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Review

Inorganic Oxyhalide By-Products in Drinking Water and Ion Chromatographic Determination Methods

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Abstract

Many drinking water utilities are changing their primary disinfectant from chlorine to alternative disinfectants such as ozone, chlorine dioxide and chloramines, which reduce regulated trihalomethanes and some organochlorine compounds levels, but often increase levels of others potentially toxicologically important compounds. The hazardous inorganic oxyhalide by-products are bromate, chlorite and chlorate, some of which have been classified as probable human carcinogens. The most important of these is bromate, formed when source waters containing bromide are ozonated. Chlorite is formed when chlorine dioxide is used, whereas chlorate is formed when chlorine, chlorine dioxide, hypochlorite acid or chloramine is used to disinfect drinking water.

This paper is a review of ion chromatographic separations of these inorganic oxyhalide disinfection by-products in drinking water and their detection using conductivity, UV/Vis or mass spectrometry detection. The critical comparison of ISO, US EPA and other methods including limits of detection, availability and costs of analyses is given. Furthermore, a review of papers concerning ion chromatography determination of inorganic oxyhalides in drinking water published during the last 20 years is presented.

Keywords: ion chromatography, bromate, chlorite, chlorate, drinking water.

Introduction

The first documented drinking water treatment can be found in Egyptian hieroglyphics, describing procedures to purify water. The basic principles were the same then as they are today: boiling, chemical treatment and filtration. The importance of drinking water quality and its influence on human health was known, but the specific contaminations would not be identified for centuries.

This situation was changed in the 19th century, when chlorine as a chemical disinfectant was introduced to water treatment. The introduction of chlorination to drinking water was followed by remarkable reductions in cholera, dysentery and typhoid worldwide.

Nowadays, water treatment by disinfection processes of drinking water has been considered the major public health achievement of the 20th century. Consequently, the identification of water contaminants shifted from microbiological to chemical. The number of chemicals determined in drinking water has grown exponentially. However, for hundreds of them, very few have been studied or have documented proof of their health effects.

Nearly half of the monitored parameters are being measured for operational reasons (e.g. iron, ammonium, pH, chloride, dissolved organic carbon, assailable organic

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carbon) and for reason of customer satisfaction (e.g. colour, taste, hardness).

Of the health-related compounds, a number of metals and small groups of organic compounds and pesticides are being measured on a regular base in a majority countries.

This concerns such chemicals as metals (antimony, arsenic aluminium, chromium, magnesium, manganium, cadmium, copper, nickel, lead, mercury, iron), inorganic ions (ammonium, fluoride, nitrite, nitrate, cyanide), organic compounds (e.g. benzo(a)pyrene, trihalomethanes, chlorobenzenes, pesticides) and recently - inorganic oxyhalide disinfection by-products such as bromate, chlorite and chlorate.

The identification of new, possibly hazardous compounds in drinking water has become an important task for water suppliers. In an ideal situation, where standards for different intake routes of exposure are fully adjusted to each other, regular monitoring of these compounds should only be necessary when these compounds are carcinogens, or if the relative contribution of drinking water to total exposure or to the tolerable daily intake is high [1]. If formation, toxicity and methods of analysis of metals and selected organic compounds are well known, determination of inorganic disinfection by-products is a new challenge for researchers.

During the 1970s it was discovered that chlorination of drinking water produced carcinogens, such as trihalomethanes, haloacetic acids and others [2, 3]. Since then, environmental regulatory agencies, as well as drinking water treatment technologists, have been carrying out extensive research for alternative disinfection methods that minimize the production of by-products with significant health risks. Ozonation has emerged as one of the most promising alternatives to chlorination.

In the last decade, the use of ozone in the treatment of drinking water to improve taste, odor, organic and inorganic micropollutants has been spreading. In the early 1980s it became obvious that application of ozonation in drinking water treatment did not only result in the formation of oxygenated compounds but, in bromide containing water, brominated organic compounds as well as bromate are formed.

Recently, bromate is the most important inorganic oxyhalide by-product whose concentration in drinking water has to be controlled. Furthermore, the subjects of interest and advanced research are chlorite and chlorate.

Formations, Toxicity and Legal Regulation of Bromate, Chlorite and Chlorate

Bromate is formed when water containing bromide is ozonated. The oxidation of bromide by molecular ozone was described by Song *et al.* [4]. From the theoretical and practical standpoint it can be seen that bromate formation can be influenced by many parameters, such as ozone dose, water pH, temperature and indigenous concentration of bromide [5].

Limitation of bromate formation may be achieved by a careful adaptation of the ozone dosage to the disinfectant demand. Other options are lowering the pH, using ozone and hydrogen peroxide, adding ammonia, removing bromide prior to ozonation, and using membrane filtration or anaerobic processes [6].

Chlorite (ClO_2^-) is the disinfection by-product formed when chlorine dioxide (ClO_2) is used to disinfect drinking water, while chlorate (ClO_3^-) is formed when chlorine dioxide or chloramine is used [7].

Chlorination using hypochlorite acid (HClO) solutions, which contain ClO_3^- as a product of HClO disproportionation, may also contribute to ClO_3^- contamination in final disinfected water.

