

# OCCURRENCE, GENERATION AND ANALYSIS OF DISINFECTION BY-PRODUCTS IN BOTTLED WATERS



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## Abstract

Due to its efficacy as germicide, ozonation has become a common practice in drinking and bottled water treatment and has given rise to concern over the formation of disinfection by-products, in particular bromate, a carcinogen. This ion is produced by oxidation of bromide naturally present in water after the ozone treatment, or through the use of hypochlorite for disinfection during the bottling process. The World Health Organization has set a guideline value of 10 µg/l for bromate in drinking water, and the latest European Directive has the even stricter limit of 3 µg/l, for bottled water. A limited survey of bromide and bromate concentrations in national and foreign samples was carried out. As commercial sodium hypochlorite has been found to contain bromate as a contaminant and this could be one of the causes in addition to the oxidation of the bromide to bromate by ozone, samples were also analysed. Some alternative technologies can be applied in order to minimize the production of bromate, but a monitoring of the levels has to be done to validate them. A highly sensitive chromatographic method based on EPA 300.1 standard was developed using a high capacity column with potassium hydroxide gradient and suppressed conductivity detection. This eluent has lower suppressed background conductivity and lower noise compared to a carbonate eluent and reduced the detection and quantitation limits for bromate. A discussion of the treatment characteristics and the oxalhalides concentrations is done in this paper after testing more than 200 samples of bottled water.

## Introduction

Although ozone is a powerful oxidant and it can be used as a primary disinfectant, one of its disadvantages is that in presence of the naturally occurring bromide ions in water, it may generate bromate. It was only recently recognized that bromate formation can pose significant health risks. US EPA has classified **bromate** as probable human **carcinogen**. Aside from bromate, other disinfection by-products may be formed, such as aldehydes and carboxylic acids. Bromate may be present in some sources of hypochlorite solutions. The formation of bromate during ozonation depends on the concentration of bromide and ozone and pH.

International regulations establish guideline limits, such as the one set by the World Health Organization (WHO) for drinking water. The current limit is 10 µg/l. More stringent limits appear on the Directive of the European Community for bottled waters (3 µg/l).

Disinfectant Byproducts	
<b>Aldehydes</b>	<b>Aldo- and Ketoacids</b>
Formaldehyde	Pyruvic acid
Acetaldehyde	<b>Brominated Byproducts*</b>
Glyoxal	Bromate ion
Methyl Glyoxal	Bromoform
<b>Acids</b>	Brominated acetic acids
Oxalic acid	Bromopicrin
Succinic acid	Brominated acetonitriles
Formic acid	<b>Others</b>
Acetic acid	Hydrogen peroxide

Factors affecting the speciation and concentrations of brominated byproducts: pH and ozone-to bromide ion and TOC-to-bromide ion ratios (Singer, 1992).

Bromate and brominated organics can be controlled during ozonation by the following techniques (Song et al., 1997):

- Low pH decreases bromate ion formation while increasing brominated organic formation;
- Ammonia addition with short ozone contact time decreases both bromate ion and brominated organic formation;
- Hydrogen peroxide decreases brominated organic formation and may increase or decrease bromate ion formation. • Low ozone DOC ratio leads to low bromate ion and brominated organic formation.

Parameter	Values	RCT	Rate of Bromate Formation
Bromide	+	-	+
pH	+	+	+
Temperature	+	+	+
Alkalinity	+	-	+
Ammonia	+	unchanged	-
NOM	+	+	-

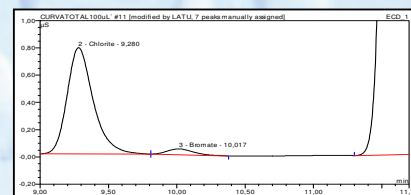
## Materials and Methods

System:

- Ion Chromatograph Dionex IC 2500
- Column Ion pack AS19 and Ion pack AG 19 guard column.
- Autosampler AS 50
- Electrochemical detector ED 50 A
- Hidroxide gradient
- Gradient pump GS 50

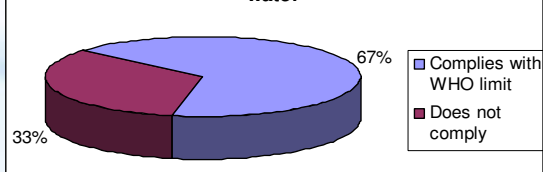


- Standard: DBP AccuStandard

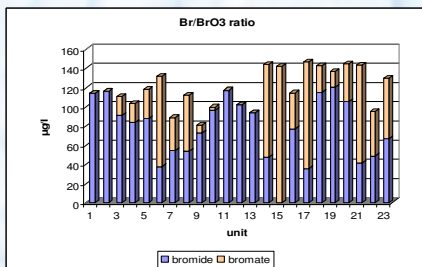


## Results

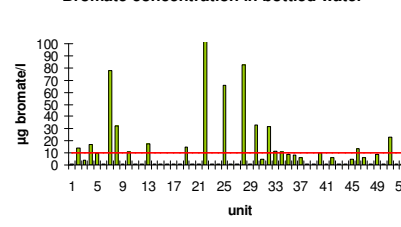
**Percentage of compliance with WHO guideline on bromate limit for drinking water**



Bromide/bromate ratio using different process.

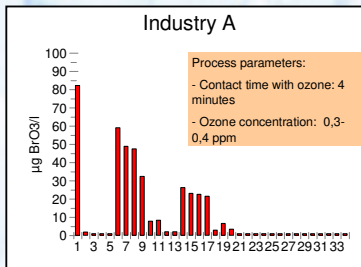


**Bromate concentration in bottled water**

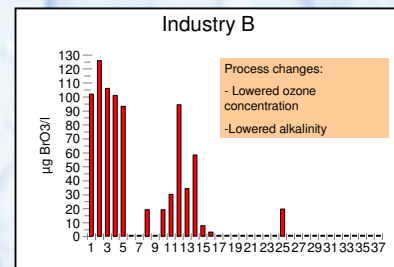


Evolution of bromate formation in the samples over time in two different companies, using different technological approaches.

**Industry A**



**Industry B**



## Conclusion

A significant number of samples were found to contain high levels of bromate. The ozone use has to be controlled to the minimum necessary to achieve disinfection in order to minimize the risk of bromate generation. Some technological options do exist, but the possibility of formation of other by-products has to be taken into account. Some other disinfection alternatives should be studied in cases where the bromide levels are high.

## References

- Guidelines for Drinking Water Quality. First Addendum to Third Edition. WHO, 2006.
- Commission Directive 2003/40/EC of 16 May 2003
- ISO 10304/1-1992
- US EPA method 300.1
- US EPA. National Center For Environmental Research. Final Report: Kinetic-Based Models for Bromate Formation in Natural Waters. EPA Grant Number: R826835
- Singer P.C. 1992. "Formation and Characterization of Disinfection Byproducts." Presented at the First International Conference on the Safety of Water Disinfection: Balancing Chemical and Microbial Risks.
- Song, R., et al. 1997. "Bromate Minimization During Ozonation." J. AWWA. 89(6):69.

