Ion Chromatography with Electrolytically Regenerated Suppressor for Water Analysis

Hui Guo, Craig Young, Steve Maury, Ruth Marfil-Vega, Shimadzu Scientific Instruments, Inc.

1. Introduction

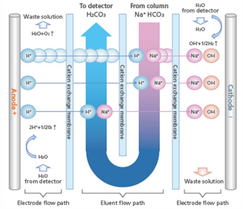
Ion chromatography (IC) continues to be the most commonly used chromatographic technique to determine the concentration of inorganic ions in waters. EPA Methods 300.0 and 300.1 are based on the use of IC for the analysis of regulated anions in various type of water. The anions in these methods are divided into common anions and inorganic disinfection by-products (DBPs). Seven common anions listed in Part A in both methods include Fluoride (F^-), Chloride (Cl^-), Nitrite (NO_2^-), Bromide (Br^-), Nitrate (NO_3^-), Phosphate (PO_4^{3-}) and Sulfate (SO_4^{2-}). DBPs listed in Part B from EPA 300.0 include Chlorite (ClO_2^-), Bromate (BrO_3^-) and Chlorate (ClO_3^-); part B from EPA 300.1 includes also Bromide (Br^-).

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 IC system with built-in electrolytically regenerated suppressor for the analysis of anions.

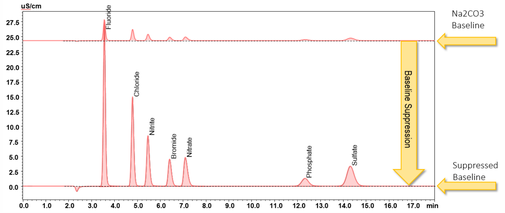
Fig. 1 Shimadzu IC



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

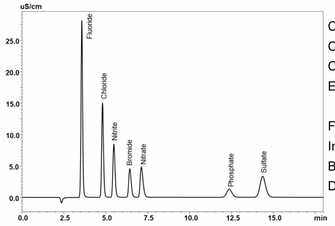
The Need for Suppressed Conductivity IC

- The conductivity of sodium carbonate solution is inherently high.
- A suppressor may be inserted between the column and detector to reduce the background signal.
- With suppression, 3 orders of magnitude lower detection limits are achieved.
- Suppression chemically alters the mobile phase.



3. Results and Discussion

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



Column Particle Size:	9 µm
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 µL
Backpressure:	~ 1020 psi
Detection:	Suppressed conductivity; 60 mA in recycle mode

Fig. 2 Separation of seven common anions

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%

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 ions. 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.

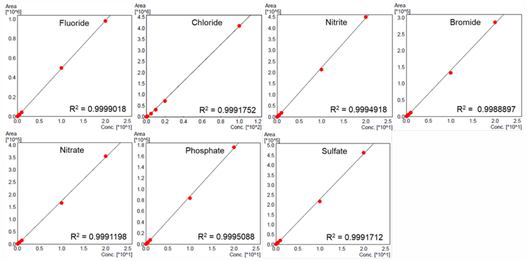
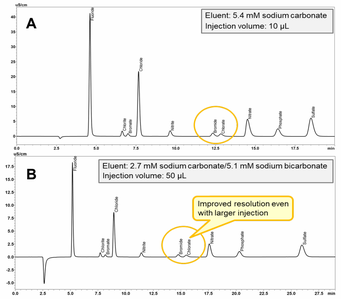


Fig. 3 Calibration curves for 7 common anions listed in EPA Method 300

Linear calibration range (Fig. 3) was established at 0.05 to 20 ppm for each anions except chloride; the latest was calibrated from 0.1 to 100 ppm. Calibration curves were acceptable with correlation coefficient (R^2) of 0.999 over 6 standard levels.

3.2. Common anions and DBPs – EPA Method 300.1



Column Particle Size:	5 µm
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
Backpressure:	~ 1400 psi
Detection:	Suppressed conductivity; 60 mA in recycle mode

Fig. 4 Separation of 10 anions listed in EPA Method 300.1

Figure 4 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.

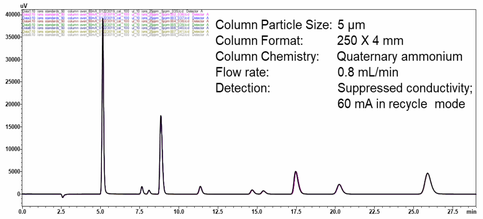


Fig. 5 Chromatographic overlay from 8 injections

Figure 5 shows chromatographic overlay from 8 injections of a mixture of 10 anions. As shown in the figure, excellent reproducibility was achieved. Retention time RSDs of 10 anions are 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.