Influence of pH, temperature and molybdate concentration on the performance of the triiodide method for the trace-level determination of bromate (EPA 326)

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Metrohm Ion analysis

Ion Chromatography

Introduction

The disinfection of drinking water destroys pathogenic microorganisms and removes compounds causing bad taste and/or odor. Most public water suppliers still disinfect their drinking water with chlorine. However, apart from its unpleasant taste, chlorine reacts with the ubiquitous organic compounds and forms harmful disinfection by-products (DBP) such as the potentially carcinogenic trihalomethanes. In order to control the formation of these DBPs several strong oxidants, including permanganate and ozone, are used. While ozone is one of the most efficient oxidants, it also oxidizes the naturally occurring bromide to bromate. Since the International Agency of Research on Cancer has classified bromate as a potential carcinogen, bromate levels in drinking and mineral water have to be controlled. The United States Environmental Protection Agency (US EPA) and the European Union currently set a maximum bromate concentration of 10 ppb in drinking water. For mineral waters the pertinent regulations stipulate a limit of 3 ppb.

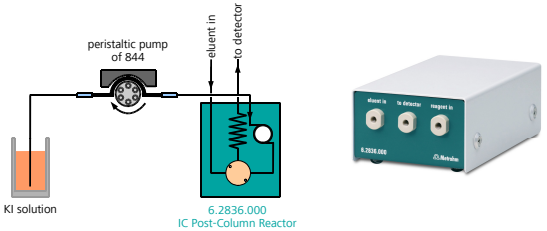
To satisfy the regulatory requirements, the determination of bromate requires very sensitive analytical methods. The most widely used methods for the quantitation of bromate are based on ion chromatography. MS detection and UV/VIS detection after post-column reaction (PCR) are the most sensitive detection modes. The post-column derivatization of bromate with o-dianisidine (ODA) according to EPA method 317 achieves a detection limit of approximately 0.2 ppb, but the potential carcinogen ODA is a major drawback. The alternative EPA method 326 stipulates post-column reaction (PCR) of bromate with the less harmful iodide, achieving a detection limit for bromate of less than 50 ng/L (= 50 ppt).

The triiodide method

The analysis is based on the Environmental Protection Agency EPA method 326. In this post-column derivatization method, bromate – aided by the catalytic effect of amonium molybdate – oxidizes iodide to triiodide in an acidic medium. The produced triiodide molecule can be detected at high sensitivity in the UV spectrum at a wavelength of 352 nm. The method described here is exclusively suited for the determination of bromate, iodate and chlorite. Any additional water constituents have to be determined separately.

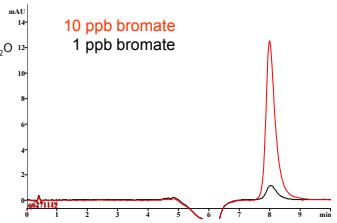
$$BrO_3^- + 3\,I^- + 3\,H^+ \rightarrow 3\,HOI + Br^-$$
$$3\,HOI + 3\,I^- + 3\,H^+ \rightarrow 3\,I_2 + 3\,H_2O$$
$$3\,I_2 + 3\,I^- \rightarrow 3\,I_3^-$$
$$BrO_3^- + 9\,I^- + 6\,H^+ \rightarrow Br^- + 3\,I_3^- + 3\,H_2O$$

The peristaltic pump transfers the KI solution to the PCR where it is mixed with the eluent. The generated triiodide is subsequently conveyed to the UV/VIS detector.

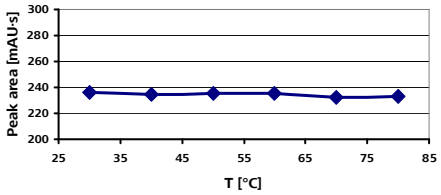


Chromatographic standard conditions

Column:	Phenomenex Star Ion A300 HC
Eluent:	100 mmol/L H_2SO_4 and 0.045 mmol/L $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$
Flow:	1 mL/min
Loop:	1000 µL
PCR reagent:	0.26 mol/L KI
PCR temperature:	25 °C
PCR flow rate:	0.25 mL/min
PCR mixing volume:	0.4 mL
Wavelength:	352 nm
Standard:	10 ppb bromate



In the following the influence of the temperature (1), the molybdate (2), the iodide (3) as well as the sulfuric acid concentration (4) on the performance of the triiodide method is investigated. If not differently cited the indicated results were obtained under the above-mentioned chromatographic conditions.

