

Health Risk Assessment for Bromate (BrO_3^-) Traces in Ozonated Indian Bottled Water

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ABSTRACT

For this study, bromide and bromate ions in various commercial brands of Indian bottled water samples were estimated using ion chromatography. The measured mean concentration of bromide and bromate ions in water samples was found to be 28.13 $\mu\text{g/L}$ and 11.17 $\mu\text{g/L}$ respectively. The average level of bromate in Indian bottled water was found to be slightly higher (~ 12%) than the acceptable limits (10 $\mu\text{g/L}$) recommended by USEPA (US Environmental Protection Agency). Though, kinetically, it is predicted that 62.5% (6.25 $\mu\text{g/L}$) of bromide in bottled water is needed to convert into bromate upon ozonation to exceed the minimum acceptable limits, but the average formation of bromate determined to be only 26.77% of the predicted concentration. Bromate concentration in bottled water showed a strong correlation with bromide suggesting that its formation in water is very much influenced and controlled by bromide content. The objective of the present study was to determine the BrO_3^- content in commercially available different brands of bottled drinking water in India and to estimate the health risks to population due to ingestion. Results of estimated excess cancer risk and chemical toxicity risk to Indian population due to ingestion of bottled water were presented and discussed.

Keywords: Bromide, Bromate, Excess Cancer Risk, Chemical Toxicity Risk, Bottled Water

1. Introduction

1.1. Genesis

During the 1970's, it was realized that the chlorination of drinking water produced carcinogenic disinfection by products (DBPs) such as trihalomethane. Since then, alternative disinfection methods that minimize the production of toxic by-products have been investigated. Ozonation has emerged as one of the most promising alternatives to chlorination [1]. Although ozonation is already an established method of water purification in the water industry, it suffers from a major problem which is attracting increasing concern, namely the formation of bromate ions due to oxidation of bromide ion.

1.2. Bromine

Bromine is an important precursor to bromate in drinking water. Bromine has both natural and anthropogenic sources. Natural sources include seawater, subsurface brines and evaporite deposits. Anthropogenic sources for bromine include pesticides, medicines and industrial solvents, gasoline additives and water purification. Hydro

chemical characteristics of bromide compounds are low concentration in most rock-forming minerals and generally low bioconcentrations in aqueous systems. Because of these characteristics, it behaves as conservative species and widely used as tracers in hydrological systems. During the evaporite deposits, bromine shows some adsorption characteristics particularly at low pH, on Kaolinite and iron oxide surface.

The sources of bottled water in India are mainly surface and subsurface water like river water, lake water and ground water. The common technique for preparation of bottled water is based on reverse osmosis, ultra filtration, ozonisation, electrolytic methods *etc.* which are itself the removal technique of bromide ion. In spite of applying the removal processes, trace quantities of bromide are found in the bottled water.

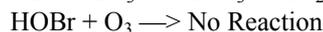
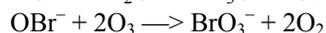
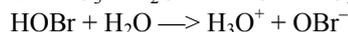
The bottled water is a highly regulated as a food product by FDA (Food Development Authority) under the Federal Food, Drug and Cosmetic Act (FFDCA), subject to federal, state, and industry standards and includes in smaller containers as well as larger containers distributed to the home and markets.

1.3. Bromate

Bromate is not normally found in water. Conversion of bromide to bromate upon ozonation may be affected by physico-chemical parameters including natural organic matter, pH, temperature and some other factors. The relative increase of bromate depends on measures used for comparison (over time or as a function of concentration of bromide (C) \times retention time with the amount of ozone (T)). The use of CT has been suggested as a more useful indicator to describe the relative rate of bromate formation because it also gives a simultaneous descriptor for disinfection efficiency [2]. The rate of formation of bromate ion may also increase with temperature [3,4]. In addition, many studies on the effect of alkalinity on the formation of bromate during ozonation indicate that increased alkalinity increases bromate formation [5]. However, the rate of formation of bromate during ozonation is also affected by ozone characteristics. Thus, a smaller CT may result because ozone becomes less stable with increasing temperature and/or alkalinity. All factors being equal, bromide concentration and ozone dose are the best predictors of bromate formation during ozonation [6]. It should be noted that some of the studies demonstrating high rates of conversion of bromide to bromate are pure laboratory studies with very high bromide levels and thus may not be representative of conversion rates at environmentally relevant doses.

In the ozonised bottled water, naturally occurring bromide causes a catalytic disintegration of ozone and forms hypobromite (OBr^-) as an intermediate product which is predominantly present at higher pH values, but at lower pH, more hypobromous acid (HOBr) is formed. Hypobromite reacts further with an excess of ozone to form bromate. Hypobromous acid does not react further with ozone; therefore, at low pH, no bromate is formed. In the presence of organic matter, HOBr leads to the formation of brominated organic compounds, such as bromoform, mono- and dibromoacetic acid, dibromoacetone, bromopicrin and especially cyanogen bromide. Under certain conditions, bromate may also be formed in concentrated hypochlorite solutions used to disinfect drinking-water [6]. This reaction is due to the presence of bromide in the raw materials (chlorine and sodium hydroxide) used in the manufacture of sodium hypochlorite and to the high pH of the concentrated solution. Bromide is not oxidized by chlorine dioxide, so the use of chlorine dioxide will not generate hypobromous acid, hypobromite ion or bromate [7]. Although bromate can be formed on simultaneous exposure to chlorine dioxide and light, the reaction is thermodynamically unfavourable and bromate is unlikely to be formed under water treatment conditions [8,9]. Bromate can also be formed

in electrolytically generated hypochlorous acid solutions when bromide is present in the brine [10]. Since bromate contains 62.5% (0.625) bromide only hence this fractions need to be converted to form bromate upon ozonation to exceed maximum acceptable concentration. The following equations show the pathway by which bromide (Br^-) is oxidized by ozone to bromate (BrO_3^-) through the intermediate formation of hypobromite (OBr^-). These equations also show that ozone does not oxidize hypobromous acid (HOBr) to bromate. Since increased acid (H_3O^+) will favor the formation of hypobromous acid, this suggests that ozonation at a low pH will tend to minimize bromate formation [11].



