

Ion Chromatographic Determination of Oxyhalides and Bromide at Trace Level Concentrations in Drinking Water Using Direct Injection

INTRODUCTION

The U.S. EPA Information Collection Rule (ICR) requires drinking water utilities serving more than 100,000 customers to report the concentration of target microorganisms present, the removal process used, and the concentration of disinfection byproducts (DBP) present in their waters.¹ The monitoring period began in July 1997 and will continue for 18 months. The ICR will affect approximately 300 drinking water utilities in the United States.

The U.S. EPA recommends Method 300.0 (B), which specifies ion chromatography with chemically suppressed conductivity detection, to monitor chlorite, bromate, and chlorate in drinking water.² Bromide, a precursor to bromate, must also be monitored down to levels as low as 10 ppb, because bromate has been classified as a potential carcinogen, even at low ppb levels, by the U.S. EPA and the World Health Organization. Under the ICR, utilities using hypochlorite solution as a disinfectant are required to monitor chlorate; those using chlorine dioxide are required to monitor chlorite, chlorate, and bromate; and those using ozone are required to monitor bromate. All utilities are required to monitor bromide.

This Application Note describes an isocratic separation using the IonPac[®] AS9-HC column to determine trace levels of oxyhalides and bromide in the presence of common anions in drinking water, as well as their detection limits and linear concentration ranges. The AS9-HC column method was developed to improve the separation between bromate and chloride, thus allowing lower detection limits of bromate in the presence of high chloride

concentrations. Unlike previous IC methods for these ions, no pretreatment cartridges are required to remove high concentrations of common ions such as chloride, bicarbonate, and sulfate. The instrumentation, techniques, and representative applications of this method are discussed in this Note.

EQUIPMENT

Dionex DX-500 Ion Chromatography system consisting of:

GP40 Gradient Pump

CD20 Conductivity Detector

AS40 Automated Sampler

LC20 Chromatography Enclosure equipped with a rear-loading injection valve

4-L Plastic bottle assemblies (for external water mode)

PeakNet Chromatography Workstation

REAGENTS AND STANDARDS

Deionized water, Type I reagent grade, 18 M Ω -cm resistance or better

0.5 M Carbonate Anion Eluent Concentrate (in deionized water) (Dionex P/N 37162)

Sodium and Potassium salts, ACS reagent grade, for preparing anion standards (see Table 1) (Fisher Scientific, EM Science)

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CONDITIONS

Columns: IonPac AS9-HC Analytical, 4 x 250 mm (P/N 51786)
IonPac AG9-HC Guard, 4 x 50 mm (P/N 51791)
Eluent: 9 mM Sodium carbonate
Run Time: 25 min
Flow Rate: 1 mL/min
Sample Vol.: 200 μ L
Detection: Suppressed conductivity, ASRS™ -II, 4 mm, AutoSuppression™ external water mode

PREPARATION OF SOLUTIONS AND REAGENTS

Standard Solutions

Stock Anion Standard Solution (1000 mg/L)

Dissolve the corresponding mass of the salt for each of the anions of interest (see Table 1) in 1000 mL of deionized water. Standards are stable for at least one month when stored at 4 °C.

Table 1 Masses of compounds used to prepare 1 liter of 1000 mg/L ion standards

Anion	Compound	Mass (g)
F ⁻	Sodium fluoride (NaF)	2.210
ClO ₂ ⁻	Sodium chlorite (NaClO ₂ •2H ₂ O)	2.409
BrO ₃ ⁻	Sodium bromate (NaBrO ₃)	1.180
Cl ⁻	Sodium chloride (NaCl)	1.648
NO ₂ ⁻	Sodium nitrite (NaNO ₂)	1.500
Br ⁻	Sodium bromide (NaBr)	1.288
ClO ₃ ⁻	Sodium chlorate (NaClO ₃)	1.276
NO ₃ ⁻	Sodium nitrate (NaNO ₃)	1.371
H ₂ PO ₄ ⁻	Potassium phosphate, monobasic (KH ₂ PO ₄)	1.433
SO ₄ ²⁻	Potassium sulfate (K ₂ SO ₄)	1.814
HCO ₃ ⁻	Sodium bicarbonate (NaHCO ₃)	1.377

Working Standard Solutions

Dilute each analyte to the required concentration with deionized water using the 1000-mg/L standards prepared above. Working standards containing less than 100- μ g/L anions should be prepared daily.

