

Advances in Bromine Speciation in Drinking Water by HPLC/ICP-MS

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Introduction

Bromine is a natural component of waters, most commonly occurring as the bromide ion (Br^-). A common procedure for purifying drinking waters, ozonolysis, also converts bromide to bromate (BrO_3^-), a known carcinogen. Therefore, it is important to measure both bromide and bromate in drinking waters.

Compared to earlier bromine separation (*speciation*) methodology¹, this work focuses on decreasing the analysis time, while also separating additional bromine-containing compounds in drinking waters.

Experimental

Hardware/Software

A PerkinElmer[®] Series 200 HPLC System (quaternary pump, autosampler, vacuum degasser and column oven; PerkinElmer Inc., Waltham, MA, USA) was used with an anion exchange column (ZirChrom Separations, Anoka, MN, USA; ZirChrom-SAX) for all separations. Detection was accomplished with an ELAN[®] DRC II (PerkinElmer SCIEX, Waltham, MA, USA); all instrument control, analysis and data processing were done with Chromera[™] software (PerkinElmer Inc., Waltham, MA, USA).

Standards and Samples

Bromide/bromate standards were prepared daily from 1000 mg/L stock solutions (Spex, Charleston, SC, USA) by dilution with 18 M Ω -cm water.

Samples were either bottled waters (purchased at local grocery stores) or tap waters. Aside from filtering samples to remove small particles, no sample preparation/dilution was required.

Table 1: Method Parameters

HPLC Conditions	
Isocratic Mobile Phase:	18 mM NH ₄ OH + 3 mM HNO ₃ ; pH 10.2
Gradient Mobile Phase Profile:	2 min at 100% A (14 mM NH ₄ OH + 6 mM HNO ₃ ; pH=7.3) Step to 100% B (18 mM NH ₄ OH + 3 mM HNO ₃ ; pH=10.2) 4 min at 100% B; 5 min re-equilibration (Equil) time
Method Conditions:	Flow Rate: 1.5 mL/min, Column Temperature: 50°C, Injection Volume: 50uL
Total Analysis Time:	Isocratic Method: 4 min; Gradient Method (with Equil): 11 min
ICP-MS Conditions	
RF Power: 1500 W; Dwell Time: 250 ms; RPq: Standard Mode: 0.25; DRC Mode: 0.50	
Analytes:	Standard Mode: ⁷⁹ Br ⁺ ; DRC Mode: ^{79,81} BrO ⁺ (m/z 95, 97)
Reaction Gas:	Standard Mode: None; DRC Mode: N ₂ O = 0.5

Results

In Figure 1, Chrom1 shows a chromatogram of a drinking-water sample in which the bromine species are well separated in under three minutes. This chromatogram was acquired using the newly developed isocratic conditions shown in the accompanying table. The S/N for the 7.4 µg/L (ppb) Br⁻ peak is ~5-6, suggesting that the limit of detection (LOD) is approximately 3 ppb (LOD = 3 x S/N). The noise was discerned from the baseline immediately after the Br⁻ peak. Larger injection volumes (> 50 µL) would allow detection of lower levels, but these must not overload the column.

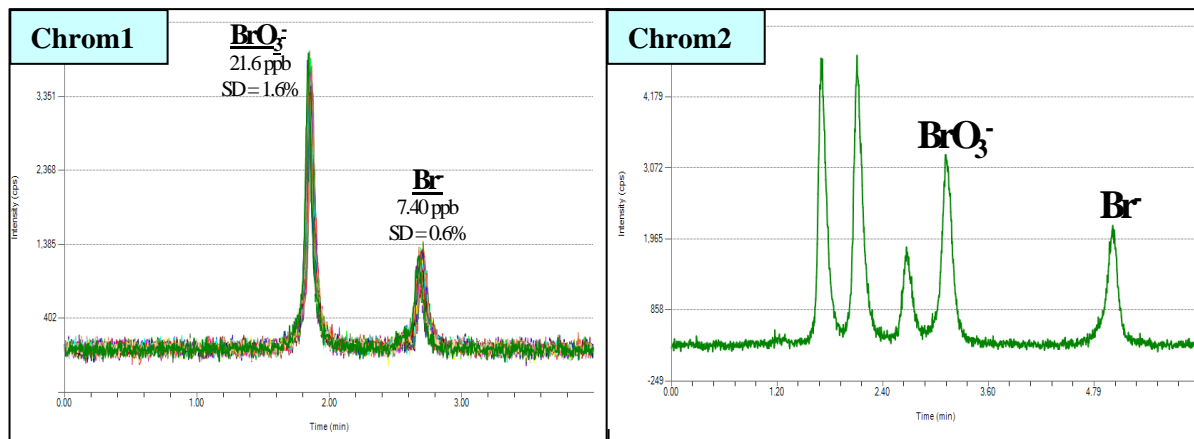


Figure 1. Chromatographic overlays of 49 consecutive bromine injections.

Figure 2. Drinking water sample containing bromine species, as well as some unknowns.

To determine the repeatability/ruggedness of the method, this same sample was analyzed 49 consecutive times over 4 hours. The corresponding chromatograms are shown overlaid in Figure 1, overlaying quite well. The concentration relative standard deviation (RSD) was <2%, and the retention time RSD was ≤0.5%.

The drinking-water samples ranged between 0-425 ppb Br⁻ and 0-125 ppb BrO₃⁻. Each sample was measured in duplicate on four non-consecutive days, with only small variations in the results. The significantly high concentrations of BrO₃⁻ in some of the drinking water samples suggest potential safety concerns.

Some samples contained additional bromine-containing components. To allow for the additional peak resolution required, a gradient HPLC method was developed. The conditions are provided in a corresponding application note². A sample that contained these additional components is shown in Figure 2. To confirm that these additional peaks were actually bromine-containing components, the samples were also analyzed using the DRC mode. This was available via the ELAN DRC II, which converted $^{79,81}\text{Br}^+$ to $^{79,81}\text{BrO}^+$ (m/z 95, 97), by reaction with N_2O in the reaction cell. The unidentified components appearing in the standard mode at m/z 79 (Br^+) were also observed for both m/z isotopes in the DRC mode, thus confirming the presence of bromine in these components.

Conclusion

This work has demonstrated a rapid, robust isocratic method for the separation and quantitation of bromide and bromate in drinking waters in three minutes. Injection-to-injection and day-to-day stability have been demonstrated. For those waters containing additional bromine species, a gradient HPLC method was established which separated all bromine species in 5 minutes.

References

1. Perrone, P.A., Reuter, W.M., Neubauer, K.R., Bosnak, C.P., Hall, G.A., Grosser, Z.A, *Bromine Speciation by HPLC/ICP-MS* (Application Note), 2005, PerkinElmer Inc.
2. Neubauer, K.R., Perrone, P.A., Reuter, W.M., *Advances in Bromine Speciation by HPLC/ICP-MS* (Application Note), 2006, PerkinElmer Inc.

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