Bromate has been identified as an animal and possible human carcinogen [8]. The International Agency for Research on Cancer (IARC) classified bromate in group B-2 (the agent is possibly carcinogenic to humans) [9].

In 1993 bromate was judged by the World Health Organization (WHO) as a potential carcinogen, initially on 25 μg/L level, which was associated with an excess lifetime cancer risk of $7 \cdot 10^{-5}$, because of the limitations in the available analytical and treatment methods. Soon, health effects research indicates it to be a suspected human carcinogen, which exhibits a potential 10^{-4} risk of cancer after a lifetime exposure in drinking water at 5.0 μg/L level and a potential 10^{-5} risk at 0.5 μg/L level.

The United States Environmental Protection Agency (US EPA) [10], as well as the Commission of the European Communities [11], has recently issued new rules that require public water supplies to control previously unregulated microorganisms and cancer-causing disinfection by-products in final treatment drinking water. According to these regulations, Maximum Admissible Level (MAL) is 10 μg/L for bromate and 1000 μg/L for chlorite.

There is no limit for chlorate due to limited knowledge about its toxicity; however, WHO recommends minimizing the level of chlorate as much as possible long as there is no reliable toxicological data. The influence of chlorate on humans is described Eysseric *et al.* [12].

The maximum admissible level for bromate has been primarily based on current analytical capability (not on toxicological considerations - the target concentration for bromate in drinking water is zero); thus, there is a need for ongoing development and refinement of analytical technologies in order to permit rapid and reliable determinations at the sub μg/L level.

Global and national agencies are continually striving to monitor bromate, chlorite and chlorate levels in drinking water in order to establish appropriate regulatory limits. Depending on results of further research, a risk model could indicate a more definitive guideline value for oxyhalides in drinking water. The higher limit sets are due mainly to the lack of sensitive analytical methods for routine laboratories. For these reasons there is a need for improving existing methods in terms of sensitivity, cost and reliability.

Unquestionably, the analysis of inorganic oxyhalide disinfection by-products in drinking water will continue in the future to lead to improvement of health conditions. In most countries the addition of bromate as a food additive is no longer allowed, making drinking water the sole source of its intake.

The problem of bromate also concerns bottled water which has become a healthier choice than tap water for many people because they believe that bottled water contain fewer contaminants, or dislike the taste of chlorinated tap water. Therefore, the annual consumption of bottled drinking water in the world is substantial [13]. It is well known that much of bottled drinking water passes through treatment processes such as filtration, deionization, reverse osmosis or ozonation to ensure its quality.

Application of Ion Chromatography in Determination of Bromate, Chlorate and Chlorite in Water

Numerous techniques are used to determine inorganic oxyhalide compounds including: colorimetry, wet chemical methods (e.g. titrimetry), electrochemical techniques (e.g. amperometry, polarography, ion-selective electrodes), UV spectrophotometry [14], capillary electrophoresis [15] and even gas chromatography [16].

Many of these methods suffer from interferences and limited sensitivity; they can be labour intensive and are often difficult to automate. Although performance criteria (trueness, precision and limit of detection) can be specified for analytical methods, it is still difficult to obtain similar results in different laboratories.

Advances in analytical instrumentation, detection systems and separation techniques have, in many instances, provided analytical chemists the tools required to continually lower method detection limits. Consequently, several methods have been proposed for low-level analysis of inorganic oxyhalide by-products in drinking and bottled waters. The idealized method for bromate, chlorite and chlorate determinations should meet the following requirements:

- determination of target ions in drinking water with limit of determination on 25% of maximum acceptable concentration (2.5 µg/L for bromate, 50 µg/L for chlorite and chlorate);
- no sample pretreatment;
- short time spent on analysis;
- low cost of single analysis;
- method availability.

The most useful analytical technique for determination of inorganic anions and cations seems to be ion chromatography [17], which is a significant addition to the ever-expanding field of chromatographic analysis.

Since its introduction, ion chromatography has seen phenomenal growth in most areas of analytical chemistry and has become a versatile and powerful technique for the analysis of a vast number of ions present in the environment or in biological tissues and fluids.

Ion chromatography is also an attractive technique for laboratories, which need to determine many anions and cations on several thousand samples, but do not have the throughput to justify the purchase of large automatic analyzers, usually based on colorimetric procedures. It eliminates the need to use hazardous reagents, which are often integral to colorimetric procedures.

The most important advantages of ion chromatography are: broad range of applications, well-developed hardware, many detection options, reliability (good accuracy and precision), high selectivity, high speed, high separation efficiency, good tolerance to sample matrices, low cost of consumables, accepted as standard methodology [18].

Initially, separation methods were based on low-capacity ion-exchangers. Therefore, injection volume and ionic strength of the sample were strictly limited to avoid column overloading. A total removal of interfering ions like chloride and sulphate is necessary. Methods without trace enrichment are usually not sensitive enough to determine oxyhalide disinfection by-products on required levels. More sophisticated methods based on bromate preconcentration step prior analysis use low-capacity anion-exchangers with suppressed conductivity detection.

In this case a total removal of sample matrix (especially chloride, sulphate and carbonate) is required. Unfortunately, these methods are not well suited for routine analysis on levels below 1 µg/L, because of expensive sample pretreatment and time spent on preconcentration and clean-up steps.