1.4. Provisional Guideline Values

Bromate is mutagenic both *in vitro* and *in vivo*. [12,13] has classified potassium bromate in Group 2B (possibly carcinogenic to humans), concluding that there is inadequate evidence of carcinogenicity in humans but sufficient evidence of carcinogenicity in experimental animals. [14] has classified bromate as a probable human carcinogen by the oral route of exposure under the 1986 EPA guidelines for Carcinogen Risk Assessment [15] on the basis of adequate evidence of carcinogenicity in male and female rats. Under the 1999 EPA draft Guidelines for Carcinogen Risk Assessment [16], bromate is likely to be a human carcinogen by the oral route; the data on the carcinogenicity of bromate via the inhalation route are inadequate for an assessment of its human carcinogenic potential. [17] has classified bromate as probably carcinogenic to humans (sufficient evidence in animals; no data in humans). At this time, there is not sufficient evidence to conclude the mode of carcinogenic action for potassium bromate [6,13,14,18]. Because of insufficient information on the mode of carcinogenic action of bromate, IPCS (2000) developed both a carcinogenicity assessment based on the linearized multistage model as well as a TDI based on a non-linear approach for the carcinogenicity of bromate. A TDI of 1 $\mu\text{g}/\text{kg}$ of body weight was calculated based on a no-effect level for the formation of renal cell tumours in rats at 1.3 mg/kg of body weight per day in the [19] study and the use of an uncertainty factor of 1000 (10 each for inter- and intraspecies variation and 10 for possible carcinogenicity). The IPCS (2000) value of 0.1 $\mu\text{g}/\text{kg}$ of body weight per day for a 10^{-5} excess lifetime cancer risk level was based on an increased incidence of renal tumours in male rats given potassium bromate in drinking-water for 2 years using the same study [19]. The upper-bound estimate of the

cancer potency for bromate is 0.19 per mg/kg of body weight per day. The concentrations in drinking water associated with upper-bound excess lifetime cancer risks of 10^{-4} , 10^{-5} and 10^{-6} are 20, 2 and 0.2 $\mu\text{g/litre}$, respectively.

Both the World Health Organization (WHO) and the U.S. Environmental Protection Agency (EPA) have judged bromate as a potential carcinogen, even at very low $\mu\text{g/L}$ levels. The U.S. EPA has estimated a potential cancer risk of 1×10^{-4} (1 in 10^4) for a lifetime exposure to drinking water containing bromate at 5 $\mu\text{g/L}$ and recently issued new rules that require public water supplies to control previously unregulated microbes (e.g., cryptosporidium and giardia) and cancer-causing DBPs in finished drinking water. The Stage 1 D/DBP Rule specifies a Maximum Contaminant Level (MCL) for bromate of 10 $\mu\text{g/L}$. The EPA intends to convene Stage 2 of the D/DBP Rule in the near future, while both Germany and Japan are considering regulatory limits for inorganic DBPs. As per WHO-1993 guidelines, the recommended level for bromate is 25 $\mu\text{g/L}$ corresponding with a cancer risk of 10^{-5} (life time exposure [20]).

2. Materials and Methods

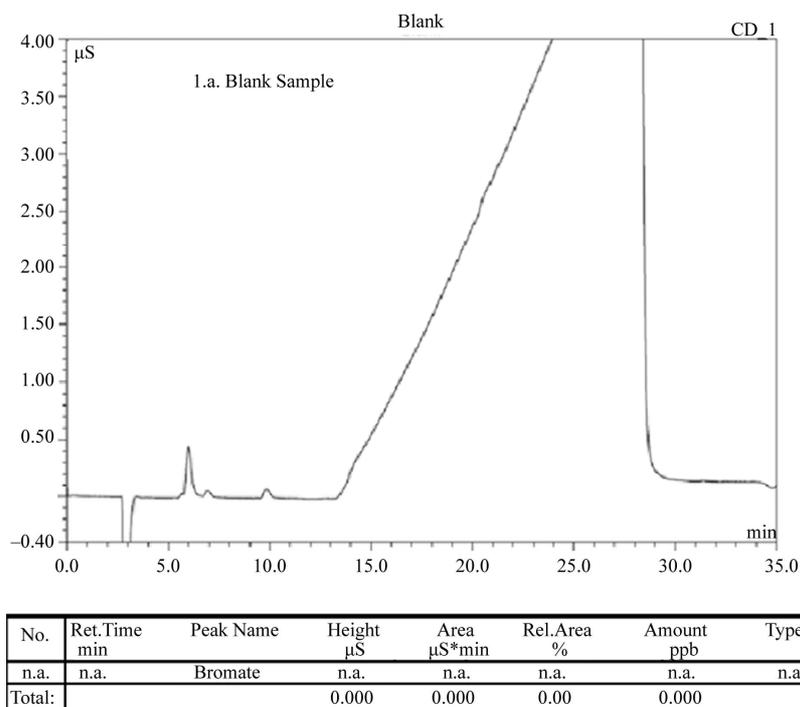
2.1. Sample Collection and Sample Preparation

