Application Note AN-U-049

Disinfection byproducts in water

Trace bromate analysis with IC-UV/VIS according to ISO 11206

Safe drinking water is essential for human life and is also quite often a privilege. Whether the source is surface or groundwater, the presence of pathogenic bacteria, poor taste, and a detectable odor requires disinfection processes to guarantee the appropriate quality for drinking water purposes [1,2]. Chlorination was introduced at the beginning of the 20th century as a standard water treatment process. This process helped to protect human health and reduce mortality from waterborne microbial infections and diseases [3,4]. However, the chlorination process forms harmful byproducts (e.g., trihalomethanes) from the reaction of chlorine with organic water components.

To avoid such reactions, modern disinfection processes use strong oxidants like permanganate or ozone. However, if the water contains bromide, ozonation and oxidation lead to the formation of bromate, a potential carcinogen. Therefore, bromate is regulated at a maximum of 10 µg/L in drinking water and requires regular monitoring to ensure the water quality. Ion chromatography (IC) provides a robust, efficient, and sensitive technique to monitor bromate even at trace levels in line with ISO 11206 and EPA Method 317. The specific post-column reaction (PCR) of bromate-forming triiodide enables the determination of concentrations as low as 1 µg/L – even in carbonate- and chloride-rich matrices.

SAMPLES AND SAMPLE PREPARATION

Spiked and unspiked tap water (Zurich, Switzerland) and mineral water (Evian) samples were analyzed to test the reliability and validity of this method. In addition to spiking Swiss tap water samples (0.2 and 1 µg/L bromate), bromate traces in carbonate- and chloride-rich matrices were also investigated to show the absence of interferences. For these tests, 0.2 µg/L bromate was added to Evian water (357 mg/L carbonate and 5 mg/L chloride) and to spiked ultrapure water (UPW containing 100–500 mg/L carbonate and 5–100 mg/L chloride).

EXPERIMENTAL

IC separation with post-column reaction (PCR) and subsequent UV/VIS detection provides a dedicated method to determine very low concentrations of bromate in water. After separation of bromate from matrix components with an analytical column, triiodide is formed via the PCR (**Reaction 1**). This reaction is very specific, enabling the sensitive determination of bromate via triiodide detection at a wavelength of 352 nm. Due to the high selectivity, the influence of interferences is significantly reduced. This allows trace bromate detection even in matrices high in carbonate and chloride.
The setup is simple (930 Compact IC Flex, 947 Professional UV/VIS detector, a sample processor, and a Dosino for precise addition of reagents) and conforms with **US EPA Method 317** and **DIN EN ISO 11206**. The separation of bromate from other anions is achieved using the **Metrosep A Supp 17 - 250/4.0** column and a sulfuric acid–molybdate eluent. The eluent, which contains molybdate as a catalyst for the PCR, is continuously pumped through the column. Before entering the reactor block, potassium iodide (**Reaction 1**) is added by a Dosino for triiodide formation and its subsequent UV/VIS detection. The calibration of this setup ranged from 1–20 µg/L using a 1000 µL injection volume.

$$BrO_3^- + 3\,I^- + 3\,H^+ \xrightarrow{Mo(VI)} 3\,HOI + Br^- \quad (a)$$
$$3\,HOI + 3\,I^- + 3\,H^+ \longrightarrow 3\,I_2 + 3\,H_2O \quad (b)$$
$$3\,I_2 + 3\,I^- \longrightarrow 3\,I_3^- \quad (c)$$
$$BrO_3^- + 9\,I^- + 6\,H^+ \xrightarrow{Mo(VI)} \boxed{3\,I_3^-} + Br^- + 3\,H_2O \quad (d)$$

UV 352 nm

Reaction 1. Reaction path of bromate with iodine and molybdate as catalyst in acidic solution forming triiodide as described in the triiodide methods in US EPA 317 and ISO 11206. The reaction occurs post-column prior to the spectral detection of triiodide at 352 nm.

