Determination of Common Anions and Oxyhalides in Environmental Samples: Selecting the Proper Mobile Phase and Column

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INTRODUCTION

Method optimization in ion chromatography involves the process of selecting the best analytical column and mobile phase to ensure the best separation for a given application, with selectivity and sensitivity being key parameters. This presentation will explore the impact of mobile phase, resin selectivity, and column capacity in optimizing ion-exchange separations.

Carbonate-based anion-exchange columns have been used extensively due to ease of eluent preparation. Several high-capacity carbonate eluent columns have recently been introduced for simultaneous analysis of inorganic anions and oxyhalides. The application of these columns with carbonate eluent systems will be demonstrated.

Hydroxide eluent systems have been shown to provide the highest detection sensitivity and lowest noise, resulting in substantially lower detection limits. Several high-capacity resins have been developed for hydroxide eluent systems for inorganic anion and organic acid separations. While many of these columns are optimized for anions and organic acids, recent developments have extended the use of hydroxide eluent systems to the separation of common inorganic anions and oxyhalides. A comparison of mobile phases and columns using real world samples will be demonstrated.

EXPERIMENTAL CONDITIONS

- All separations were performed on the ICS-3000 Dual Chromatography System (Dionex, Sunnyvale, CA USA) equipped with Dual Pump, Eluent Generator, Conductivity Detector and ASRS® ULTRA II 2 mm in Auto Recycle mode.
- Columns used were Dionex IonPac® AG18, AS18 and AG22, AS22 2 mm for the analysis of common anions, and IonPac AG19, AS19 and AG23, AS23 2 mm for analysis of common anions and oxyhalides.
- Dionex Chromeleon® 6.7 Chromatography Management Software was used for system control and data processing.

RESULTS

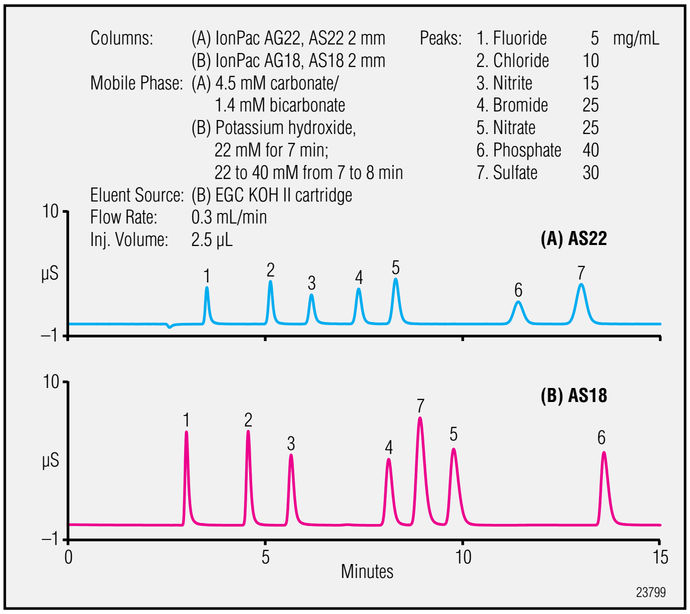

Figure 1. Comparison of IonPac AS22 and AS18 2 mm columns for separation of seven common anions using their appropriate eluents.

The IonPac AS22 demonstrates excellent separation of fluoride, chloride, nitrite, bromide, nitrate, phosphate, and sulfate using carbonate/bicarbonate eluent. The IonPac AS18 also provides excellent separation of the same analytes using an electrolytically generated hydroxide mobile phase. Note the hydroxide eluent system provides higher sensitivity with the same amount of sample injected onto both columns.

