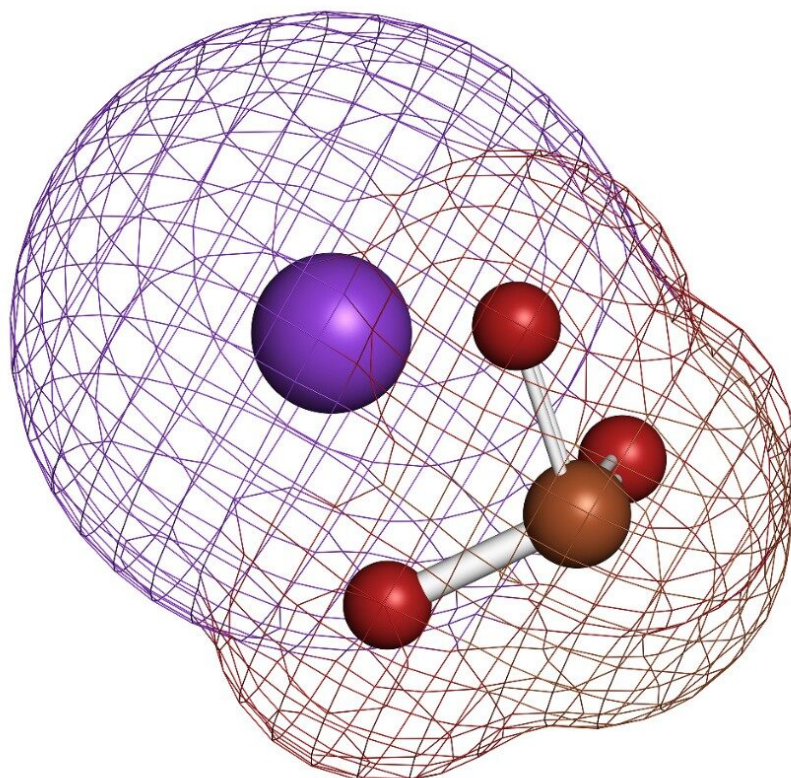


Nota de aplicación

Analysis of Free Bromate Ions in Tap Water using an ACQUITY UPLC BEH Amide Column

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Abstract

This application note demonstrates the feasibility of analyzing bromate ions in tap water using the HILIC separation mode and flexible LC-MS instrumentation that already exists in many laboratories worldwide.

Benefits

- The BEH Amide column used under HILIC conditions improves both the retention and detection of the free bromate ion without the need for post-column derivatization.
- The versatility of LC-MS detection provides a reliable and sensitive assay compared to commonly-used ion-chromatography (IC) methods.

Introduction

Bromates found in drinking water pose a toxic health risk to humans if ingested in significant quantities. Even at very low concentration, the presence of bromate in drinking water has the potential for adverse long-term health effects. Bromate is not endogenous to natural sources of water; however, bromate contamination is created as a by-product of advanced ozone water treatments. Ozone reacts with natural sources of elemental bromine found in water supplies and the level of bromine can vary from source to source. To date, there are no practical methods for removing the bromine or the bromate by-product, and the only solution is to limit the bromate formation during the water treatment process. This requires careful monitoring of the bromate concentration so that it does not exceed safe drinking water standards. The World Health Organization (WHO) drinking quality standards recommendation is limited to 10 ppb ($\mu\text{g/L}$) bromate in drinking water.¹

Experimental

Sample Preparation:

All standard solutions were prepared using 90% acetonitrile:10% de-ionized water. Samples of tap water were prepared by diluting 5-fold with acetonitrile.