Modern ion chromatography is faster, more convenient and has greater separating ability than classical methods. The improved performance stems largely from the four factors: better chromatographic components, more efficient ion-exchange resins and columns, smaller samples and automatic detection of separated sample substances.

Ion chromatography is now considered a well-established, mature technique for the analysis of ionic species. Many organisations, such as the International Standardisation Organisation (ISO), the US EPA and the American Society for Testing and Materials (ASTM) have standard or regulatory methods of analysis based upon ion chromatography.

The review of ISO, US EPA, ASTM and Dionex (the world leading manufacturer of ion chromatography equipment) methods for determining inorganic oxyhalide by-products are given in Table 1 (ISO Standards), Table 2 (US EPA and ASTM methods) and Table 3 (Dionex Co. methods).

In the mid-1990s, the ISO worked on Method 15061 for bromate [19] and Method 10304-4 [20] for chlorite, chloride and chlorate determination. ISO 15061 standard specifies a method for determination of dissolved bromate in drinking water, raw water, surface water, partially ozonated water and swimming pool water. Measurement of bromate is made in the range of 0.5 µg/L to 1000 µg/L with or without sample preconcentration. If preconcentration is necessary, 6 ml of sample is passed through three cation exchange cartridges in the Ba-, Ag- and H-forms to reducing total ionic strength.

Table 1. ISO standards for the determination of inorganic oxyhalides in water.

Method number	Method name	Inorganic oxyhalides ions determined	Detection mode	Range [μg/L]	Interferences
ISO 15061 (2001)	Water Quality. Determination of Dissolved Bromate – Method by Liquid Chromatography of Ions.	BrO_3^-	Conductivity. UV detector (λ = 190 - 205 nm) is suitable to confirm the conductivity results only.	0.5 - 1 000	The presence of nitrate, chloride, carbonate and sulfate may affect the capacity of the concentrator column and lead to poor recovery of bromate Metals, selected organic acids, solid particles and organic compounds (such as mineral oils, detergents, and humic acids) shorten the life-time of the concentrator and separator column.
ISO 10304-4 (1997)	Water Quality. Determination of Dissolved Anions by Liquid Chromatography of Ions – Part 4: Determination of Chlorate, Chloride and Chlorite in Water with Low Contamination.	ClO_3^-	Conductivity	0.03 - 10	Organics acids such us mono- and dicarboxylic acids or disinfectants by products (e.g. chloroacetic acids) and the presence of high concentration of fluoride, chloride, nitrite, nitrate and sulphate ions can negatively influence on analysis. Dissolved organic substances can react with working electrode of the amperometric detector, causing a decrease in sensitivity.
		ClO_2^-	Conductivity	0.05 – 1	
			UV (λ=207 – 220 nm)	0.1 - 1	
			Amperometry (0.4 – 1.0 V)	0.01 - 1	

ISO 10304-4 standard specifies a method for the determination of dissolved chlorite, chloride and chlorate anions in water with low contamination (e.g. drinking water, raw water, swimming pool water). An appropriate sample pretreatment and use conductivity, UV or amperometric detector make the working ranges from 0.03 μg/L to 10 μg/L (chlorate) to 0.01 μg/L to 1000 μg/L (chlorite).

The review of the methods of ion chromatographic determination of inorganic disinfection by-products published by the US EPA are described by Hautman *et al.* [21].

In 1987 the US EPA presented a draft of Method 300.0, which was recommended for determining common anions (fluoride, chloride, nitrate and sulphate) on mg/L levels using standard low capacity anion exchange column and conductivity detection.

Soon this Method was updated to include part B for the determination of bromate and other inorganic disinfection by-products using a modern high capacity anion exchange column with carbonate/bicarbonate eluent. The limit of detection using this column was still on a dissatisfied level. In 1997 US EPA Method 300.1 was published as a update to Method 300.0. This new 300.1 Method was developed as a more sensitive method by identifying specific parameters (columns, eluent and injection volume) which could be utilized to provide quantification of lower concentrations of bromate in drinking water, even in the presence of up to 50 mg/L of chloride ions. This Method incorporated a new high-capacity anion-exchange column of more efficiency resolving trace bromate from the common anions.

By using a high-capacity anion-exchange column it is possible to determine bromate at a level lower than 1 μg/L by direct injection of a very large volume (up to 1 mL) without any sample preconcentration or pretreatment [22].

In 2000 the US EPA published Method 317.0, which uses a post column derivatization with *o*-dianisidine that reacts with the eluting bromate to form chromophore which is then measured at UV/Vis detector. This Method offers excellent bromate, chlorite and chlorate limits of detection below 1 μg/L.

US EPA Method 321.8 specifies the use of an anion exchange column and detection of bromate using ICP-MS detection in atmospheric pressure mode. This approach can achieve limit of determination for bromate on 0.3 μg/L, although the sample must first be pre-treated to remove haloacetic acids and separation conditions must be chosen to provide complete resolution of bromate from brominated haloacetic acids, because these species can interfere with bromate [23].

The newest US EPA method 326.0, has been developed for the analysis of ultra trace bromate concentrations in drinking waters using post column derivatization reaction with Mo(VI). This Method provides comparable results to Method 317.0. [24].

Besides methods recommended by the ISO and US EPA, there are a lot of methods worked out by manufacturers of chromatography equipment.