In present work, 31 different brands of 500 mL ozonated bottled water samples were collected from different regions of India during the months of September and Oc-

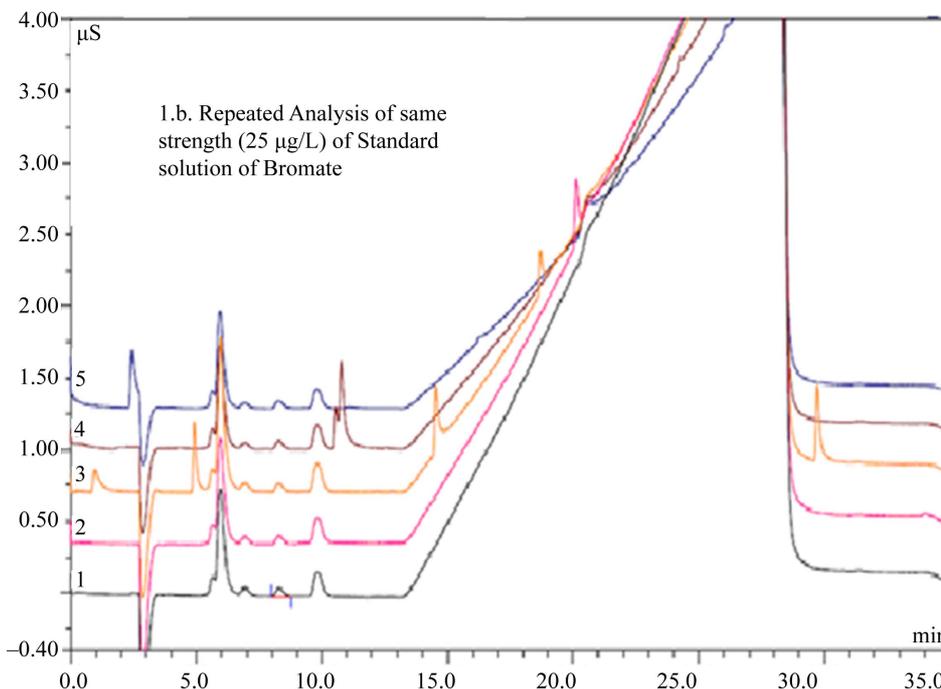
tober, 2010. During collection of bottled water, ozonation for purification as well as date of packing were taken care of to avoid any discrepancies. The collected bottled water samples were filtered through 0.45 μ filter paper, acidified with 0.01M of nitric acid (AR Grade, Merck, Mumbai, India) and stored in a pre-cleaned plastic bottle of 500 ml capacity. The bottles were thoroughly washed and rinsed with acid followed by demineralised water prior to storing the samples.

2.2. Measurement and Standardization of Bromide and Bromate in Bottled Water

Bromide and bromate in bottled water were estimated by conductivity suppressed ion chromatography system (DI-ONEX600) using an Ion Pac AS17 (anion-exchange column) as a stationary phase with 15 mM of NaOH (0 – 15 mts) as a mobile phase and an IonPac AS19 (anion-exchange column) as a stationary phase with 10 mM (0 - 15 mts) and 10 - 45 mM (15 - 35 mts.) of NaOH as a mobile phase respectively. For estimation of bromate ion, the instrument was calibrated in the range of 1 - 100 $\mu\text{g/L}$ using a stock solution of standard which was prepared by dissolving 1.31 g of potassium bromate (KBrO_3) in 1 L of Millipore elix-3 water. Similarly, for bromide ion, calibration and standardization were done in the range of 1 - 10 mg/L with the stock solution of Fluka standard. **Figure 1** shows the chromatogram of blank sample, standard solution of bromated and bromide as

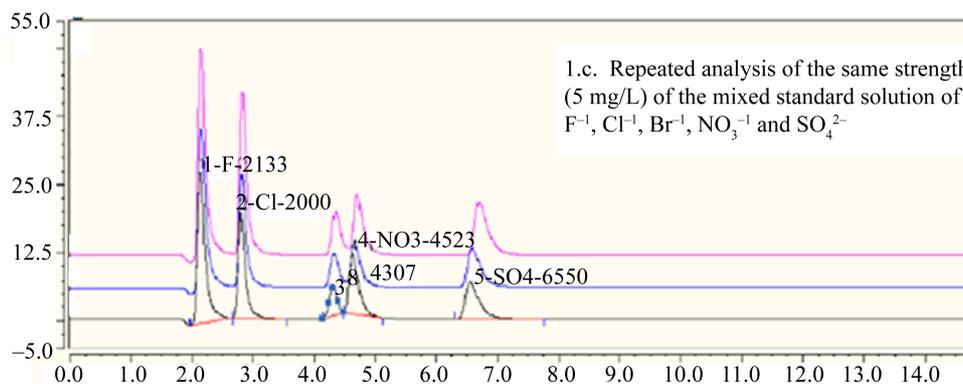


(a)