LC System:	ACQUITY UPLC
Detector:	ACQUITY SQD (-ve ESI, SIR mode <i>m/z</i> 128.9)
Column:	ACQUITY UPLC BEH Amide, 2.1 x 100 mm, 1.7 μ m, part number 186004801
Column Temp.:	40 °C
Injection Volume:	20 μ L
Injection Mode:	Full loop
Flow Rate:	0.3 mL/min
Isocratic Mobile Phase:	90% acetonitrile: 10% 50 mM aqueous ammonium formate (unbuffered)
Weak Needle Wash:	Acetonitrile
Strong Needle Wash:	Water
Seal Wash:	50% acetonitrile:50% water
Data Management:	MassLynx, version 4.1

Results and Discussion

Challenges Faced using Conventional Methods

1. A low limit of detection (1 μ g/L) for bromate is required to ensure quality monitoring of tap water conforming to WHO guidelines

2. Ion-chromatography (IC) with post-column (PC) derivatization:
 3. a) Natural sources with high organic carbon levels mask the bromate ion content, resulting in erroneous data
 - b) Naturally high concentrations of carbonate/bicarbonate interfere with bromate analysis
 - c) The strong acids used for the post-column reaction increase instrument down-time, and the high maintenance requirements make the assay non-user friendly
4. Ion-chromatography (IC) with mass spectrometric detection (IC-MS/MS)
 5. a) The mobile phases used for IC suppress ionization during MS analysis, which decreases both bromate sensitivity and robustness of the assay
 - b) IC-MS is only useful for ionizable species
 - c) Not widely adopted by drinking water laboratories

HILIC-LC/MS Approach to Bromate Analysis

1. Using the BEH Amide column under HILIC conditions retains bromate with MS-friendly mobile phases
2. The high acetonitrile content in the mobile phase facilitates good detector response without the need for derivatization
3. The versatile LC-MS system can be used for a wide variety of assays, thus increasing instrument utilization and flexibility

		Bromate Analysis		
		IC-PC	IC/MS	HILIC-LC/MS
Sample Preparation		Not Required	Not Required	Required (dilution)
Post-column Reaction with Strong Acids		Required	Not Required	Not Required
Post-column Addition of Strong Organic Solvent		Not Required	Required	Not Required
Quantitation	Standard	1	0.1	0.1
Limit (ppb)	Tap Water	1	0.1	0.5
Recovery of 1 ppb Standard Solution (%RSD)		5~6	2~3	2~3
Qualitative Analysis (screening)		No	Yes	Yes
Versatility		No	No	Yes

Table 1. Comparison of bromate analysis methods. The LOQ for the HILIC method is based on a signal-to-noise (S/N) ratio of 10.

Sensitivity

To establish reliable data, it is recommended that the analytical method be at least 10-fold more sensitive than the action limit imposed for the assay. By following the 10 ppb WHO guideline for bromate, this would require that the analyte be detectable at 1 ppb or lower. Typical IC methods can detect bromate at these very low levels; however, the methods used for IC are more labor intensive and require a rigorous instrument maintenance schedule due to the reagents used for the post-column reaction. In contrast, HILIC chromatography coupled with MS detection provides both ease of use and high sensitivity. Figure 1 shows single ion recording (SIR) MS chromatograms in the range of 0.05 – 1 ppb. The mass-to charge ratio monitored for the bromate ion was 128.9 Da.