The ion chromatography method for inorganic disinfection by-product determination can be divided into three

Table 2. US EPA and ASTM methods recommended determination of inorganic oxyhalides in water.

Method number	Method name	Inorganic oxyhalide ions determined	Columns	Eluent	Sample injection volume [μL]	Detection mode	Limit of detection [μg/L]
US EPA							
300.0 part B (1993)	The Determination of Inorganic Anions in Water by Ion Chromatography	BrO_3^- ClO_2^- ClO_3^-	Dionex IonPac AG9 +AS9 (or equivalent)	1.7 mM $NaHCO_3$ + 1.8 mM Na_2CO_3	50	Suppressed conductivity	BrO_3^- - 20 ClO_2^- - 10 ClO_3^- - 3
300.1 (1997)	The Determination of Inorganic Anions in Water by Ion Chromatography	BrO_3^- ClO_2^- ClO_3^-	Dionex IonPac AG9-HC +AS9-HC (or equivalent)	9.0 mM Na_2CO_3	200	Suppressed conductivity	BrO_3^- - 1.32 ClO_2^- - 1.44 ClO_3^- - 2.55
317.0 (2000)	Determination of Inorganic Oxyhalide Disinfection By-products in Drinking Water Using Ion Chromatography with the Addition of a Postcolumn Reagent for Trace Bromate Analysis.	BrO_3^- ClO_2^- ClO_3^-	Dionex IonPac AG9-HC +AS9-HC (or equivalent)	9.0 mM Na_2CO_3	225	Suppressed conductivity followed in series with UV post column derivatization with o-dianisidine	Conductivity ClO_2^- - 0.80 ClO_3^- - 0.56 BrO_3^- - 0.64 (UV) BrO_3^- - 0.11
321.8 (1997)	Determination of Bromate Ions in Waters Using Ion Chromatography with Inductively Coupled Plasma Mass Spectrometry	BrO_3^-	Dionex PA-100	5.0 mM HNO_3 + 25.0 mM NH_4NO_3	580	ICP-MS	BrO_3^- - 0.30
326.0 (2002)	Determination of Inorganic Oxyhalide Disinfection By-Products in Drinking Water Using Ion Chromatography Incorporating the Addition of a Suppressor Acidified Postcolumn Reagent for Trace Bromate Analysis.	BrO_3^- ClO_2^- ClO_3^-	Dionex IonPac AG9-HC +AS9-HC (or equivalent)	9.0 mM Na_2CO_3	225	Suppressed conductivity followed in series with UV post column derivatization with Mo(VI)	UV/Vis: BrO_3^- - 0.17 ClO_2^- - 2.0 ClO_3^- - 1.7 Conductivity: BrO_3^- - 1.2
ASTM							
D 6581-00 (2000)	Standard Test Method for Bromate, Bromide, Chlorate, and Chlorite in Drinking Water by Chemically Suppressed Ion Chromatography	BrO_3^- ClO_2^- ClO_3^-	Dionex IonPac AG9-HC +AS9-HC (or equivalent)	9.0 mM Na_2CO_3	200	Suppressed conductivity	BrO_3^- - 5 ClO_2^- - 20 ClO_3^- - 20

groups [25]. All of them are based on ion chromatography separation and different detection methods. The first one is the most popular conductivity detection, the second is based on UV/Vis detection after post-column derivatisation and the third on mass spectrometry detection.

The review of published papers, including applied columns, eluents, detection mode and obtained detection limits, are given in Table 4 (ion chromatography with conductivity detection), Table 5 (ion chromatography with UV/Vis detection) and Table 6 (ion chromatography with mass spectrometry detection).

A review of method of determination of bromate in drinking water is described by Koscielna [69]. The determination of bromate in waters that have been chlorinated using sodium hypochlorite are described by Weinberg *et al.* [70].

The experimental results described by Columbini *et al.* [28] showed that the matrix effect, due to inorganic ions contained in drinking water, strongly influenced the chromatographic behaviour of bromate peak. The increase of total ion content let to a correlated decrease in the efficiency of the analyte peak so that effective detection limits depended on the matrix composition.

Table 3. Methods of the determination of inorganic oxyhalides in water recommended by Dionex.