However, if bromate needs to be determined in very low concentrations **below 1 µg/L** and especially **next to high concentrations of chloride or carbonate**, the setup can be easily modified to meet these requirements. Also in this case, the PCR and subsequent UV/VIS detection is used to guarantee a selective bromate determination. For the analytical separation of bromate in a complex matrix, the high-capacity column **Metrosep A Supp 10 - 100/4.0** and an alkaline bicarbonate eluent is used. To provide more baseline stability and the best reaction conditions, **chemical suppression** is used prior to adding the PCR reagents (**Figure 1**). Using an injection volume of 1325 µL in this case allows reliable detection of bromate from **0.05–5 µg/L**.

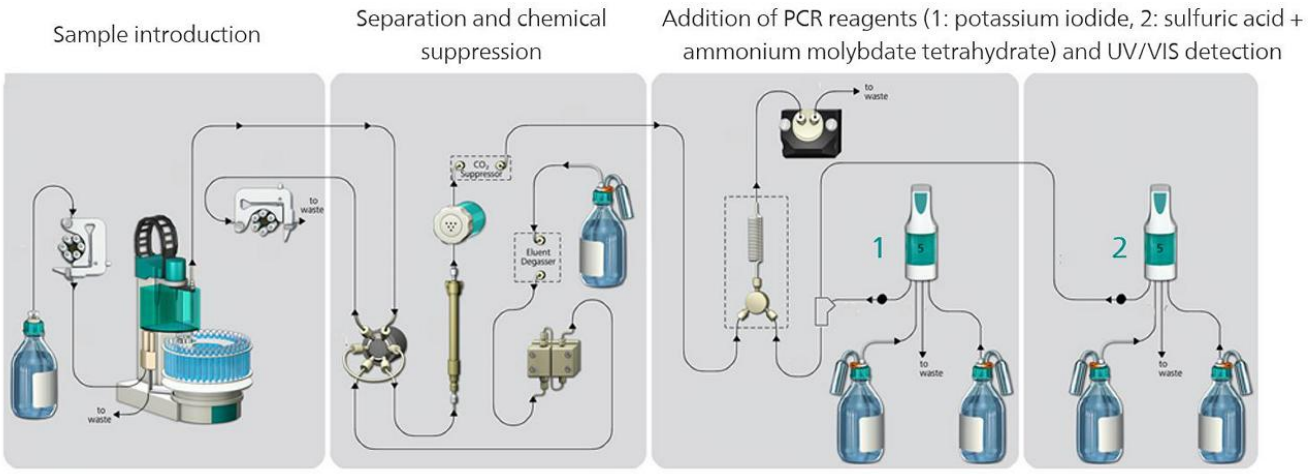


Figure 1. IC system configuration for the determination of trace bromate concentrations in water with the Metrosep A Supp 10 column, chemical suppression, PCR, and UV/VIS detection.

RESULTS AND DISCUSSION

Figure 2A shows the results of the determination of bromate with the Metrosep A Supp 17 column and acidic eluent. With the simple setup (i.e., one Dosino for reagent addition) and a 1000 µL injection volume, bromate concentrations from 1–20 µg/L can be determined with high accuracy.

The presence of chloride or carbonate in the sample matrix can impact the retention time and peak shape of bromate. To overcome this, the high capacity Metrosep A Supp 10 column efficiently separates bromate from these matrix components before PCR and UV/VIS detection. Thus the detection of bromate down to 0.05 µg/L in matrices containing up to 200 mg/L carbonate and 100 mg/L chloride is possible (Figure 2B). The retention time for bromate in both setups is comparable, eluting in less than 10 minutes, which permits analysis of at least 100 samples per day.

Sample spike recoveries for artificially prepared samples with high-matrix UPW and for Swiss tap water ranged from 85–105%. The tap water samples contained some bromate (2.3 µg/L). However, no bromate was detected in the carbonate- and chloride-rich Evian samples. Trace level spikes of 0.2 µg/L were determined with a recovery of 85%.

A wavelength of 352 nm was chosen for the UV/VIS detection. This decreases the baseline noise because some species from the eluent and samples do not absorb at that wavelength.

