Trace Level Analysis of Perchlorate and Bromate in Various Water Matrices using Suppresed Ion Chromatography

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Ion Chromatography

Summary

- Perchlorate salts are used as "rocket fuel" in electroplating and other industries; yet, in 1999 (C&EN article) it was scientifically proven to inhibit the human thyroid gland's absorption of iodine — which, in turn, may cause thyroid-related diseases. Perchlorate detection/analysis in varying water matrices can be a challenge. How do we overcome the obstacles?
- Bromide is ubiquitously found in drinking water. It is introduced into source water either by contact with bromide-containing soils or seawater having a high bromide content. Bromide converts into bromate during water disinfection, for example by ozonation. Bromate can also enter drinking water when sodium hypochlorite is used as disinfectant, as it is a common impurity in sodium hypochlorite production. The International Agency for the Research of Cancer has determined that bromate is a possible carcinogen. Therefore, monitoring of bromate and its precursor bromide in drinking water is required.

While much research has been done to develop methods to analyze for bromate and bromide including several Environmental Protection Agency (EPA) methods, most of this work requires specialized instrumentation such as two-dimensional ion chromatography, expensive sample preparation or post-column reactions techniques.

This work describes a method for determining the concentration of bromate and bromide ions at ppb levels in drinking water using a simple isocratic IC with loop injection. Bottled water and tap water samples were used to validate the method. Spiked water samples were used to verify quantification.

➢ Metrohm 940 Professional IC Anion – MSMHC / MCS

Trace level Perchlorate determination is performed by USEPA method 314.0 – Suppressed Conductivity Detection.

In this method QA/QC section mandates to test for Maximum Conductivity Threshold (MCT) study. This study is designed to test column capacity and maximum ion loading without distorting peak symmetry at lowest possible concentration of Perchlorate in matrix of 3000 parts per million Total Dissolved Solids (TDS). Hence, as Matrix ions specially Chloride, Carbonate and Sulfate are increased, it becomes difficult to measure Perchlorate at trace level by Ion Chromatography and suppressed conductivity detection.

This poster presentation demonstrate trace level (1 parts per billion) Perchlorate analysis in High Ionic Matrix (3000ppm TDS) where 3000ppm TDS = 1000ppm each of Chloride, Carbonate and Sulfate ions. Sodium Salt of these ions was used to prepare standards.

Sample preparation

Typical samples may be in various phases (aqueous and organics), solid material like mud and particles. It may require centrifugation, filtration etc. before the ion analysis. Metrohm provides automated in-line sample filtration device that eliminates use of syringe filters for these type of samples.

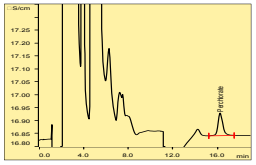
Perchlorate Analysis

a) Suppressed Ion Chromatography (Perchlorate with Dual4 column)

USEPA Method 314.0 enhanced:

Anionic functionalized Monolith column specially designed for Perchlorate analysis

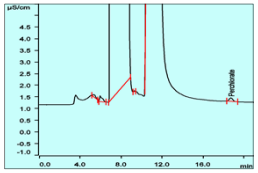
Column: Metrosep Dual4 - 100
Column temp.: 45 °C
Eluent: 5.5 mmol/L LiOH + 10mM 4-Cyanophenol
Flow: 1.5 mL/min
Loop: 1000 µL
Detection: Sequential Suppressed Conductivity



b) Suppressed Ion Chromatography (Perchlorate with ASUPP7 column)

Confirmation column – High Resolution Anion Exchange column

Column: Metrosep ASUPP7 - 250/4.0
Column temp.: 45 °C
Eluent: 10.5 mmol/L Na_2CO_3 + 25% Acetonitrile
Flow: 0.7 mL/min
Loop: 1000 µL
Detection: Sequential Suppressed Conductivity