Method number	Method name	Inorganic oxyhalides ions determined	Columns	Eluent	Detection mode	Limit of detection [µg/L]
AN 81	Ion Chromatographic Determination of Oxyhalide and Bromide at Trace Level Concentrations in Drinking Water Using Direct Injection	BrO_3^- ClO_2^- ClO_3^-	Dionex IonPac AG9-HC + AS9-HC	9.0 mM Na_2CO_3	Suppressed conductivity	BrO_3^- - 1.73 ClO_2^- - 2.38 ClO_3^- - 1.07
AN 101	Trace Level Determination of Bromate in Ozonated Water Using Ion Chromatography	BrO_3^- ClO_2^- ClO_3^-	Dionex IonPac AG9-SC + AS9-SC + AG10	40 mM H_3BO_3 + 20 mM NaOH or 200 mM H_3BO_3 + 100 mM NaOH	Suppressed conductivity	BrO_3^- - 7.3 ClO_2^- - 3.4 ClO_3^- - 9.4
AN 136	Determination of Inorganic Oxyhalide Disinfection By-Products Anions and Bromide in Drinking Water Using Ion Chromatography with the Addition of a Post-Column Reagent for Trace Bromate Analysis	BrO_3^- ClO_2^- ClO_3^-	Dionex IonPac AG9-HC + AS9-HC	9.0 mM Na_2CO_3	Suppressed conductivity + UV/Vis with o-dianisidine post column derivatization	UV/Vis: BrO_3^- - 0.09 ClO_2^- - 1.80 ClO_3^- - 1.85 Conductivity: BrO_3^- - 1.22
AN 149	Determination of Chlorite, Bromate, Bromide and Chlorate in Drinking water By Ion Chromatography with an On-Line Generated Post-Column Reagent for Sub-µg/L Bromate Analysis	BrO_3^- ClO_2^- ClO_3^-	Dionex IonPac AG9-HC + AS9-HC	9.0 mM Na_2CO_3	Suppressed conductivity + UV/Vis with KI and H_2SO_4 post column derivatization	UV/Vis: BrO_3^- - 0.06 ClO_2^- - 1.10 ClO_3^- - 0.85 Conductivity: BrO_3^- - 0.82

The interferences of chlorite are a significant problem during bromate determination. A number of procedures were investigated as a means to preferentially remove chlorite without adversely affecting bromate levels. Of these, the procedure that employs Fe(II) in acidic solution was found to be most effective. The elimination of these interference problems was the final step toward the development of the EPA Method 317.0 [54].

Considering these drawbacks, methods based on post-column derivatization and UV/Vis detection are attractive alternatives. The use of UV/Vis detection with a variety of post-column reagents, including chlorpromazine, *o*-dianisidine, fuchsine or excess bromide (or iodide) under acidic conditions, has been shown to allow sub-µg/L for bromate.

However, it is not easy to select one post-column derivatization method for bromate analysis from the various options because each option has its advantages and disadvantages.

For example, the method which uses a mixture of nitric acid, potassium bromide and *o*-dianisidine is the simplest method among the post-column derivatization techniques currently proposed [50]. Nevertheless, the *o*-dianisidine used in this method is a possible carcinogen that require special handling of waste from the system.

Chiu *et al.* [71] reported a simple and rapid method, which was based on the strong absorption of the tribromide, converted from bromide under an excess of hydrobromic acid. This procedure was used to determine bromate by using ion chromatography with post column derivatization [45, 46, 48-51]. A stable tribromide species is formed and detected by UV at 267 nm. The commonly occurring anions in typical drinking water are invisible to the detector and therefore do not interfere with analyzed bromate ions.

Sensitivity for bromate determination is improved by more than a factor of 10 through the use of post column derivatization reaction in which HI generated *in situ* from KI reacts with bromate to form the triiodide anions (I_3^-). These anions have very high molar absorbivity of 38,200 l/mol/cm at 288 nm. Chlorate, however cannot be measured by these methods due to its very low reactivity towards iodide.

Echigo *et al.* [50] described a comparison of three post column methods for the analysis of bromate in drinking water. They checked potassium iodide-ammonium heptamolybdate, *o*-dianisidine and sodium bromide-sodium nitrate methods. The three methods are all compatible with conductivity detection and bromate limits of detection were 0.17 µg/L, 0.24 µg/L and 0.19 µg/L, respectively.

Table 4. An examples of determination of bromate, chlorate and chlorite in water by ion chromatography with conductivity detection.

Columns	Eluent	Limit of detection [µg/L]	References
Dionex IonPac AG9-HC + AS9-HC	1.7 mM $NaHCO_3$ + 1.8 mM Na_2CO_3 or 9.0 mM Na_2CO_3	BrO_3^- - 1.73 ClO_2^- - 2.38 ClO_3^- - 1.07	[26]
Biotronik BT S AG + BT I ANS	1.7 mM Na_2CO_3 + 1.5 mM $NaHCO_3$	BrO_3^- - 15	[27]
Dionex IonPac AG9-HC + AS9-HC	9.0 mM Na_2CO_3	BrO_3^- - 1	[28]
Dionex IonPac AG9-SC + AS9-SC	5mM $Na_2B_4O_7$	BrO_3^- - 0.5	[29]
Dionex IonPac AG9-SC + AS9-SC	40 mM H_3BO_3 + 20 mM NaOH	BrO_3^- - 1.0	[30]
Dionex IonPac AG9-SC + AS9-SC	1.8 mM Na_2CO_3 + 1.7 mM $NaHCO_3$ or 30 mM NaOH + 120 mM H_3BO_3	Conductivity: BrO_3^- - 7.3 ClO_2^- - 3.4 ClO_3^- - 9.4 UV/Vis: BrO_3^- - 10.3 ClO_2^- - 9.4	[31]
Dionex IonPac AG11-HC + AS11-HC	11.5 mM Na_2CO_3	BrO_3^- - 0.06 ClO_3^- - 0.08	[32]
Dionex IonPac AG16 + AS16	5mM -100 mM NaOH (gradient)	BrO_3^- - 0.1 ClO_3^- - 0.6	[33]
Graphitzed carbon column	2 mM Na_2CO_3 + 1 mM TBA-OH + acetonitrile	BrO_3^- - 1	[34]
Dionex IonPac AG11-HC + AS11-HC	11.5 mM NaOH	BrO_3^- - 2.5	[35]
Dionex IonPac AG9-HC + AS9-HC	1.7 mM $NaHCO_3$ + 1.8 mM Na_2CO_3	ClO_2^- - 10.0 ClO_3^- - 5.0	[36]
Dionex IonPac AG9-HC + AS9-HC	1.7 mM $NaHCO_3$ + 1.8 mM Na_2CO_3	ClO_2^- - 10.0 ClO_3^- - 5.0	[37]
Dionex IonPac AG4A-SC + AS4A-SC	1 mM – 30 mM KOH (gradient)	BrO_3^- - 1	[38]
Dionex IonPac AG9-HC + AS9-HC	11.5 mM Na_2CO_3	BrO_3^- - 0.1 ClO_3^- - 0.9	[39]