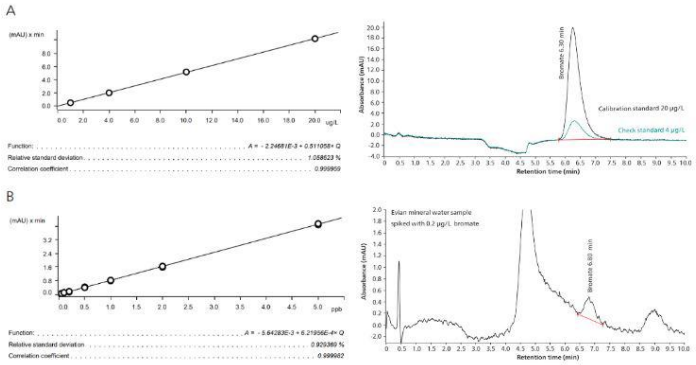


Figure 2. Bromate determination according to US EPA 317 and ISO 11206 using the Metrosep A Supp 17 column (A) and in carbonate-rich matrices with the Metrosep A Supp 10 column (B). The calibration for the simple setup with the Metrosep A Supp 17 column (A) ranged from 1–20 µg/L bromate. The chromatogram shows the UV/VIS absorbance from bromate standards of 20 µg/L and 4 µg/L. The bromate calibration at trace levels using the Metrosep A Supp 10 column (B) ranged from 0.05–5.0 µg/L (standard bracketing). The chromatogram shows a spiked Evian mineral water sample (0.2 µg/L bromate in the carbonate- and chloride-rich matrix, spike recovery of 85%).

CONCLUSION

Water disinfection (e.g., chlorination) is a necessary process to protect us from disease. Unfortunately, it can come with disadvantages like an unpleasant chemical smell and formation of dangerous disinfection byproducts (e.g., carcinogenic trihalomethanes). Although modern technologies like ozonation impart better water flavor, carcinogenic byproducts such as bromate or haloacetic acids can be produced if bromide or other halogens are present in the source water before treatment. Therefore, monitoring drinking water for such disinfection byproducts is of great importance. EU and US EPA regulations set the maximum allowable bromate concentration in drinking water at 10 µg/L. The EPA has attempted to stipulate even lower bromate concentration limits with a maximum contaminant goal of zero for drinking water [5]. For bottled natural mineral and spring waters disinfected by ozone, the EU has reduced the limit of bromate to 3 µg/L [6]. Regarding wastewater treatment, bromate formation can become a critical threat for the environment, as treated effluent directly enters rivers and other water sources. Sensitive bromate detection is essential and requires flexibility to be applicable for various matrices as well as the low detection limits.

IC with PCR and UV/VIS detection offers a specific and sensitive method for bromate analysis in line with the requirements of EPA Method 317 and ISO 11206. As this technique is highly flexible, drinking water can be analyzed just as easily as water samples with a high matrix load. Only minor adjustments are necessary for the separation column and the PCR reagents. Additionally, the technique is automated, allowing efficient analysis and a high sample throughput ideal for routine operation. The complete setup can be upgraded with inline sample preparation techniques (e.g., ultrafiltration or dilution), further increasing the method efficiency and broadening the application scope to more complex sample matrices.