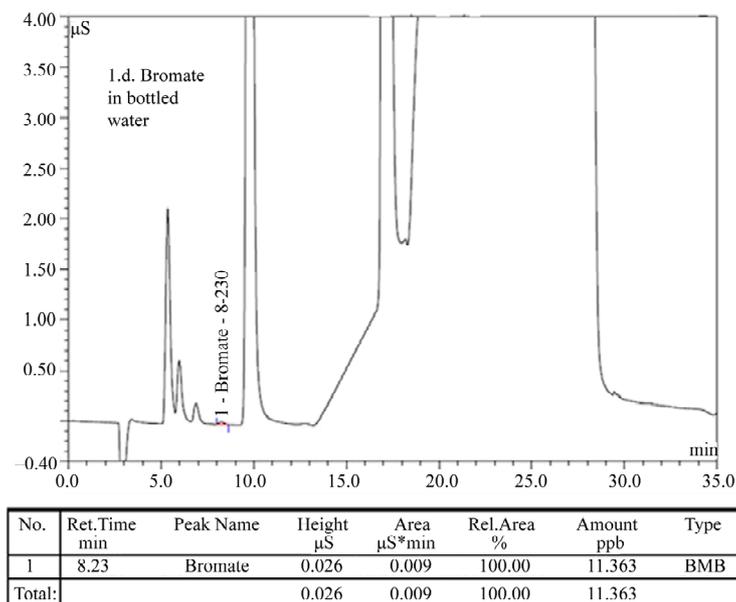
Sample No.	Sample Name	Ret.Time min	Area µS*min	Height µS	Amount ppb	Type	Plates (BP)
4	Standard/1	8.253	0.0193	0.056	25.336	Bromate	Bromate
5	Standard/2	8.307	0.0186	0.058	24.323	BMB	3897
6	Standard/3	8.277	0.0182	0.057	23.827	BMB	4049
7	Standard/4	8.273	0.0187	0.059	24.502	BMB	4076
8	Standard/5	8.283	0.0194	0.060	25.412	BMB	4042
Average		8.279	0.019	0.058	24.680		4047
Rel.Std.Dev:		0.232%	2.759%	2.610%	2.759%		2.447%

(b)



A	B	C	D	E	F	G	H
Sample No.	Sample Name	Ret.Time min	Area µS*min	Height µS	Amount ppb	Type	Plates (EP)
		Br	Br	Br	Br	Br	Br
		ECD 1	ECD 1	ECD 1	ECD 1	ECD 1	ECD 1
1	Standard/1	4.307	0.7322	4.9982	5.0000	BMB	5318
2	Standard/2	4.327	0.8498	5.5794	5.8029	BMB	5086
3	Standard/3	4.353	0.7463	5.9456	5.0963	BMB	6702
Average		4.329	0.7761	5.5077	5.2997		5685
Rel.Std.Dev:		0.541%	8.273%	8.673%	8.273%		15.684%

(c)



(d)

Figure 1. Chromatogram (Conductivity vs retention time) of blank sample (Figure 1(a)), standard solution of Bromate (Figure 1(b)) and Bromide (Figure 1(c)) ions as well as bromate contents in bottled water (Figure 1(d)) using conductivity suppressed ion-chromatography system.

well as bromated content in bottled water using conductivity suppressed ion chromatography. In the chromatogram, the concentration of ions in unknown sample was analyzed by measuring their peak area as conductivity and comparing it with the standard curve. Finally, the concentration of unknown ion in the unknown solution was identified by retention time. The relative standard deviation (2.6% - 8.27%) in the measurement was evaluated by repeated analysis of same strength of standard solution of bromide and bromate ions. Quality assurance was made by spike recovery, replicate analysis and cross method checking. The blank sample containing Millipore elix-3 water was also measured for the concentration of both ions. All the reagents used for experimental work were of ultrapure/ analytical grade, by Merck, Mumbai, India. Bromate and bromide ions were estimated under the following conditions: 1) Separation of Bromate in blank, standard solution and bottled water using gradient method: separator column: IonPac AS19 (4 mm), eluent: 10 mM (0 - 15 mts) and 10 - 45 mM (15 - 35 mts.) of NaOH, flow rate: 1 mL/min, temperature: 30°C, detection: anion self-regenerating suppressor-ULTRA, auto suppression - recycle mode, expected background conductivity: <2 µS.

2) Separation of Bromide in the same strength of mixed standard solution using isocratic method: separator column: Ion Pac AS17 (2 mm), eluent: 15 mM NaOH, flow rate: 0.25 mL/min, injection volume: 25 µL, temperature: 30°C, detection: anion self-regenerating suppressor- ULTRA, auto suppression - recycle mode, expected

background conductivity: <2 µS.

2.3. Risk Assessment

For this study, two types of risks were evaluated, separately, because the human health effects can be classified as carcinogenic risk and chemical toxicity risk. Firstly, the excess cancer risk due to ingestion of bromate in bottled water was evaluated based on the general US EPA standard method.

2.3.1. Methodology of Excess Cancer Risk Assessment

The Individual excess cancer risk (IECR), as defined in USEPA, 2000 a, can be evaluated by the following expression

$$IECR = UR_0 X C_{bw} \quad (\text{Equation (1)})$$

where UR_0 is the risk factor expressed as $(\mu\text{g}\cdot\text{L}^{-1})^{-1}$ due to ingestion of drinking water and US EPA, has considered the toxicological values of inorganic bromate for the cancer risk calculation at the case-study area, $UR_0 = 2 \times 10^{-5} (\mu\text{g}\cdot\text{L}^{-1})^{-1}$. C_{bw} is the estimated concentration of bromate in bottled water, expressed as $\mu\text{g}\cdot\text{L}^{-1}$.