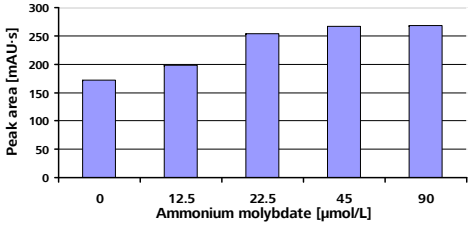


PCR temperature: 30, 40, 50, 60, 70 and 80 °C

The variation of temperature only slightly affects the response of the «bromate peak». Thus post-column derivatization can be performed at room temperature.

(2) Influence of molybdate concentration

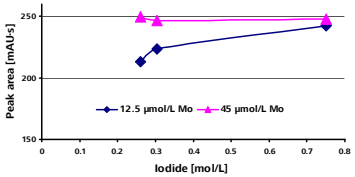
Different molybdate concentrations in the eluent were used to evaluate the response of the 10 ppb bromate standard.



Eluent: 100 mmol/L H_2SO_4 and 0, 12.5, 22.5, 45 and 90 µmol/L $(NH_4)_6Mo_7O_{24} \cdot 4\,H_2O$

No significant enhancement in sensitivity was observed for concentrations exceeding 45 µmol/L ammonium molybdate. Lower concentrations result in a loss of sensitivity. Without any molybdate ions the post column reaction proceeds to 70%.

(3) Influence of iodide concentration

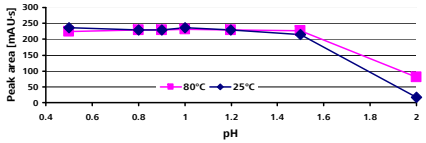


PCR reagent: 0.26, 0.305 and 0.75 mol/L KI · 4 H_2O

In the range investigated the variation of the iodide concentration has no significant effect on the sensitivity of the triiodide method.

(4) Influence of sulfuric acid concentration

By varying the concentration of sulfuric acid the influence of the pH on the response of the «bromate peak» can be evaluated. The pH values after the mixing of eluent and reagent in the PCR were calculated as a function of the sulfuric acid concentration and plotted versus the response of the «bromate peak».



x (H_2SO_4, eluent) (mmol/L)	calculated pH in the detector	measured pH of the eluent
381.0	0.5	0.56
185.0	0.8	0.81
144.0	0.9	0.91
122.0	1.0	1.01
67.6	1.2	1.18
30.8	1.5	1.43
8.0	2.0	1.88

Eluent: x mmol/L H_2SO_4 and 45 µmol/L $(NH_4)_6Mo_7O_{24} \cdot 4\,H_2O$

No sensitivity improvement was attained for a pH below 1.5. Above this treshold value the response of the «bromate peak» decreases rapidly. Additionally, increasing pH results in increasing retention times, thus extending analysis time.

Summary

Ozonolysis of bromide-containing drinking water results in the formation of bromate, a suspected carcinogen. Bromate is effectively detected at trace-level by ion chromatography followed by post column derivatization with iodide, according to the US EPA Method 326. In this work the derivatization reaction in the post-column reactor was optimized for sensitivity. The bromate response was neither dependent on the investigated reaction temperatures (30…80 °C) nor on the examined iodide concentrations (0.26…0.75 mol/L KI). In contrast, varying molybdate and sulfuric acid concentrations had a significant influence on method sensitivity. Increasing sulfuric acid concentrations (pH < 1.5) improved sensitivity and shifted the «bromate peak» to shorter retention times. Ammonium molybdate concentrations of 45 and 90 µM in the eluent provided the best results. Applying the optimum conditions for the triiodide method, a detection limit for bromate of less than 50 ng/L (= 50 ppt) is attained.

Literature

Kitamaki Y. and Takeuchi T., Cyclodextrin-aided determination of iodate and bromate in drinking water by microcolumn ion chromatography with precolumn enrichment, Analytical Sciences **20** (2004) 1399-1402.

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