REFERENCES

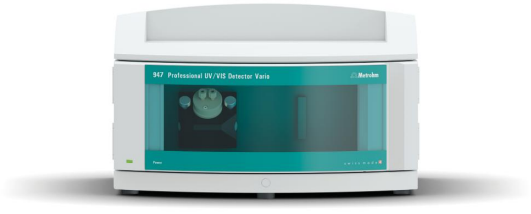
1. Boorman, G. A.; Dellarco, V.; Dunnick, J. K.; et al. Drinking Water Disinfection Byproducts: Review and Approach to Toxicity Evaluation. *Environmental Health Perspectives* **1999**, *107*, 207–217. https://doi.org/10.2307/3434484.
2. Wille, A.; Proost, R.; Steinbach, A. Spurenbestimmung von Bromat in Wasser. *Österreichische Wasser- und Abfallwirtschaft* **2010**, *62* (11/12), 27–30.
3. Mughal, F. Chlorination of Drinking Water and Cancer: *A Review. J Environ Pathol Toxicol Oncol* **1992**, *11* (5–6), 287–292.
4. Evans, S.; Campbell, C.; Naidenko, O. V. Analysis of Cumulative Cancer Risk Associated with Disinfection Byproducts in United States Drinking Water. *Int J Environ Res Public Health* **2020**, *17* (6), 2149. https://doi.org/10.3390/ijerph17062149.
5. Bonacquisti, T. P. A Drinking Water Utility's Perspective on Bromide, Bromate, and Ozonation. *Toxicology* **2006**, *221* (2–3), 145–148. https://doi.org/10.1016/j.tox.2006.02.010 .
6. European Commission. Commission Directive 2003/40/EC. Establishing the List, Concentration Limits and Labelling Requirements for the Constituents of Natural Mineral Waters and the Conditions for Using Ozone-Enriched Air for the Treatment of Natural Mineral Waters and Spring Waters. *Off J of EU 2003*.

Internal references: AW IC CH6-1398-052020; AW IC AE-0126-112020

CONTACT

メトロームジャパン株式会社
143-0006 東京都大田区平和島6-1-1
null 東京流通センター アネックス9階
metrohm.jp@metrohm.jp

CONFIGURATION



947 Professional UV/VIS Detector Vario SW

インテリシェントな単一波長検出器　947 Professional UV/VIS Detector Vario SW は、紫外線や可視光線範囲でアクティフな物質を安全かつ確実に検出することかてきます。波長を一つ選択することかてきます。

Metrosep A Supp 17 - 250/4.0

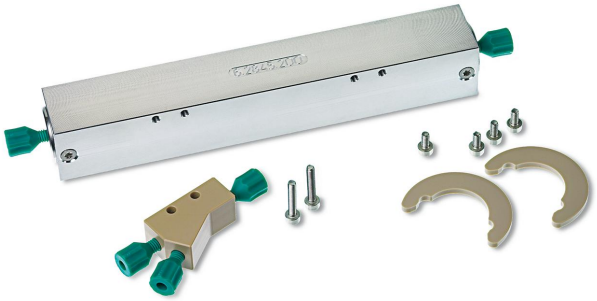
Metrosep A Supp 17 - 250/4.0ては高い分離性能と高いコストハフォーマンスか組み合わされており、カラムオーフンを必要としません。使用されているホリスチレン/シヒニルヘンセンの基本材料により、カラムの長期耐用を保証します。このカラムては、複雑な分離課題を解決することかてきます。

930 Compact IC Flex Oven/Deg

930 コンハクト IC Flex Oven/Deg は**カラムオーフン**と内蔵式**脱気装置**を備えた**サフレッションの無い**インテリシェントコンハクトIC装置てす。この装置は任意の分離メソットおよび検出メソットによって使用することかてきます。

典型的な使用領域:

- 電気伝導度検出器によるサフレッション無しの陰イオンおよび陽イオンの測定
- UV/VIS検出器またはアンヘロメトリック検出器によるシンフルな使用



Reactor complete to 6.2845.100

Spare reactor for the reactor plate

Metrosep A Supp 10 - 100/4.0

Metrosep A Supp 10 - 100/4.0分離カラムは、粒子径たった4.6 µmの大容量ホリスチレン・シヒニルヘンセン共重合体をヘースとしています。このカラムの特徴は、理論段数と選択性の高さてす。そのため、溶離液に有機性修飾剤を添加しなくても、亜硫酸塩と硫酸塩を確実に分離することかてきます。カラム温度、流量、溶離液の構成成分における柔軟性の高さか、この特性を補完します。

頑丈な造り、極めて高いコストハフォーマンス、非常に優れた分離性能、適度なクロマトクラフィーの分析時間により、Metrosep A Supp 10 - 100/4.0は汎用的に使用可能な陰イオンカラムてす。