

Anions Analysis in Drinking water by a Novel Modular Ion Chromatograph

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1. Introduction

Ion chromatography (IC) continues to be the most commonly used chromatographic technique to determine the concentration of inorganic ions in waters. EPA Methods 300.0 and 300.1 are two regulatory IC methods for water analysis including surface water, ground water and drinking water.

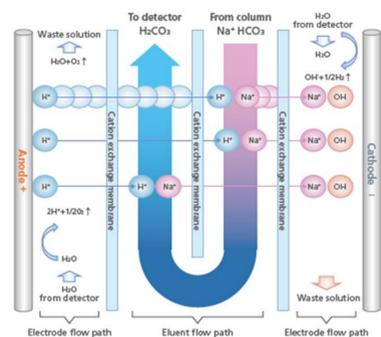
Since the baseline conductivity of typical mobile phases for ion chromatography is quite high, the detection limits for common anions can be poor (low ppm). Background suppression is used to effectively reduce the conductivity of the mobile phase, thus reducing the detection limits for the analytes by 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 inorganic anions according to methods EPA 300.

2. Experimental

Experiments were performed using a modular Shimadzu Prominence IC system with built-in electrolytically regenerated suppressor for the analysis of anions.



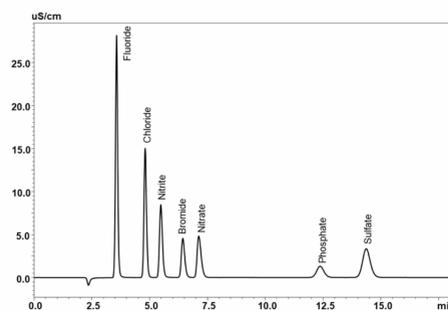
Fig. 1 Shimadzu Prominence IC



Cations in mobile phase are exchanged with hydronium ions that are continuously generated from water electrolysis.

3. Results and Discussion

3.1. Common anions analysis- EPA Method 300, Part A



Column Particle Size: 9 μ m
Column Dimension: 250 X 4 mm
Column Chemistry: Quaternary ammonium
Eluent: 1.8 mM sodium carbonate
1.7 mM sodium bicarbonate
Flow rate: 1 mL/min
Injection Vol: 50 μ L
Backpressure: ~ 1020 psi
Detection: Suppressed conductivity,
180 mA in recycle mode

Fig. 2 Separation of seven common anions

Figure 2 shows the experimental conditions and separation of seven common anions listed in EPA Method 300 Part A. As shown in the figure, the target analytes were separated in 15 minutes. Method reproducibility was evaluated using a 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 1 show excellent reproducibility in terms of retention time and peak area over the time of the study.

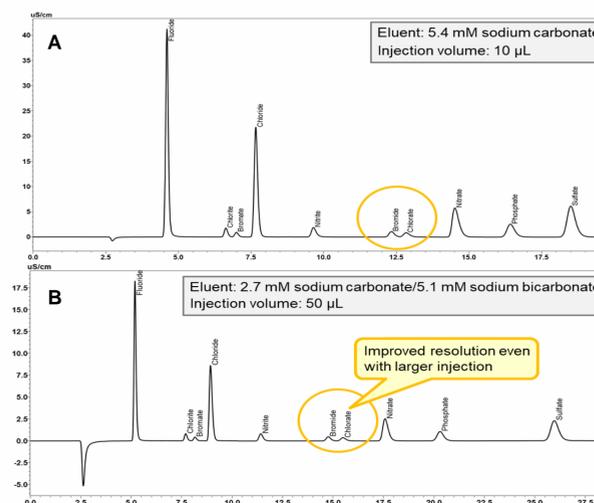
Table 1 Retention time and peak area reproducibility

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%

3.2. Common anions and DBPs – EPA Method 300.1

Figure 3 shows separation results from using two high-resolution methods. As shown in the figure, mobile phase composition and injection volume used were different

between these two methods. All anions are eluted in less than 20 minutes using method A. Although the run time is longer using method B, the advantage of this method is the resolution of bromide and chlorate is higher even with larger injection volume. Hence, method B is more suitable for trace chlorate and bromide analysis.



Column Particle Size: 5 μ m
Column Dimension: 250 X 4 mm
Column Chemistry: Quaternary ammonium
Eluent A: 5.4 mM sodium carbonate
Eluent B: 2.7 mM sodium bicarbonate
5.1 mM sodium bicarbonate
Flow rate: 0.8 mL/min

Fig. 3 Separation of 10 anions listed in EPA Method 300.1

The system produces linear response with coefficient of determination greater than 0.999 in a broader concentration range for all 10 anions from using method B as shown in Figure 4. Method reproducibility was evaluated using a mixed standard with concentration of 10 ppm for each ion. Excellent reproducibility was achieved from 8 injections of a mixture of 10 anions. Retention time RSDs of 10 anions are

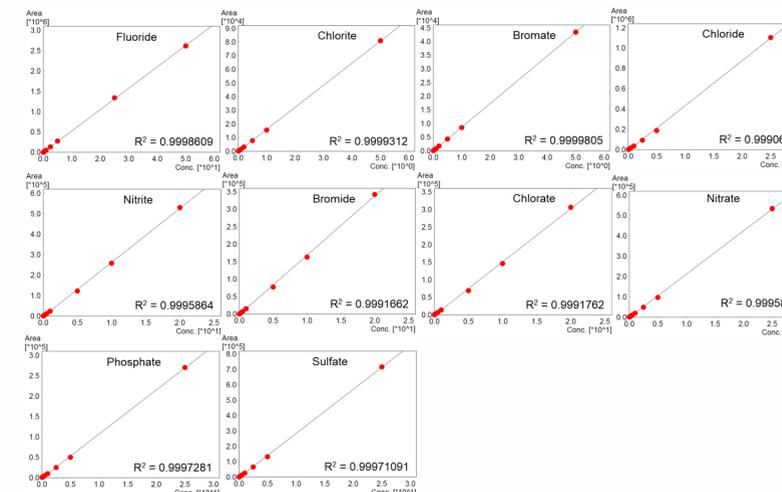


Fig. 4 Calibration curves for 10 anions listed in EPA Method 300.1

from 0.02 to 0.08% and peak area RSDs are from 0.23 to 0.42% for all the anions.

4. Conclusion

This study demonstrates that the robust and reliable performance of the Shimadzu ion chromatography with electrolytically regenerated suppression is achieved for the determination of common inorganic anions and DBPs listed in EPA Methods 300.0 and 300.1. Three methods are used in this study. One method is used to determine the seven common anions listed in Part A of the EPA Methods 300. The other two high-resolution methods using different mobile phase are performed to determine both common anions and DBPs simultaneously. More specifically, one high-resolution method can be used for rapid analysis of 10 anions, the other high-resolution method provides improved resolution of bromide and chlorate, even with a larger sample injection, making it more applicable to trace-level analysis of DBPs in more complex water matrices.