Eluent Solution

9 mM Sodium carbonate

Dilute 18 mL of 0.5 M sodium carbonate concentrate to 1 L with deionized water. Transfer to an eluent container and blanket with helium at 0.055 MPa (8 psi).

Preservation Solution

45 g/L Ethylenediamine preservation solution

Dilute 10 mL of 99% ethylenediamine (Fluka) to 200 mL with water. Use 1 mL of this solution per liter of sample.

SAMPLE PREPARATION

Spurge samples for 5 minutes to remove any reactive gases (e.g., chlorine dioxide or ozone). To prevent oxidation of chlorite to chlorate or formation of bromate from hypobromite, preserve samples by adding 1 mL of ethylenediamine preservation solution per liter of sample.

DISCUSSION AND RESULTS

The IonPac AS9-HC provides baseline separation of chlorite, chlorate, bromate, and bromide from common anions and provides good resolution between bromate and chloride to allow a low detection level of 5 μ g/L (5 ppb) for bromate in the presence of a high chloride (50 mg/L) concentration. Figure 1 shows a typical chromatogram of a separation of common anions and oxyhalides on the IonPac AS9-HC column.

For the best performance at low levels, it is critical that baseline noise be kept to a minimum. From start up, a system for trace analysis typically requires about 5 hours to

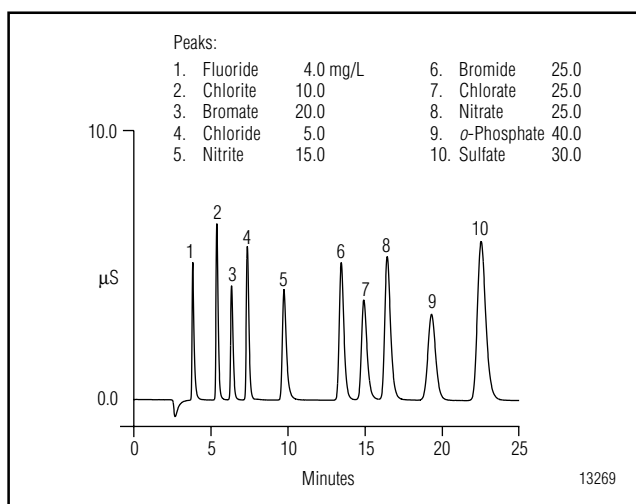


Figure 1 Separation of common anions and oxyhalides on the IonPac AS9-HC column.

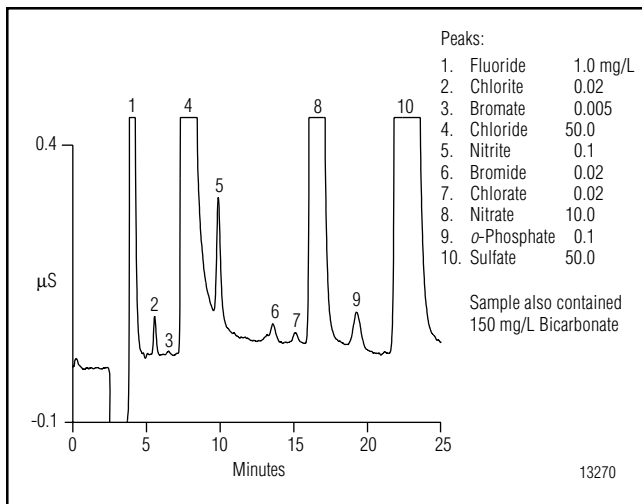


Figure 2 Determination of µg/L levels of oxyhalides and bromide in simulated drinking water.

establish a stable background conductivity. For this reason, it is best to keep the system running continuously. Ensure that there is an adequate supply of the eluents, external water, and waste containers to allow the system to run unattended. An equilibrated system will have a background conductivity between 20–24 µS. To keep a conductivity background at that low level throughout a whole day without significant drift, it is absolutely necessary to use external water mode rather than recycle mode. Peak-to-peak noise is typically 6–10 nS. Figure 2 shows the determination of low levels of oxyhalides and bromide in simulated drinking water. Seven injections of this same concentration standard were made to determine method detection limits of oxyhalides and bromide in simulated drinking water. Table 2 shows the results.