2.3.2. Methodology of Chemical Risk Assessment

Secondly, to evaluate the hazard quotient for bromate, the chemical toxicity risk as lifetime average daily dose (LADD) was estimated with the help of Equation (3) [21-23] and was compared with the reference dose (RfD) of 0.372 µg/kg/day which is calculated on the basis of maximum acceptable level of bromate (10 µg/L) in

drinking water as per guide lines of US EPA, 1999. Here, the water ingestion rate was set as $2 \text{ L}\cdot\text{day}^{-1}$ which is similar to the upper-bound level of adult daily intake recommended by US EPA [24]. 350 days for exposure frequency [24]. 63.7 years for total exposure duration i.e. the average all India life expectancy for both males and females [25], 23250 days for average time [25] and $51.5 \pm 8.5 \text{ kg}$ for body weight [26]. The hazard quotient (HQ) and chemical toxicity risk (LADD) was calculated through ingestion of bottled water by the following formula:

$$HQ = \frac{LADD}{RfD} \quad (\text{Equation (2)})$$

$$LADD(\mu\text{g}/\text{kg}/\text{day}) = \frac{C_i \times IR \times EF \times LE}{BW \times AT} \quad (\text{Equation (3)})$$

where, C_i = Concentration of bromate in bottled water ($\mu\text{g}/\text{L}$)

IR = Ingestion rate (L/day)

EF = Exposure frequency (days/year)

LE = Life expectancy (years)

AT = Average Time (days)

BW = Body Weight (kg)

RfD = Reference Dose ($\mu\text{g}\cdot\text{kg}^{-1}\cdot\text{day}^{-1}$)

$LADD$ = lifetime average daily dose, ($\mu\text{g}\cdot\text{kg}^{-1}\cdot\text{day}^{-1}$)

2.4. Uncertainty Analysis and Statistical Methods

To analyze the uncertainty on estimation of excess cancer risk and lifetime average daily dose (LADD), the input distributions on exposure frequency and body weight were assumed as triangular distribution and normal distribution respectively. Normality test for bromate (concentration) distribution was also tested by Shapiro-Wilk 'W' statistical method which is a semi-nonparametric analysis of variance that detects a broad range of different types of normality in a sample of data (Origin Software, Version 8.1). At 5% significant level, the calculated probability value (W) was found to be lower than the tabulated value. This indicates that the bromate distribution can be assumed as a normal distribution. Ingestion rate of drinking water, total exposure duration and averaging time were considered as constant input values as given in **Table 1**.

3. Results and Discussions

3.1. Physico-Chemical Characteristics of Bottled water

The physicochemical analyses of the bottled water samples are presented in **Table 2**. The pH of bottled water was slightly alkaline and varied within narrow range of 7.1 - 7.3. TDS (Total Dissolved Solids) of water samples

were in the range of 150 - 170 mg/L. The concentration of major ions in bottled water was observed to be far below the permissible limits as per drinking water guideline of Bureau of Indian standard [27].

3.2. Bromide and Bromate Levels in Bottled Water

The mean concentration of Br^- and BrO_3^- in different brands of packaged drinking water samples was found to be $11.17 \mu\text{g}/\text{L}$ (range: 2 - 30 $\mu\text{g}/\text{L}$) and $28.13 \mu\text{g}/\text{L}$ (range: 6 - 65 $\mu\text{g}/\text{L}$) respectively. It was observed that, 45.16% bottled water were above the acceptable limits as per drinking water guidelines of US, EPA for bromate levels. At present, the International Bottled Water Association (IBWA) based on USEPA has set a self-regulatory limit for bromate in bottled water of 10 $\mu\text{g}/\text{L}$ whereas the World Health Organization (WHO) have set a guideline value of 25 $\mu\text{g}/\text{L}$ which is under review and the proposed new guideline value is 10 $\mu\text{g}/\text{L}$. The average ratio of measured $\text{BrO}_3^-/\text{Br}^-$ was observed as 0.43 with the range of 0.16 - 0.62, whereas, chemical kinetically, this ratio is predicted to be 1.6 because it is derived that 62.5% (6.25 $\mu\text{g}/\text{L}$) of bromide in bottled water is needed to convert into bromate upon ozonation to exceed the minimum contamination level (10 $\mu\text{g}/\text{L}$). The formation of bromate in bottled water was not found to be completely 100% in opposition to predicted concentration. The actual formation of bromate ranged from 0.45% to 39.06% with mean value of 25.86% against predicted concentration. **Table 3** shows the measured bromide and bromate concentration, their ratios and percentage formation of bromate in bottled water of various regions of India and consequently risks (excess Cancer risk and chemical toxicity risk) due to ingestion. The reduction in bromate levels may be because of not favoring the formation of intermediate species as hypobromite (OBr^-) at measured pH range of bottled water. In the pH range of 7 - 8, only 1% - 10% of hypobromous acid $[\text{HOBr}]_{\text{total}}$ (in the form of OBr^-) takes part in reactions with molecular ozone [7]. The oxidation of hypobromous acid by ozone is very slow and therefore, does not contribute significantly to bromate formation. Moreover, the concentration of bromate is also dependent on the amount of bromide in the source water, ozone concentration and duration of contact.

3.3. Correlation Analysis

To establish a correlation of Bromide and bromate content in bottled water, Pearson coefficients of correlation was used and showed a fairly high degree of correlation with coefficient (r) = 0.78 with the intercept +2.17 and slope +0.31. This implies that bromate content in bottled water was very much influenced and controlled by bromide content. Moreover, there are also some other

Table 1. Probability distribution of input parameters used to forecast excess cancer risk and LADD.