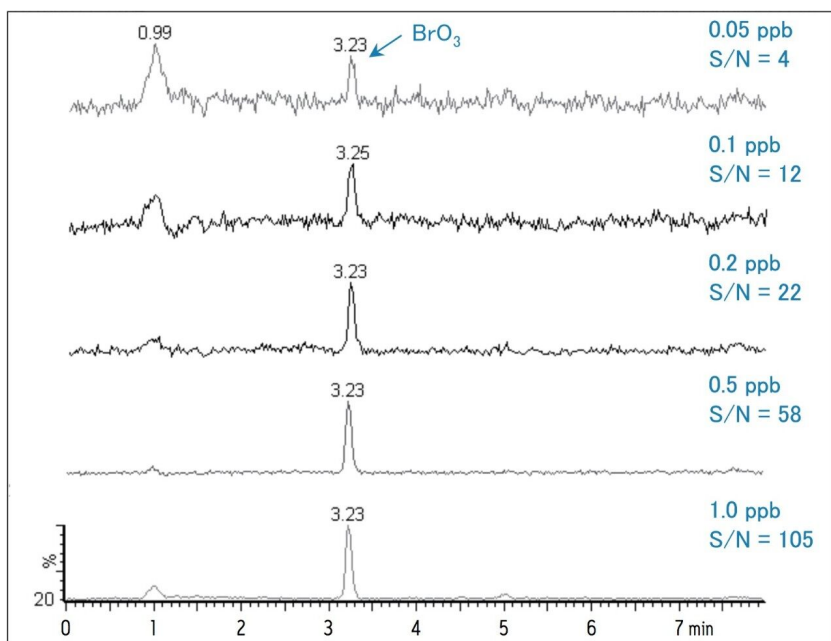


Figure 1. SIR chromatograms (m/z 128.9) of standard bromate solutions.

Recovery

Table 2 summarizes the recovery data of a spiking experiment in tap water. Figure 2 provides detailed chromatograms for the spiking experiment. The recovery of bromate in the tap water was greater than 95% for both spike levels.

Bromate (ppb)			
Spiked Concentration	Measured Concentration	Calculated Concentration	% Recovery
0	0.24	1.21	-
1	0.44	2.18	97.0

Table 2. Recovery data for tap water samples spiked with bromate. The recovery values have been corrected for bromate levels found in blank samples. The tap water used in the spiking study contained a native level of 1.21 ppb bromate.

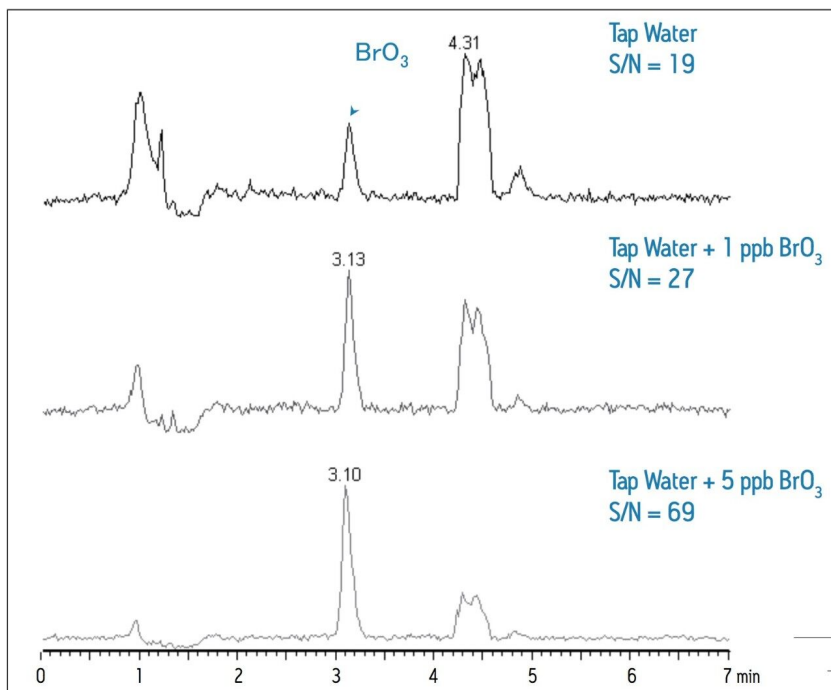


Figure 2. SIR chromatograms of a spiked water sample at 1 ppb and 5 ppb. The tap water sample has a native level of 1.21 ppb.

Reproducibility

The reproducibility data for standard bromate solutions and tap water spiked with 1 ppb of bromate (N=9) is shown in Table 3. The relative standard deviation of the 1 ppb standard bromate solution and a 1 ppb spiked water sample is 1.7% and 6.1%, respectively, and shows good linearity over the spiking range (Figure 3).

Bromate Sample	Average (n = 9)	σ	%RSD
1.0 ppb standard	1657	29	1.7
0.5 ppb standard	880	40	4.6
0.2 ppb standard	357	18	5.1
0.1 ppb standard	164	18	11.0
Tap water + 1.0 ppb	605	37	6.7

Table 3. Reproducibility (n=9) of the SIR peak area for standard bromate solutions and a 1 ppb spiked sample of tap water. The bromate concentration of the injected samples was 0.2 ppb (equivalent to 1 ppb undiluted sample).