The choice of the most convenient and the best method for determination of specific oxyhalide depends on many factors, such as: expected concentrations of analyte, sample matrix, limit of determination obtained by the method used and their availability [50, 72].

Much lower detection limits are obtained using hyphenated techniques such as ion chromatography coupled with mass spectrometry detection. When in 1986 the first paper of application of inductively coupled plasma with mass spectrometry (ICP-MS) as a multi-elemental detector for liquid chromatography was published, the number of publications in the field had been increasing exponentially [73]. ICP-MS coupling with ion chromatography offers the capability of speciation with multi-elemental detection, excellent sensitivity and detection limits, and a wide dynamic range.

The obvious disadvantages of MS-based detection techniques is that they each add considerable complexicity and significant cost to the analysis, and to date no international ion chromatography method based ion MS or ICP-MS detection has been promulgated for the regulatory monitoring of bromate or any other disinfection by-product anions.

Other combinations include ion chromatography combined with negative thermal ionization isotope dilution mass spectrometry (IC-NTI-IDMS) analysis [58] and ion chromatography coupled with electro spray ion tandem mass spectrometry (IC-MS-MS) [62]. The application of atmospheric pressure ionization mass spectrometry (API-MS), coupled with ion chromatography, showed a performance comparable to that of IC-MS/MS and IC-ICP-MS [67]. Contrary to IC-API-MS, IC-ICP-MS can tolerate a higher salt concentration in eluent, which allows the use of high-capacity columns and a larger sample volume. This lowered the detection limits by one order of magnitude for ICP-MS detection mode compare to API-MS.

Hyphenated techniques are very sensitive and single analysis is cheap, but they are highly sophisticated, and the instrumentation is very expensive. Thus, these methods are not for routine analysis.

Table 5. Examples of determination of bromate, chlorate and chlorite in water by ion chromatography with UV/Vis detection.

Columns	Eluent	Limit of detection [μg/L]	Post column derivatisation reagent	Detection wavelength [nm]	References
Dionex IonPac AG9-HC + AS9-HC	9.0 mM Na_2CO_3	BrO_3^- - 0.1	0.26 M KI + 43 μM $(NH_4)_6Mo_7O_{24}$	352	[40]
Dionex IonPac AG9-HC + AS9-HC	50 mM $Na_2B_4O_7$ + 6 mM HCOONa	BrO_3^- - 0.1	0.1 KI + 0.1 mM OsO_4 + 5 mM NaOH + 5% C_2H_5OH	288	[41]
Dionex IonPac AG12 + AS12	0.3 mM $NaHCO_3$ + 2.7 mM Na_2CO_3	BrO_3^- - 0.2	0.145 mM $NaNO_2$ + 2 M NaBr	267	[42]
Dionex IonPac AG9-HC + AS9-HC	25 mM $Na_2B_4O_7$	BrO_3^- - 0.3	Fuchsine	520	[43]
Dionex IonPac AG9-HC + AS9-HC	9.0 mM Na_2CO_3	BrO_3^- - 0.5	o-dianisidine	450	[44]
Excelpak ICS-A1G+ICS-A13x2	1.0 mM $NaHCO_3$ + 5.0 mM Na_2CO_3	BrO_3^- - 0.35	5 mg/L $NaNO_2$ + 0.5 M NaBr	268	[45]
Dionex IonPac AG9-HC + AS9-HC	9.0 mM Na_2CO_3	BrO_3^- - 0.25	0.5 M NaBr + 20 mg/L $NaNO_2$	267	[46]
Dionex IonPac AG4A-SC + AS4A-SC	2.7 mM Na_2CO_3 + 0.3 mM $NaHCO_3$	BrO_3^- - 0.1	Fuchsin	530	[47]
Dionex IonPac AG12 + AS12	2.7 mM Na_2CO_3 + 0.3 mM $NaHCO_3$	BrO_3^- - 0.2	5 mg/L $NaNO_2$ + 0.5 M NaBr	267	[48]
Excelpak ICS-A23 + ICS13	5.0 mM Na_2CO_3 + 1.0 mM $NaHCO_3$	BrO_3^- - 0.35	5 mg/L $NaNO_2$ + 0.5 M NaBr	268	[49]
Dionex IonPac AG9-HC + AS9-HC	9.0 mM Na_2CO_3	BrO_3^- - 0.17	1.0 M NaBr + 0.295 mM $NaNO_2$	267	[50]
Dionex IonPac AG9-HC + AS9-HC	9.0 mM Na_2CO_3	BrO_3^- - 0.24	o-dianisidine	450	[50]
Dionex IonPac AG9-HC + AS9-HC	9.0 mM Na_2CO_3	BrO_3^- - 0.19	0.26 M KI + 43 μM $(NH_4)_6Mo_7O_{24}$	352	[50]
Dionex IonPac AG9-HC + AS9-HC	9.0 mM Na_2CO_3	BrO_3^- - 0.05 ClO_2^- - 0.1	0.145 mM $NaNO_2$ + 2 M NaBr	267	[51]
Self-made high-capacity polystyrene-divilylbenzene copolymer.	70 mM NaOH + 0.5 mM $HClO_4$	UV/Vis: BrO_3^- - 0.7 ClO_2^- - 3.5	chlorpromazine	530	[52]
Dionex IonPac AG9-SC + AS9-SC	1.60 g of NaOH and 12.3 g of H_3BO_3 in 2 L	BrO_3^- - 0.5	chlorpromazine	530	[53]
Dionex IonPac AG9-HC + AS9-HC	9.0 mM Na_2CO_3	BrO_3^- - 0.24	o-dianisidine	450	[54]
Dionex IonPac AG9-SC + AS9-SC	40.0 mM H_3BO_3 + 20.0 mM NaOH	BrO_3^- - 0.2	chlorpromazine	525	[55]
Vydac 302 IC	1 mM potassium hydrogen-phtalate	ClO_2^- - 0.18 ClO_3^- - 0.15	direct UV	254	[56]