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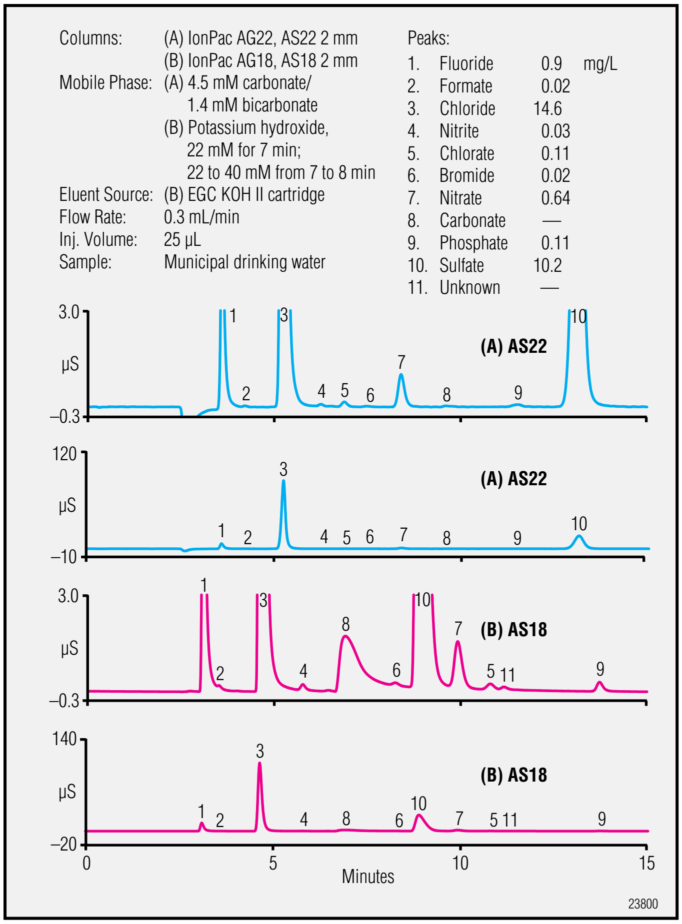

Figure 2. Comparison of IonPac AS22 and AS18 2 mm columns for analysis of a municipal drinking water sample.

The IonPac AS22 and AS18 both show excellent results using their appropriate eluents. Note, however, that both columns show different selectivity for the various common anions. Both columns are solvent compatible which permits easy column clean-up after analysis of samples containing hydrophobic components.

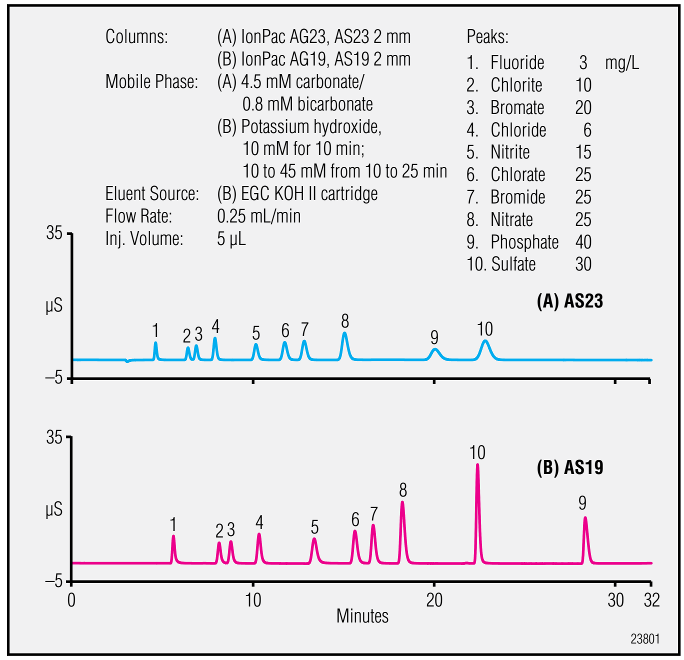

Figure 3. Comparison of IonPac AS23 and AS19 2 mm for separation of common anions and oxyhalides using their appropriate eluents.

The IonPac AS23 is designed for separation of oxyhalides and common inorganic anions in a variety of sample matrices. These analytes can easily be separated in approximately 24 min using isocratic carbonate/bicarbonate eluent with suppressed conductivity.

The IonPac AS19 is a hydroxide-selective column also designed for separation of oxyhalides and common inorganic anions in a variety of sample matrices. Again, note that hydroxide mobile phase along with gradient elution shows much higher sensitivity as compared to isocratic carbonate eluent when the same amount of sample is injected on both columns (AS23 and AS19).

