Bromate in Drinking Water – Which Method to Use in Ion Chromatography

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Determination of bromate in drinking water using ion chromatography with suppressed conductivity detection and two different post column reaction procedures with UV/Vis detection.

Introduction

Bromate in drinking water is a by-product of water purification by ozone and chlorination. This anion is suspected to be harmful and therefore has to be monitored in water quality control. The concentrations usually encountered are in the low ppb range and below, that is close to the detection limit of ion chromatography with suppressed conductivity detection. As an alternative, ion chromatography with post column reaction and optical detection may be used. The two methods known are:

- post column reaction with o-dianisidine (as described in EPA 317.0)
- post column reaction with iodide (as described in EPA 326.0)

Examples of each method are given in this paper.

Instrumentation

The analyses have been performed on a Metrohm Advanced IC System (Metrohm Ltd., Herisau, Switzerland) comprising a 818 IC Pump, 820 IC Separation Center with one injector and the Metrohm Suppressor Module (MSM), 819 IC Detector, 833 IC Liquid Handling Pump Unit, 830 IC Interface and Metrodata IC Net 2.3. For the post column reaction the following equipment has been added: 6.2836.000 Post Column Reactor (Figure 1), 833 IC Liquid Handling Pump Unit, 782 Column Thermostat (for the o-dianisidine method) and a Lambda 1010 UV/Vis detector (Bischoff Analysentechnik, Leonberg, Germany).

Figure 1: Metrohm Post Column Reactor.

Experimental Conditions

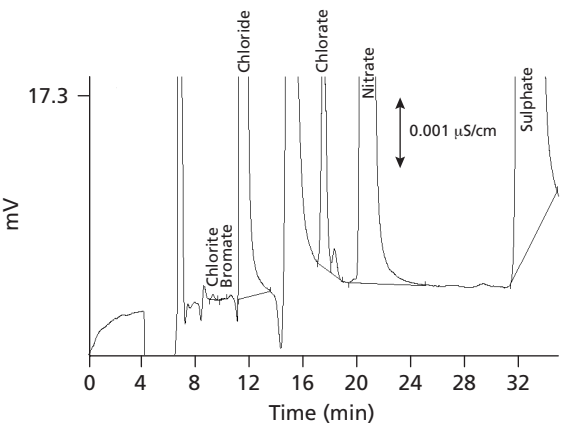
Drinking water samples and standard solutions were injected directly.

Chromatographic Conditions

Suppressed conductivity detection (Figure 2):

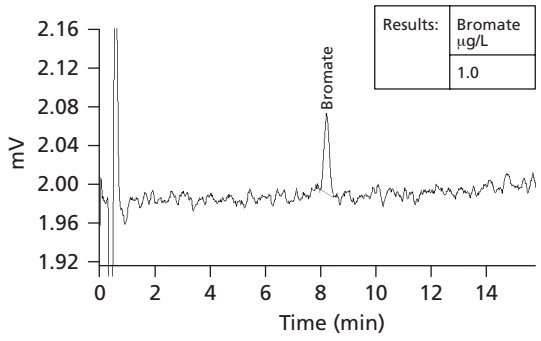
Column:	6.1006.530 Metrosep A SUPP 5 – 250
	6.1005.340 Metrosep A SUPP 1 Guard
Eluent:	1.0 mmol/L sodium hydrogen carbonate
	3.2 mmol/L sodium carbonate
Suppressor:	MSM, 50 mmol/L H2SO4
Flow:	0.7 mL/min
Injection Volume:	100 µL

Figure 2: Chromatogram and results table taken from Metrohm IC Application Note S-170, "Oxyhalides besides standard anions in mineral water." Conditions as given in text.



Results:	Chlorite µg/L	Bromate µg/L	Chloride	Chlorate µg/L	Bromide µg/L	Nitrate	Sulphate
	1.17	0.623	n.q.	26.7	7.84	n.q.	n.q.