Input parameters	Mean Value	Standard Deviation	Distribution	References
Bromate levels (µg/l)	11.16	7.24	Normal	This study
IR (l/day)	2	-	-	US EPA, 1991
BW (kg)	51.5	8.5	Normal	H.S. Dang et al. 1995
EF (days/year)	350 (180-365)	-	Triangular	US EPA, 1991
LE (Years)	63.7	-	-	HDR, India, 2009

US EPA: United States, Environmental Protection Agency, EF: Exposure Frequency, LE: Life Expectancy, HDR: Human Development Report, BW: Body Weight, IR: Ingestion Rate.

Table 2. Physiochemical characteristics of Indian bottled water samples.

Parameters	pH	TDS (mg/L)	Hardness (mg/L)	HCO ₃ ⁻ (mg/L)	Cl ⁻ (mg/L)	NO ₃ ⁻ (mg/L)	SO ₄ ⁻ (mg/L)	Na ⁺ (mg/L)	K ⁺ (mg/L)	Mg ⁺⁺ (mg/L)	Ca ⁺⁺ (mg/L)
Range	7.1 - 7.3	150 - 170	60 - 70	55 - 65	2.06 - 28.3	0.3 - 10.7	0.1 - 11.5	1 - 40	0.02 - 2.04	0.03 - 8	0.2 - 25

Table 3. Measured Bromide and Bromate concentration, their ratios and percentage formation of bromate in bottled water of various regions of India and consequently risks (Excess Cancer risk and chemical toxicity risk) due to ingestion.

Bottled Water code	Locations	Measured concentration of Br ⁻ (µg/L)	Measured concentration of BrO ₃ ⁻ (µg/L)	Measured BrO ₃ ⁻ concentration / measured Br ⁻ concentration	Percentage formation of measured BrO ₃ ⁻ against predicted concentration (%)	Excess Cancer Risk (× 10 ⁻⁴)	Chemical Risk	
							LADD (µg·kg ⁻¹ ·day ⁻¹)	HQ (Hazard quotient)
BW-1	Mumbai	36	22	0.61	38.19	4.40	0.818	2.2
BW-2	Mumbai	11	4	0.36	22.72	0.80	0.149	0.4
BW-3	Mumbai	62	10	0.16	10.08	2.00	0.372	1
BW-4	Mumbai	32	12	0.37	23.43	2.40	0.446	1.2
BW-5	Mumbai	10	6	0.59	37.50	1.20	0.223	0.6
BW-6	Mumbai	10	5	0.50	31.25	1.00	0.186	0.5
BW-7	Mumbai	31	16	0.52	32.25	3.20	0.595	1.6
BW-8	Mumbai	59	13	0.22	13.77	2.60	0.484	1.3
BW-9	Mumbai	22	9	0.41	25.56	1.80	0.335	0.9
BW-10	Mumbai	53	24	0.43	27.12	4.80	0.855	2.3
BW-11	Mumbai	8	2	0.25	15.62	0.40	0.074	0.2
BW-12	Pune	16	10	0.62	39.06	2.00	0.372	1
BW-13	Bangalore	39	20	0.51	32.05	4.40	0.744	2
BW-14	Bangalore	17	6	0.35	22.05	1.20	0.223	0.6
BW-15	Bangalore	6	3	0.50	31.25	0.60	0.111	0.3
BW-16	Chennai	21	12	0.57	35.71	2.40	0.446	1.2
BW-17	Hyderabad	7	2	0.28	17.85	0.40	0.074	0.2
BW-18	Surat	39	8	0.20	12.82	1.60	0.298	0.8
BW-19	Surat	8	5	0.62	39.06	1.00	0.186	0.5
BW-20	Surat	35	9	0.26	16.07	1.80	0.335	0.9
BW-21	Surat	9	5	0.56	34.72	1.00	0.186	0.5
BW-22	Baroda	18	11	0.61	38.19	2.20	0.409	1.1
BW-23	Baroda	57	26	0.46	28.50	5.20	0.967	2.6
BW-24	Ahmadabad	33	9	0.27	17.04	1.80	0.335	0.9
BW-25	Jaipur	15	7	0.46	29.16	1.40	0.260	0.7
BW-26	Delhi	10	5	0.50	31.25	1.00	0.186	0.5
BW-27	Delhi	65	30	0.46	28.84	6.00	1.116	3
BW-28	Dehradun	29	14	0.48	30.17	2.80	0.521	1.4
BW-29	Shimla	38	17	0.45	27.96	3.40	0.632	1.7
BW-30	Allahabad	41	8	0.19	12.19	1.60	0.297	0.8
BW-31	Patna	35	16	0.46	28.57	3.20	0.595	1.6

factors which can influence the concentration of bromide in bottled water. **Figure 2** showed a correlation analysis of bromide & bromate concentration in bottled water.

3.4. Risk Assessment due to Oral Ingestion of Bromate in Bottled Water

3.4.1. Individual Excess Cancer Risk

The present study determined the bromate concentration in the bottled water of each area and estimated the individual excess cancer risk. The individual excess cancer risk due to ingestion of bromate in bottled water at an average of 2 L/day over the lifetime expectancy of 63.7 years for an Indian adult observed to be in the range of 4×10^{-5} - 6×10^{-4} with a mean value of 2.24×10^{-4} which showed about one order of magnitude higher than the maximum acceptable level (2×10^{-5}) as per guide lines of US EPA. In the worst case (95th percentile), the excess cancer risk was expected to be about 6 per 10 thousand people which is 30 times higher than the acceptable risk.

