



Application Note AN-U-049

水中的消毒副产物

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

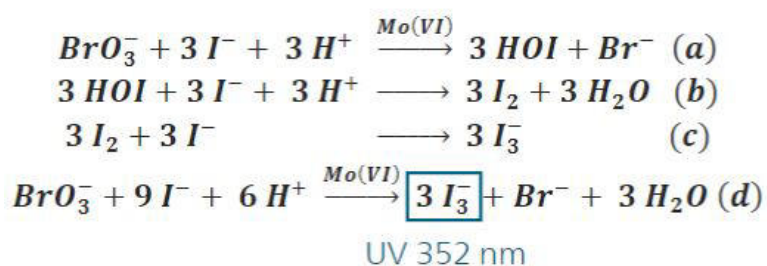
Spiked and unspiked tap water (Zurich, Switzerland) and mineral water (Evian) samples were analyzed to test the reliability and validity of this method. In addition to spiking Swiss tap water samples (0.2 and 1 µg/L bromate), bromate traces in carbonate- and chloride-rich matrices were also investigated 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.



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**.

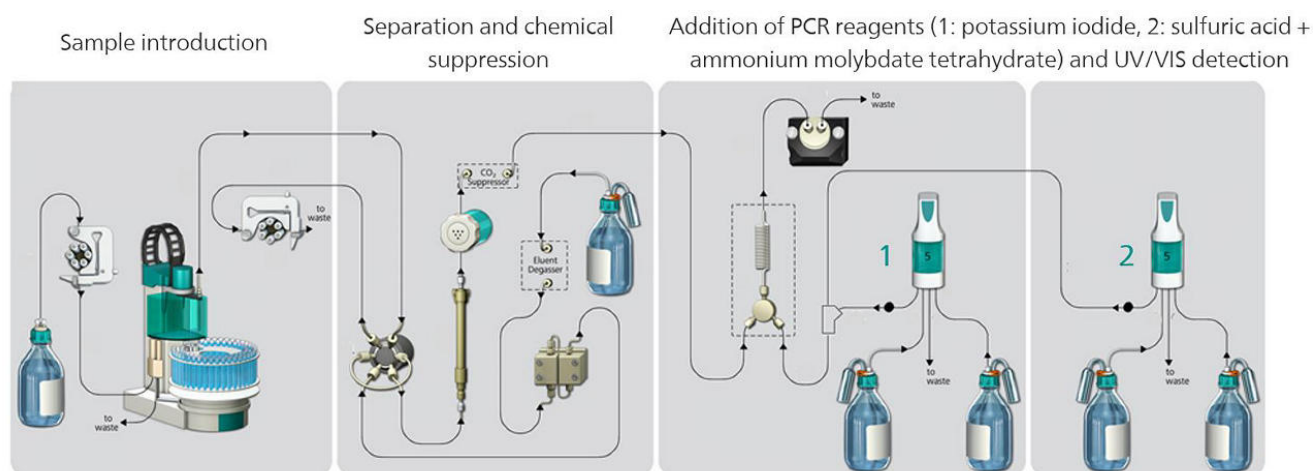


Figure 1. IC system configuration for the determination of trace bromate concentrations in water with the Metrosep A Supp 10 column, chemical suppression, PCR, and UV/VIS detection.

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 $\mu\text{g/L}$ 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 $\mu\text{g/L}$ 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 $\mu\text{g/L}$). However, no bromate was detected in the carbonate- and chloride-rich Evian samples. Trace level spikes of 0.2 $\mu\text{g/L}$ 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.

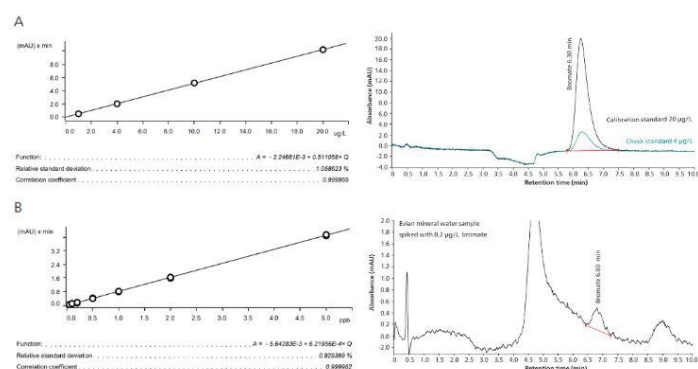


Figure 2. Bromate determination according to US EPA 317 and ISO 11206 using the Metrosep A Supp 17 column (A) and in carbonate-rich matrices with the Metrosep A Supp 10 column (B). The calibration for the simple setup with the Metrosep A Supp 17 column (A) ranged from 1–20 µg/L bromate. The chromatogram 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

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Internal references: AW IC CH6-1398-052020;

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CONTACT

Metrohm Taiwan Ltd.
開封街二段 46 號 5 樓
108 台北市

info@metrohm.com.tw

CONFIGURATION



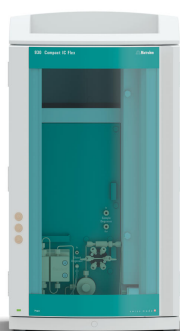
947 Professional UV/VIS Detector Vario SW

智能单波长 检测器, 947 Professional UV/VIS Detector Vario SW, 可对紫外光或可见光区域内的活性物质进行安全可靠的定量操作。可选择一种波长。



Metrosep A Supp 17 - 250/4.0

Metrosep A Supp 17 - 250/4.0 是高分离率和出色性价比的组合,不需要柱加热炉。所使用的基本材料聚苯乙烯/二乙烯基苯可以确保分离柱的长使用寿命。在该柱上可以完成复杂的分离任务。

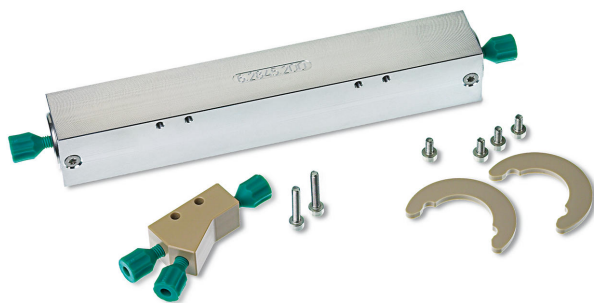


930 Compact IC Flex Oven/Deg

930 Compact IC Flex Oven/Deg 是智能型带柱加热炉、无抑制的 Compact IC 仪器,并且内置脱气装置。该仪器可使用各种分离和检测方法。

典型的应用范围:

- 阴离子和阳离子测定,无抑制的电导检测
- 使用 UV-VIS 或安培检测的简单应用



6.2845.100

板式反应器的备用反应器



Metrosep A Supp 10 - 100/4.0

Metrosep A Supp 10 - 100/4.0 分离柱基于高容量聚苯乙烯/二乙烯基苯共聚物,其颗粒大小仅为 4.6 μm 。该分离柱具有基数高、选择性大的特点。无需添加有机改性剂便可在淋洗液中可靠地分离亚硫酸盐和硫酸盐。此外,该分离柱还具有柱温、流速和淋洗液组成灵活性高的属性。

它结构稳固、性价比优越且分离效率高,同时其所需的色谱分析时间适中,这些特点使 Metrosep A Supp 10 - 100/4.0 成为可通用的离子分离柱。