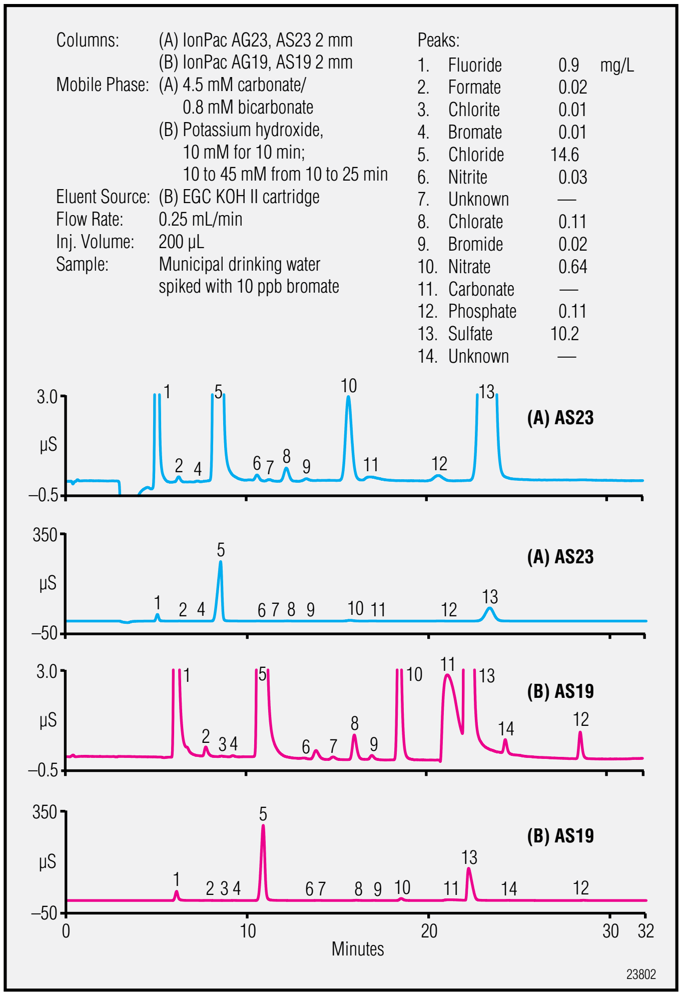

Figure 4. Comparison of AS23 and AS19 2 mm for analysis of municipal drinking water.

The IonPac AS23 and AS19 demonstrate excellent results for analysis of common anions and oxyhalides using their appropriate eluents. However, when low-level detection of bromate is required, the best results are achieved using the IonPac AS19 along with electrolytically-generated hydroxide eluent.

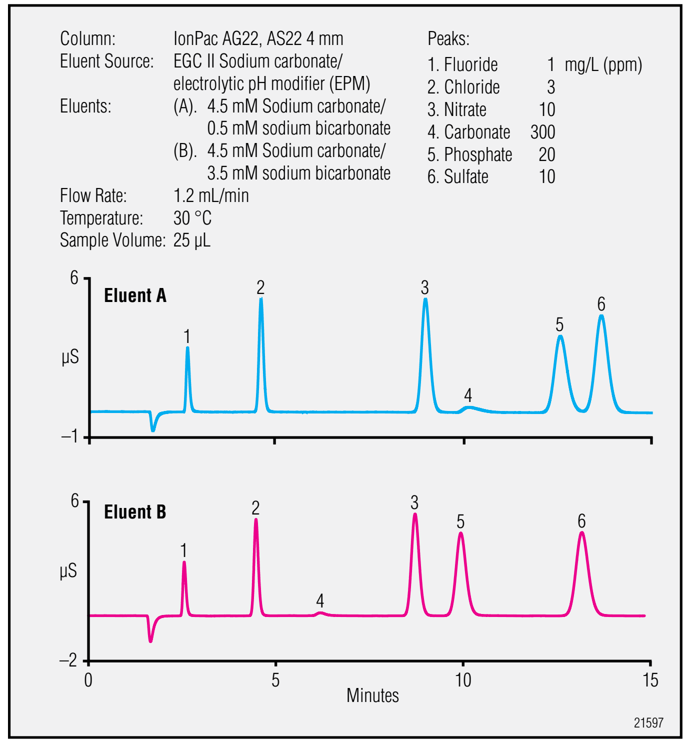

Figure 5. Effect of eluent pH on IonPac AS22 selectivity.