3.4.2. Chemical Toxicity Risk

To evaluate the chemical toxicity risk of bromate, the lifetime average daily dose (LADD) of bromate through ingestion was estimated at different percentile and compared it with the reference dose (RfD) of 0.372 $\mu\text{g}/\text{kg}/\text{day}$ and thereby produced a hazard quotient. The life time average daily dose (LADD) worked out to be 0.414 $\mu\text{g}/\text{kg}/\text{day}$ as a mean with a range of 0.074 $\mu\text{g}/\text{kg}/\text{day}$ - 1.116 $\mu\text{g}/\text{kg}/\text{day}$ by considering the body weight as 51.5 ± 8.5 kg of an adult Indian reference man. The mean of hazard quotient (LADD/RfD) was also found to be slightly greater than unity indicating that bromate in Indian bottled water is under alarming situation from the chemical toxicity point of view. In the worst case based on very conservative assumptions (at 95th percentile), the exposure dose determined to be 0.967 $\mu\text{g}/\text{kg}/\text{day}$ which is 2 - 3 times higher than RfD. The Basic statistical pa-

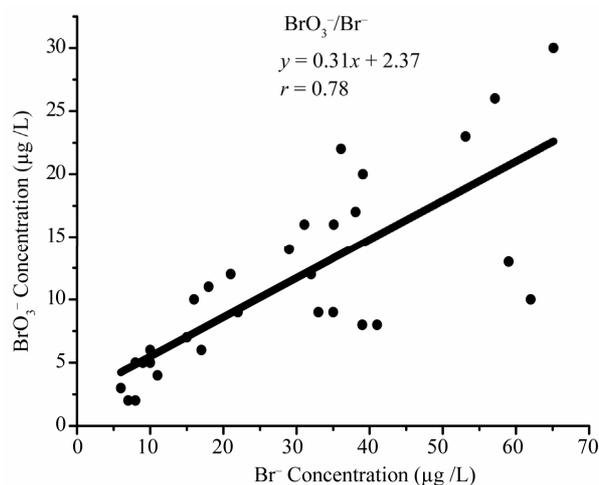


Figure 2. A correlation analysis of bromide & bromate concentration in bottled water.

rameters of bromide and bromate content in Indian bottled water including risks (Excess Cancer risk and chemical toxicity risk) at different percentiles (5th - 95th) due to ingestion of bromated are presented in **Table 4**.

4. Conclusions

This study was carried out with a view to bring the awareness of Indian centralized regulatory authorities who have not recommended any acceptable limits in this prospect. However, in developed countries like Europe and America, the limits for bromate are well prescribed. Lack of awareness in this respect has led to various manufactures, which are using it without proper regulation. There are limited methods currently available to remove bromate from water. The average exposure level of bromate was comparatively high and the chemical toxicity in turn is also presumed to be greater. Therefore, it is suggested that either bromide (precursor of bromate)

Table 4. The Basic statistical parameters of bromide and bromate content in Indian bottled water including risks (Excess Cancer risk and chemical toxicity risk) at different percentiles (5th - 95th) due to ingestion of bromate.

	Mean	Median	Minimum	Maximum	Range	5 th percentile	25 th Percentile	75 th Percentile	95 th percentile	Inter Quartile Range (IQR)
Bromide (Br^-)	28.13	29	6	65	59	7	10	39	62	29
Bromate (BrO_3^-)	11.16	9	2	30	28	2	5	16	26	11
Excess Cancer Risk ($\times 10^{-4}$)	2.24	1.84	0.40	6	5.6	0.40	1	3.2	5.20	2.20
Chemical Toxicity risk (LADD)	0.414	0.335	0.074	1.116	1.042	0.074	0.186	0.595	0.967	0.409
Hazard Quotient (HQ)	1.113	0.90	0.2	3	2.8	0.2	0.5	1.6	2.6	1.2

should be removed using different techniques like membrane filtration, ion exchange, precipitation *etc* prior to ozonolysis [28,29] or to restrict bromate formation during the ozonation process by decreasing the pH to 6.8 [30]. Under low pH conditions, ozone appears less effective as an oxidant and the formation of unwanted brominated organic DBPs is also more favoured. Because of the large number of factors that influence bromate production, it will be necessary to optimize treatment by balancing the advantages and disadvantages of various measures on an individual basis for each water supply.