Table 2 Method detection limits for oxyhalides and bromide in simulated drinking water based on a 200-µL injection volume using the IonPac AS9-HC column

	Conc. (µg/L)	Std. Dev. (µg/L)	RSD (%)	MDL* (µg/L)
Chlorite	10	0.76	7.99	2.38
Bromate	5	0.55	12.55	1.73
Bromide	10	0.57	5.45	1.78
Chlorate	10	0.34	4.38	1.07

*MDL = SD x $t_{s,99}$ where $t_{s,99} = 3.14$ for $n = 7$

Sample also contained: Chloride 50 mg/L
Bicarbonate 150 mg/L
Sulfate 50 mg/L

The data demonstrate that this method achieves the required method detection limits and exceeds the standard deviation requirements of the current ICR. It is important to establish a linear concentration range to accurately quantify oxyhalides and bromide in the presence of common anions in drinking water. Table 3 summarizes the results of the linearity analyses. In these analyses, seven different concentrations of each analyte were analyzed using a 200-µL sample injection. Table 3 shows that bromate is linear between 5–40 µg/L, and chlorite, chlorate, and bromide are linear between 20–500 µg/L.

Table 3 Linear concentration range study of oxyhalides and bromide in simulated drinking water using the IonPac AS9-HC

	Conc. Range (µg/L)	Std. Dev.* of Resp. Factor (µg/L)	RSD (%)	r ²
Bromate	5–40	2.09	1.17	0.9998
Chlorite	20–500	20.07	4.42	0.9999
Bromide	20–500	10.32	4.17	0.9991
Chlorate	20–500	4.05	1.46	0.9999

* Standard deviation was calculated as a function of the response factor. Response factor equals the ratio of area count to concentration.

The chosen ranges for oxyhalides and bromide are characteristic for the amounts of those analytes commonly found in drinking water. Concentrations outside these ranges were not tested. However, it is expected that the method is linear to higher concentrations. The linearity data also demonstrate method ruggedness and good column performance, which allow accurate and precise achievement of the ICR requirements. The concentration range experiment was repeated with the addition of ethylenediamine preservation solution to all of the samples to establish whether the presence of ethylenediamine would have any significant effect on chromatography and recovery of oxyhalides. No significant differences were observed.

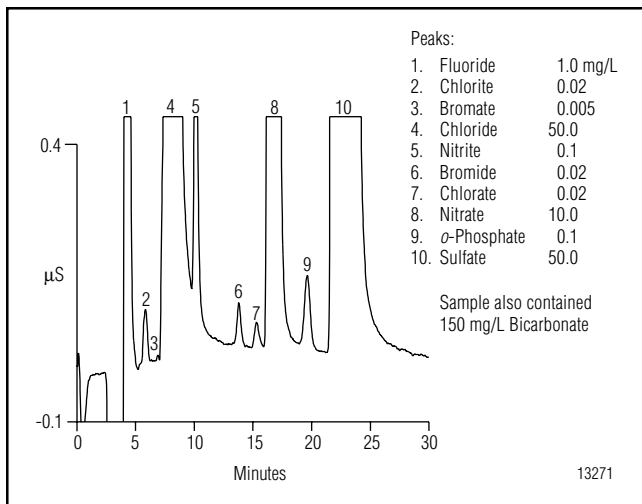


Figure 3 Large loop injection for µg/L-level oxyhalide analysis.

The effect of injection volume on simulated drinking water analysis was investigated. Figure 3 illustrates that a 500-µL injection is the largest amount of the simulated drinking water sample that can be injected onto the column without considerable loss of resolution between bromate and chloride. With a 750-µL injection, column ion-exchange sites are overloaded, which causes coelution of bromate and chloride. The IonPac AS9-HC column allows large sample loop injections (e.g., 200 µL) to achieve low detection limits even in the presence of high concentrations of chloride, sulfate, and bicarbonate.

SUMMARY

An improved column and method for the determination of oxyhalides and bromide in drinking water have been developed. Using this method, these anions can be detected in a concentration range that exceeds the ICR requirements. Linear concentration ranges have been established to accurately quantitate the oxyhalides and bromide in drinking water samples.

REFERENCES

1. Fed. Regist. **1996**, 61(94), 24354.
2. U.S. Environmental Protection Agency. *U.S. EPA Method 300.0*. "The Determination of Inorganic Anions in Water by Ion Chromatography," August 1993.

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