Another chromatographic approach for disinfection oxyhalide by-products is the application of reversed phase chromatography using commercially RP_{18} column with ion pair reagents such as tetrakisdecylammonium bromide [74] or tetrabutylammonium acetate [75].

Trace determinations of bromate in drinking waters using a flow injection system with ion-exchange column coupled with ICP-MS was reported by Elwaer *et al.* [76], Farrell *et al.* [77] and Wang *et at.* [78]. A chemiluminescent flow system for bromate determination, based on the reaction of bromate with sulphite in acid medium, is described by Silva *et al.* [79].

Table 6. Examples of determination of bromate, chlorate and chlorite in water by ion chromatography with mass spectrometry detection.

Columns	Eluent	Limit of detection [μg/L]	Mass spectrometry mode	References
Dionex IonPac AG12A + AS12A	11 mM $(NH_4)_2CO_3$	BrO_3^- - 0.67 ClO_2^- - 69 ClO_3^- - 47	ICP-MS	[57]
Column filled with Dowex AG1-X8	0.25 M NH_4NO_3	BrO_3^- 0.03 – 0.09	NTI-IDMS or ICP-MS	[58]
Dionex IonPac AS10 or AS12 or AG10 + suitable guard columns	100 mM NaOH	BrO_3^- 0.1-0.2	ICP-MS	[59]
Self-made high-capacity polystyrene-divilylbenzene copolymer.	NH_4NO_3	BrO_3^- -0.05	ICP-MS	[60]
Waters IC-Pak A	5 mM KNO_3	ClO_2^- - 500 ClO_3^- - 500	ICP-MS	[61]
Dionex IonPac AG9-SC + AS9-SC	27.5 mg/L $(NH_4)_2NO_3$ + water : methanol (10:90)	ClO_2^- - 1.0 ClO_3^- - 0.05 BrO_3^- - 0.05	IS-MS/MS	[62]
Waters IC-Pak Anion HR	5.0 mM Na_2CO_3	ClO_3^- - 0.05 BrO_3^- - 0.05	API-MS	[63]
Dionex IonPac AG9-SC + AS9-SC	27.5 mg/L $(NH_4)_2SO_4$ + water: methanol (10:90)	BrO_3^- -0.1	ESI-MS/MS	[64]
Dionex IonPac AG11-HC + AS11-HC	100 mM $(NH_4)_2NO_3$ + water: methanol (10:90)	BrO_3^- -0.13	ICP-MS	[65]
Dionex IonPac AG12A + AS12A	7.0 mM $NaHCO_3$ + 15.0 mM Na_2CO_3	BrO_3^- - 1 ClO_3^- - 1.5	ICP-MS	[66]
Waters IC – Pak Anion HR	5.0 mM Na_2CO_3	BrO_3^- -0.06	ICP-MS	[67]
Dionex IonPac AG12A + AS12A	7.0 mM $NaHCO_3$ + 15.0 mM Na_2CO_3	ClO_2^- - 4.5 ClO_3^- - 6.5	ICP-MS	[68]
Dionex IonPac AG9-SC + AS9-SC	8.0 mM $NaHCO_3$ + 8.0 mM Na_2CO_3	BrO_3^- - 0.1	ICP-MS	[55]

In 2000 an interlaboratory trial was organised involving 26 European laboratories using the draft standard ISO 15061 ion chromatography method with conductivity detection and/or alternative methods. Three alternative laboratory-based methods were developed, based on ion chromatography coupled with different detection systems: ICP-MS, colorimetry or fluorimetry. The performance data of the three methods are at least comparable to the respective data of standard ion chromatography with conductivity detection [80, 81].