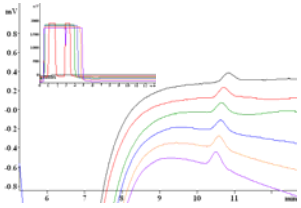
USEPA Method 314.0 – MCT study data

Metrosep Dual 4 – 100 mm

1 Perchlorate in Reagent Water

50 ppm Cl^-, HCO_3^-, SO_4^{2-}
250 ppm Cl^-, HCO_3^-, SO_4^{2-}
500 ppm Cl^-, HCO_3^-, SO_4^{2-}
750 ppm Cl^-, HCO_3^-, SO_4^{2-}
1'000 ppm Cl^-, HCO_3^-, SO_4^{2-}

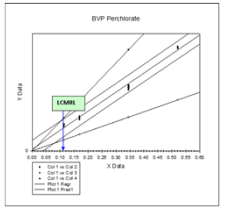
LiOH/p-cyanophenol; 5/12 mM; 1.75 mL/min; 1000 µL



Precision, Recovery and LCMRL

Conc. [ppb]	Mean [n=7]	SD	RSD [%]	Recovery [%]
0.113	0.133	0.0041	3.1	118
0.17	0.168	0.0065	3.8	99
0.345	0.323	0.0078	2.4	94
0.521	0.529	0.0033	0.6	102
0.95	0.959	0.0313	3.3	101
1.976	1.984	0.0772	3.9	100

Lowest Concentration Method Reporting Level: 0.113 ppb
(calculated by the USEPA)

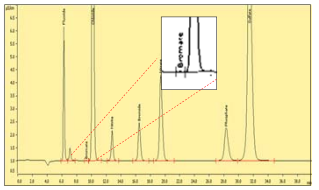


Bromate Analysis

The International Agency of Research on Cancer (IARC) has classified bromate as a possible carcinogen. Based on renal cell tumors in rats, a concentration of 3 µg/L bromate corresponds to an excess lifetime cancer risk of $1 \cdot 10^{-5}$. Due to the difficulty of bromide and bromate removal from water, combined with the limitations of available analytical techniques, the World Health Organization (WHO) recommended a guideline value of 25 µg/L bromate. This value is associated with an excess lifetime cancer risk of $7 \cdot 10^{-5}$.

The United States Environmental Protection Agency (U.S. EPA) has set a maximum contaminant level (MCL) of 10 µg/L bromate in drinking water and as of June 2008, the European Community lowered the MCL to 3 µg/L bromate. The U.S. EPA maximum contaminant level goal (MCLG) is zero ppb bromate.

Column: Metrosep ASUPP7- 250/4.0 + ASUPP16 Guard
Column temp.: 45 °C
Eluent: 3.5 mmol/L Sodium Carbonate
Flow: 0.7 mL/min
Loop: 100 µL
Detection: Sequential Suppressed Conductivity



MDL Study

Sample	Bromate	Bromide
	[µg/L]	
MDL 1-1	0.551	2.502
MDL 1-2	0.534	2.511
MDL 1-3	0.542	2.504
MDL 1-4	0.549	2.549
MDL 1-5	0.555	2.498
MDL 1-6	0.539	2.501
MDL 1-7	0.549	2.532
Mean value	0.546	2.514
SD	0.0074	0.0193
MDL	0.023	0.060

Conclusion:

In 2004, Metrohm developed and provided functionalized monolith column for Perchlorate analysis. Even though Perchlorate is inorganic anion, it behaves like organic molecule (hydrophobic), hence monolith column provides platform to wash off hydrophilic matrix ions (TDS) and retains Perchlorate for analysis.

Bromide in itself is a natural and harmless ion, ubiquitously found in water, that, when exposed to the disinfection process of ozonation, may form the potential carcinogen bromate. Sea water extrusion in coastal areas indicates high levels of bromide in tap water. However, if ozonation is not used for water disinfection then bromate is not formed.

References

(1) Metrohm Application Works – *AW US6 0071* – Determination of Perchlorate in Various waters (Dual4)
(2) Metrohm Application Works – *AW US6 0130* – Determination of Perchlorate in Various waters (ASUPP7)
(3) Metrohm Application Works – *AW CH6 0968* – Simultaneous Analysis of Anions and Oxyhalides as per USEPA method 300

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