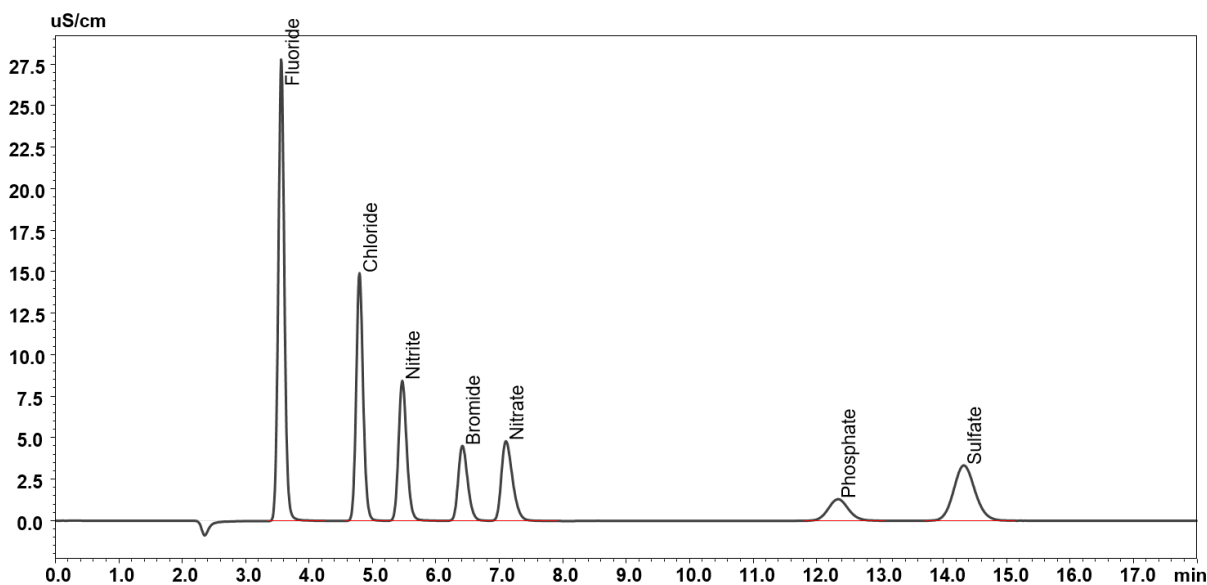


Figure 1: Separation of seven anions using the Shodex IC SI-90 4E column.
Peaks: 1. Fluoride (5 ppm), 2. Chloride (5 ppm), 3. Nitrite (5 ppm), 4. Bromide (5 ppm), 5. Nitrate (5 ppm), 6. Phosphate (5 ppm), 7. Sulfate (5 ppm)