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REFERENCES

- [1] J. Lawrence, H. Tosine, F. I. Onuska and M. E. Comba, "The Ozonation of Natural Waters: Product Identification," *Ozone: Science and Engineering*, Vol. 2, No. 1, 1980, pp. 55-64. [doi:10.1080/01919518008550868](https://doi.org/10.1080/01919518008550868)
- [2] U. Von Gunten and J. Hoigné, "Bromate Formation during Ozonation of Bromide Containing Waters: Interaction of Ozone and Hydroxyl Radical Reactions," *Environmental Science & Technology*, Vol. 28, No. 7, 1994, pp. 1234-1242. [doi:10.1021/es00056a009](https://doi.org/10.1021/es00056a009)
- [3] AWWARF, "Disinfection By-Products Database and Model Project," Denver, CO, American Water Works Association Research Foundation, 1991.
- [4] M. S. Siddiqui and G. Amy, "Factors Affecting DBP Formation during Ozone-Bromide Reactions," *Journal of the American Water Works Association*, Vol. 85, No. 1, 1993, pp. 63-72.
- [5] M. Siddiqui, G. Amy, K. Ozekin, W. Zhai and P. Westerhof, "Alternative Strategies for Removing Bromate," *Journal of the American Water Works Association*, Vol. 86, 1994, pp. 81-96.
- [6] IPCS, "Disinfectants and Disinfectant By-Products," World Health Organization, Geneva, 2000.
- [7] W. R. Haag and J. Hoigné, "Ozonation of Bromide-Containing Waters: Kinetics of Formation of Hypobromous Acid and Bromide," *Environmental Science & Technology*, Vol. 17, 1983, pp. 261-267. [doi:10.1021/es00111a004](https://doi.org/10.1021/es00111a004)
- [8] R. G. Rice and M. Gomez-Taylor, "Occurrence of By-Products of Strong Oxidants Reacting with Drinking Water Contaminants—Scope of the Problem," *Environmental Health Perspectives*, Vol. 69, 1986, pp. 31-44. [doi:10.1289/ehp.866931](https://doi.org/10.1289/ehp.866931)
- [9] G. Gordon and G. L. Emmert, "Bromate Ion Formation in Water When Chlorine Dioxide Is Photolyzed in the Presence of Bromide Ion," *Proceedings of the Water Quality Technology Conference*, Denver, CO, American Water Works Association, New Orleans, 1996.
- [10] M. Fielding and J. Hutchison, "Formation of Bromate and Other Ozonation By-Products in Water Treatment," *Proceedings of the IWSA International Workshop on Bromate and Water Treatment*, Paris, 1993, London, International Water Supply Association, 1993, pp. 81-84.
- [11] J. Hoigné and H. Bader, "Kinetics of Reactions of Chlorine Dioxide (OCIO) in Water—I. Rate Constants for Inorganic and Organic Compounds," *Water Research*, Vol. 28, No. 1, 1994, pp. 45-55.
- [12] IARC, "Some Naturally Occurring and Synthetic Food Components, Furocoumarins and Ultraviolet Radiation," International Agency for Research on Cancer, (IARC Monographs on the Evaluation of Carcinogenic Risks to Humans, Lyon, Vol. 40, 1986, pp. 207-220.
- [13] IARC, "Some Chemicals That Cause Tumours of the Kidney or Urinary Bladder in Rodents and Some Other Substances," IARC Monographs on the Evaluation of Carcinogenic Risks to Humans, International Agency for Research on Cancer, Lyon, Vol. 73, 1999, pp. 481-496.
- [14] US EPA, "Toxicological Review of Bromate in Support of Integrated Risk Information System (IRIS)," US Environmental Protection Agency, Washington DC, 2001.
- [15] US EPA, "Guidelines for Carcinogen Risk Assessment," US Environmental Protection Agency, Federal Register, Vol. 51, No. 185, 1999, pp. 33992-34003.
- [16] US EPA, "Guidelines for Carcinogen Risk Assessment (SAB Review Draft)," Washington, DC, US Environmental Protection Agency, Risk Assessment Forum (NCEA-F-0644), 1986.
- [17] US EPA, "Guidelines for Carcinogen Risk Assessment," SAB Review Draft, US Environmental Protection Agency, Risk Assessment Forum (NCEA-F-0644), Washington DC, 1999.
- [18] Health Canada, "Bromate. Guidelines for Canadian Drinking Water Quality—Supporting Document," Health Canada, Environmental Health Directorate, Health Protection Branch, Ottawa, Ontario, 1999.
- [19] Y. Kurokawa, "Dose-Response Studies on the Carcinogenicity of Potassium Bromate in F344 Rats after Long-Term Oral Administration," *Journal of the National Cancer Institute*, Vol. 77, 1986, pp. 977-982.
- [20] WHO, "Guidelines for Drinking Water Quality," Geneva, Vol. 1. 1993.
- [21] US EPA (United States Environmental Protection Agency), "Preliminary Health Risk Reduction and Cost Analysis, Revised National Primary Drinking Water Standards for Radionuclides," Review Draft, Washington DC, 2000.
- [22] Health Canada, "Summary of Guidelines for Canadian Drinking Water Quality," Federal-Provincial Subcommittee on Drinking Water of the Federal Provincial-Territorial Committee on Environmental and Occupational health, Ottawa, Ontario, Canada, 1999.
- [23] WHO (World Health Organisation), "Guidelines for Drinking Water Quality," Addendum to: Health Criteria

- and Other Supporting Information, WHO/EOS/98.1, Geneva, Vol. 2, 2nd Edition, 1998, p. 283.
- [24] US EPA (United States Environmental Protection Agency), "EPA Standard Default Exposure Factors," Washington DC, 1991.
- [25] HDR (Human Development Report), "National Resource Centre for urban poverty and All India Institute of Local Self Government, Mumbai, India," 2009.
- [26] H. S. Dang, D. D. Jaiswal, M. Parmeshwran and S. Krishnamony, "Physical, Anatomical, Physiological and Metabolic Data for Reference Indian Man: A Proposal," BARC/1994/E/03, Board of Research in Nuclear Sciences, Mumbai, India, 1994.
- [27] Indian Standard, "Drinking Water—Specification (First Revision) IS-10500," BIS, New Delhi, India, 1991.
- [28] S. W. Krasner, M. J. McGuire, J. G. Jacangelo, N. L. Patania, K. M. Reagan and E. M. Aieta, "The Occurrence of Disinfection By-Products in US Drinking Water," *Journal of the American Water Works Association*, Vol. 81, No. 41, 1989, pp. 41-53.
- [29] S. W. Krasner, W. H. Glaze, H. S. Weinberg, D. A. Daniel and I. M. Najm, "Formation and Control of Bromate during Ozonation of Waters Containing Bromide," *Journal of the American Water Works Association*, Vol. 85, No. 1, January 1993, pp. 73-81.
- [30] J. C. Kruithof and J. C. Schippers, "The Formation and Removal of Bromate," *Water Supply*, Vol. 11, No. 1, 1993, pp. 149-155.