Figure 3: Chromatogram and results table taken from Metrohm IC Application Note S-169, "Bromate with post column reaction (o-dianisidine method)." Conditions as given in text.



o-Dianisidine post column reaction method (Figure 3):

Column:	6.1006.530 Metrosep A SUPP 5 – 250
Eluent:	1.0 mmol/L sodium hydrogen carbonate 3.2 mmol/L sodium carbonate
Suppressor:	Metrohm Suppressor Module (MSM, 50 mmol/L H2SO4)
Flow:	0.7 mL/min
Temperature:	75 °C
Injection Volume:	100 µL
PCR Reagent:	80 mL/L nitric acid (70%), 5 g/L potassium bromide, 500 mg/L 3,3' dimethoxidine dihydrochloride (o-dianisidine) 20 % methanol
PCR Flow:	0.5 mL/min
Detection:	450 nm

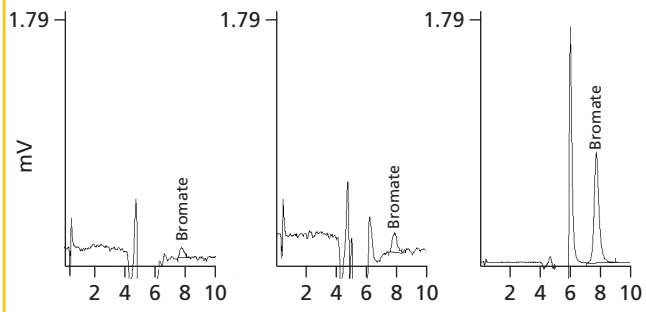
Triiodide post column reaction method (Figure 4):

Column:	6.1005.110 Bromate column
Eluent:	100 mmol/L sulfuric acid, 45 µmol/L ammonium molybdate (catalyses the oxidation of iodide)
Flow:	1.0 mL/min
Injection Volume:	1000 µL
PCR Reagent:	0.26 M potassium iodide (puriss. p.a.)
PCR Flow:	0.24 mL/min
Detection:	352 nm

Results

In terms of instrumentation and ease of use, IC with suppressed conductivity detection is the most straightforward setup. It also allows to determine the other oxyhalides as well as the standard anions in the same run (Figure 2). Due to the very high selectivity of the Metrosep A Supp 5–250 column, the bromate is well separated from chlorite and chloride as well as from the organic acids. Detection limits for bromate are in the range of 0.5 µg/L. The chromatogram and results table are shown in Figure 2. The bromate concentration in this drinking water sample is close to the limit of detection. In instances where a higher selectivity is needed or bromate is the only ion of interest, the two PCR methods are the methods of choice.

Figure 4: Chromatogram and results table taken from Metrohm IC Application Note N-47, "Bromate in drinking water with post column reaction (triiodide method)." Conditions as given in text.



Results:	Bromate (LOD) µg/L	Bromate (Herisau) µg/L	Bromate (UK) µg/L
	0.050	0.134	6.31

The o-dianisidine method is fairly well known, but requires toxic chemicals at elevated temperatures. The detection limit is higher (>1 µg/L) than that of the method with conductivity detection. The chromatogram and results table are shown in Figure 3.

The triiodide method, on the other hand, works at room temperature with ordinary chemicals. The method as described in EPA Method 326.0 uses an alkaline eluent which has to be acidified by chemical suppression. The PCR reagent is an acidic mixture of potassium iodide and a catalytic amount of molybdate. This solution is not very stable and has to be made up rather frequently. The application performed in this paper uses an acidic eluent already containing the catalyst for the reaction as well as a common and very stable iodide solution as the PCR reagent. The acidic eluent renders the suppressor device obsolete whereas the separation of acid and catalyst from the iodide markedly improves the stability of the solutions used. The special high capacity bromate column allows to inject 1 mL of sample, which yields a ten times lower detection limit (50 ng/L) than the above methods. Chromatograms of a standard solution at the limit of detection as well as of two drinking water samples are given in Figure 4.

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