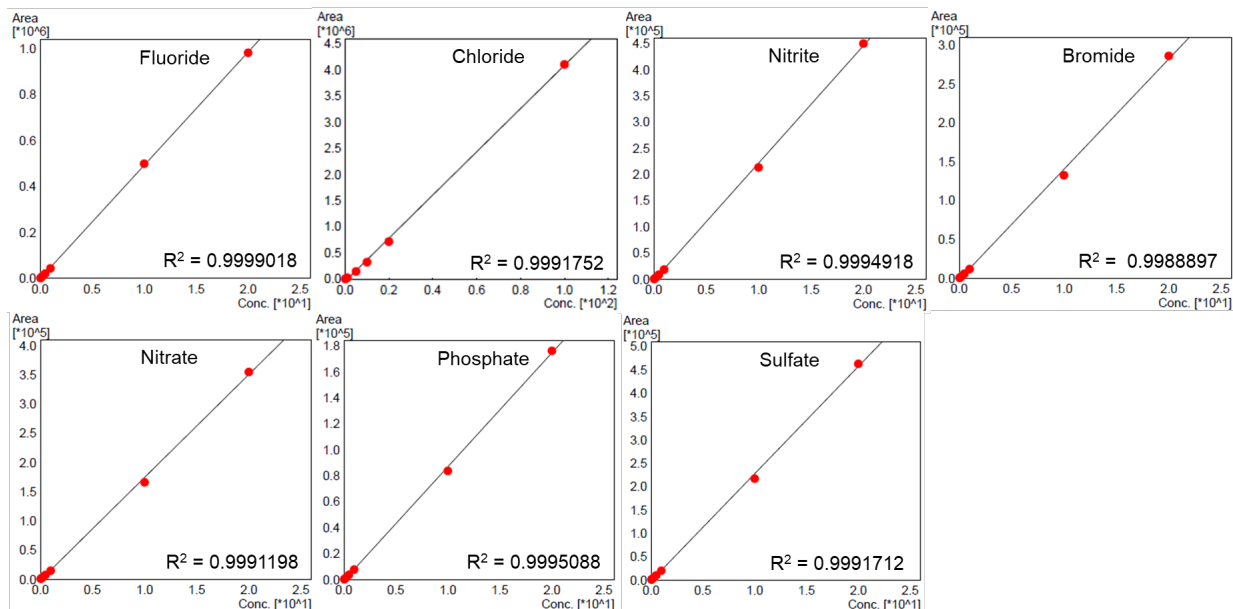


Figure 2: Calibration curves for seven anions contained in EPA Method 300

Reproducibility and Accuracy

Method reproducibility was performed using mixed standard with concentration of 10 ppm for each ion. Samples were continuously injected over four days. Reproducibility of retention time and peak area of all seven ions from five replicates from each day were analyzed. Results in table 2 show excellent reproducibility in terms of retention time and peak area over the time of the study.

Method accuracy was performed by fortifying blank DI water and tap water with 2 ppm concentration of each standard analyte. Very good recoveries were obtained from different water matrices when using this method and instrument as shown in table 3.

Table 2: Retention time and peak area reproducibility

Anions	1 day		4 days	
	T _r precision (RSD)	Area precision (RSD)	T _r precision (RSD)	Area precision (RSD)
Fluoride (F ⁻)	0.06%	0.07%	0.12%	0.72%
Chloride (Cl ⁻)	0.06%	0.07%	0.15%	0.78%
Nitrite (NO ₂ ⁻)	0.06%	0.14%	0.18%	0.70%
Bromide (Br ⁻)	0.07%	0.24%	0.20%	0.75%
Nitrate (NO ₃ ⁻)	0.08%	0.20%	0.22%	0.97%
Phosphate (PO ₄ ³⁻)	0.15%	0.25%	0.24%	0.64%
Sulfate (SO ₄ ²⁻)	0.13%	0.18%	0.30%	0.63%

Table 3: Recoveries in blank DI and tap waters

Anions	Added Concentration (ppm)	DI water	Tap water
		Recovery (%)	Recovery (%)
Fluoride (F ⁻)	2	93.9	99.4
Chloride (Cl ⁻)	2	94.0	96.2
Nitrite (NO ₂ ⁻)	2	96.1	95.2
Bromide (Br ⁻)	2	97.1	91.2
Nitrate (NO ₃ ⁻)	2	98	106
Phosphate (PO ₄ ³⁻)	2	98.4	103
Sulfate (SO ₄ ²⁻)	2	98.3	92.6

Water analysis

Figure 3 shows the chromatogram of three water samples obtained from the Shodex IC SI-90 4E column. A summary of quantitative results for various water samples is shown in Table 4.

The negative peak, also called water dip, in IC corresponds to injected water. It is also an indication of the hold-up volume of the IC system. Overlap of fluoride peak and water-dip is very common issue in water analysis. Figure 3 shows that the water-dip and fluoride peak are totally resolved using a Shimadzu Suppressed Conductivity System and column.