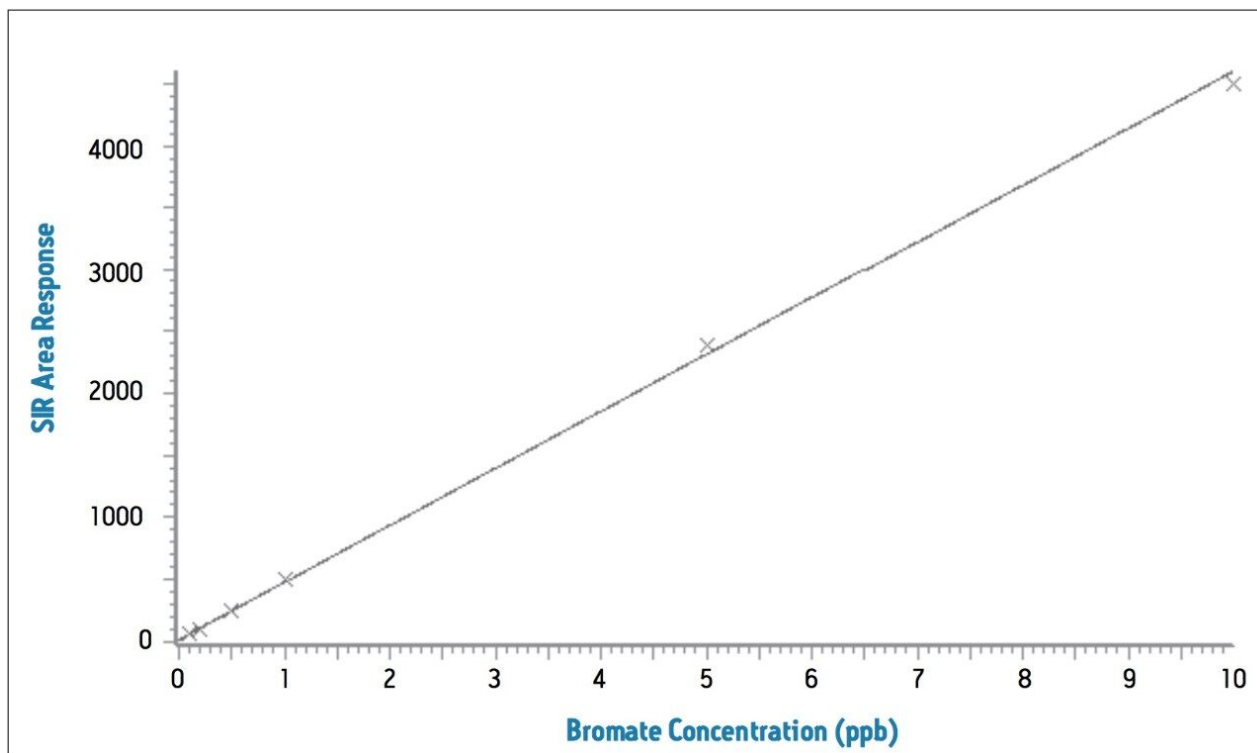


Figure 3. Calibration curve for bromate (0.1 ppb - 10 ppb).

Conclusion

The sensitivity offered by the HILIC-LC/MS method was found to be highly effective for the trace level detection of bromate ions in tap water at levels near 0.1 ppb without the need for post-column derivatization of the sample. This application demonstrates the feasibility of analyzing bromate ions in tap water using the HILIC separation mode and flexible LC-MS instrumentation that already exists in many laboratories worldwide.

References

1. WHO (2005) Background document for Development of WHO Guidelines for Drinking-Water Quality: Bromate in Drinking Water. World Health Organization, WHO/SDE/WSH/05.08/78.

2. Japan Waterworks Act Water Quality Standard.

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