The IonPac AS22 and AS23 stationary phases offer a unique advantage for the location of the carbonate peak. Unlike with other stationary phases, the carbonate peak can be placed anywhere between nitrite and sulfate depending upon the pH of the eluent as shown in Figure 5 using IonPac AS22 column.

	Range (mg/L)	Linearity (r^2)	Retention Time[a] RSD (%)	Peak Area RSD (%)	MDL Standard (µg/L)	Calculated MDL (µg/L)
	IonPac AS19 4 mm Column					
Analyte						
Chlorite	2–50	0.9999	0.04	1.20	1.0	0.18
Bromate	1–25	0.9995	0.03	1.40	2.0	0.31
Chlorate	2–50	0.9999	0.01	0.54	1.0	0.28
	IonPac AS23 4 mm Column					
Chlorite	10–50	0.9999	0.07	2.20	5.0	1.02
Bromate	5–25	0.9998	0.07	2.63	5.0	1.63
Chlorate	10–50	0.9998	0.11	2.48	9.0	2.05

[a]RSD = relative standard deviation, n = 10 for a standard consisting of 10 ppb bromate and 20 ppb each of chlorite and chlorate using 250 µL injection volume.

Table 1. Calibration data, retention time, peak area precisions, and method detection limits for disinfection byproduct anions using carbonate/bicarbonate and hydroxide mobile phases.

This table shows improved sensitivity for bromate using hydroxide mobile phase. The IonPac AS19 with electrolytically-generated hydroxide eluent is recommended for laboratories that must comply with a maximum of 3 mg/L bromate in municipal waters treated with ozone.

DISCUSSION AND CONCLUSION

1. The IonPac AS18 column is recommended for analysis of common anions when using hydroxide eluent. Due to the low background of the hydroxide eluent, the carbonate peak may interfere with quantification of one of the common anions such as bromide. However, this carbonate interference may be removed by using the Carbonate Removal Device (CRD 200). The AS18 column demonstrates higher detection limits compared to the AS22 column.

2. The IonPac AS22 column is recommended for analysis of common anions when using carbonate/bicarbonate eluent. The AS22 stationary phase offers a unique advantage for the location of carbonate peak (carbonate elutes after nitrate) unlike any other column for this application. Due to the higher background conductivity of the carbonate eluent, the carbonate peak does not interfere with the analysis of most of the common anions. However, achieving very low detection limits using carbonate/bicarbonate eluent system can prove difficult.

3. The IonPac AS19 column is recommended for analysis of common anions and oxyhalides when using hydroxide as a mobile phase. The low background conductivity of this eluent provides significantly lower detection limits compared to carbonate/bicarbonate.

4. The IonPac AS23 column is recommended for analysis of common anions and oxyhalides using carbonate/bicarbonate eluent. The AS23 column provides the required sensitivity to meet the maximum permissible limit of 10 µg/L bromate. The stationary phase of this column also offers a unique advantage for the location of carbonate peak, which elutes after nitrate.

Recommended Column Based on the Mobile Phase Along with Its Advantages				
Application	**Column Type**	**Mobile Phase**	**Eluent**	**Advantages**
Common Anions	IonPac AG18, AS18	Potassium hydroxide	22 mM KOH for 7 min and 22 to 40 mM from 7 to 8 min	High sensitivity and low method detection limits
Common Anions	IonPac AG22, AS22	Sodium carbonate/ bicarbonate	4.5 mM carbonate/ 1.4 mM bicarbonate	Faster analysis time and lower level of carbonate interference
Common Anions and Oxyhalides	IonPac AG19, AS19	Potassium hydroxide	10 mM KOH for 10 min and 10 to 45 mM from 10 to 25 min	High sensitivty and low method detection limits
Common Anions and Oxyhalides	IonPac AG23, AS23	Sodium carbonate/ bicarbonate	4.5 mM carbonate/ 0.8 mM bicarbonate	Faster analysis time and lower level of carbonate interference

REFERENCES

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