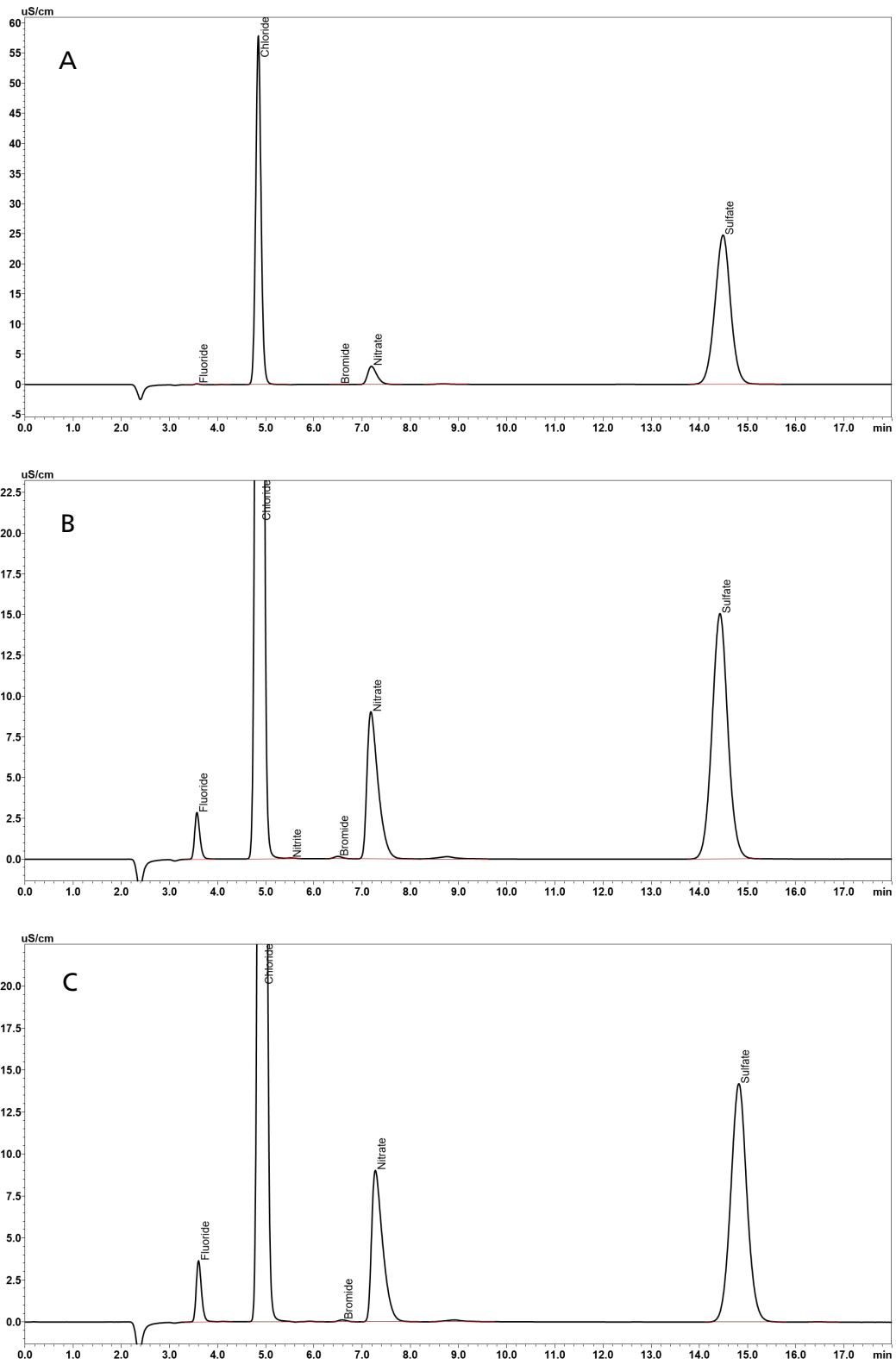


Figure 3: Inorganic anions analysis of water samples using the Shodex IC SI-90 4E column. Panels: A. bottle water, B. dispenser water, C. tap water Peaks: 1. Fluoride, 2. Chloride, 3. Nitrite, 4. Bromide, 5. Nitrate, 6. Phosphate, 7. Sulfate

Table 4: Inorganic anions analysis

Anions	Bottle water (ppm)	Dispenser water (ppm)	Lab tap water (ppm)
1. Fluoride (F ⁻)	0.08	0.50	0.64
2. Chloride (Cl ⁻)	12.99	41.06	39.69
3. Nitrite (NO ₂ ⁻)	--	0.25	--
4. Bromide (Br ⁻)	0.27	0.39	0.36
5. Nitrate(NO ₃ ⁻)	2.66	8.93	8.87
6. Phosphate(PO ₄ ³⁻)	--	--	--
7. Sulfate (SO ₄ ²⁻)	25.88	15.95	15.37

■ **Conclusion**

The Shimadzu modular IC system with electrolytic suppression provides sensitive and reliable performance for determination of common inorganic anions listed in EPA Method 300 including Fluoride (F⁻), Chloride (Cl⁻), Nitrite (NO₂⁻), Bromide (Br⁻), Nitrate (NO₃⁻), Phosphate (PO₄³⁻) and Sulfate (SO₄²⁻).

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