To support the implementation of the European Directive, the European Commission funded a 30-month project aimed at identifying interference of the current ion chromatography with conductivity detection method, the means to remove them and automation of the pre-treatment and injection steps [55].

A comparison of ion chromatographic methods based on conductivity detection, post-column-reaction and on-line-coupling IC-ICP-MS for the determination of bromate described Schminke and Seubert [52]. The most sensitive and rugged method was shown IC-ICP-MS, followed by ion chromatography with post column derivatisation and UV/Vis detection. The lowest sensitivity is shown by the ion chromatography with conductivity detection method as the slowest method compared, which, in addition, requires a sample pretreatment.

Conclusions

All ion chromatographic methods using for bromate, chlorite and chlorate analyses have some advantages and disadvantages. The main interferences in conductivity detection method are chloride, sulphate, and bicarbonate present in the sample, which should be removed. The pretreatment consists in the removal of chloride, sulphate, carbonate and organic matter with several cartridges (respectively: On-guard -Ag, -Ba, -H and RP-forms). Less involved and time consuming than manual pretreatment are using an automatic solid phase extraction unit or evaporation techniques [32, 33].

Interesting and promising alternatives are methods based on the separation of oxyhalides by ion chromatography method and using a specific post-column derivatization with e.g. *o*-dianisidine, chlorpromazine, fuchsine, KBr, KI or Mo(VI). These methods can be carried out in series with conductometric detection allowing a double detection of oxyhalides and thus immediate confirmation. Moreover, the simultaneous separation and determination of oxyhalides and common inorganic anions is possible.

The coupling of ion chromatography with mass spectrometry detector is a fast and reliable technique which allows the determination of bromate at the level below 1 μg/L without preconcentration step. Unfortunately, these methods are still expensive and are not available for routine laboratories.

Compared to non ion chromatographic methods of bromate, chlorite and chlorate determination, ion chromatography is usually faster, more accurate and reliable, less susceptible of sample matrix and gives much more information about sample composition. Furthermore, for the moment ion chromatography is the only accepted standard method for inorganic disinfectant oxyhalide by-product analysis.

From among three groups of ion chromatography methods reviewed in this paper, all are at least comparable and comply with the requirements of the World directives concerning inorganic oxyhalide by-products in drinking water. The future application and choice of the methods will depend on equipment of laboratories and on the number and type of samples to be analyzed.

References

1. DIJK-LOOIJAARD A.M., GENDEREN J. Levels of exposure from drinking water. Food Chem. Toxicol. **38** , 37, **2000**.
2. BULL R.J., BIRNBAUM L.S., CANTOR K.P,. ROSE J.B., BUTTERWORTH B.E., PEGRAM R., TUOMISTO J. Water chlorination: essential process or cancer hazard? Fund. Appl. Toxicol. **28**, 155, **1995**.
3. BOORMAN G.A., DELLARCO V., DUNNICK J.K., CHAPIN R.E., HUNTER S., HAUCHMAN F., GARDNER H., COX M., SILLS R.C. Drinking water disinfection by-products: Review and approach to toxicity evaluation. Environ. Health Persp. **107**, 207, **1999**.
4. SONG R., DONOHOE Ch., MINEAR R., WESTERHOFF P., OZEKIN K., AMY G. Empirical modelling of bromate formation during ozonation of bromide-containing waters. Wat. Res. **30**, 1161, **1996**.
5. VAN GUNTEN U., OLIVERAS Y. Advanced oxidation of bromide-containing waters: Bromate formation mechanisms. Environ. Sci. Technol. **32**, 63, **1998**.
6. CAMEL V., BERMOND A. The use of ozone and associated oxidation process in drinking water treatment (Review). Wat. Res. **32**, 3208, **1998**.
7. AIETA E.M., ROBETS P.V. A review of chlorine dioxide in drinking water treatment. J. Am. Wat. Works Assoc. **78**, 62, **1986**.
8. KUROKAWA Y., MAEKAWA A., TAKAHASAHI M. Toxicity and carcinogenicity of potassium bromate--a new renal carcinogen. Environ. Health Perspect. **87**, 309, **1990**.
9. IARC. Some naturally occurring and synthetic food components, furocoumaris and ultraviolet radiation: potassium bromate. Monographs on the Evaluation of the Carcinogenic Risk to Human. Vol.40, Geneva, **1990**.
10. US EPA Stage 1: Disinfectants and disinfection by-products rule. A quick reference guide. EPA 816-F-01-010, **1998**.
11. Council directive concerning the quality of water intended for human consumption. Directive 98/89/CE. Commission of the European Union. Brussels, **1998**.
12. EYSSERIC H., VINCENT F., PEOC'H M., MARKA C., AITKEN Y., BARRET L. A fatal case of chlorate poisoning: Confirmation by ion chromatography of body fluids. J. Forens. Sci. **45**, 474, **2000**.
13. DABEKA R.W., CONACHER H.B.S., LAWRENCE J.F., NEWSOME W.H., McKENZIE A., WAGNER H.P., CHADHA R.K.H., PEPPER K. Survey of bottled drinking waters sold in Canada for chlorate, bromide, bromate, lead, cadmium and other trace elements. Food Add. Contamin. **19**, 721, **2002**.
14. WILLIAMS J. Anions Determination. PWN, Warszawa, **1985**. [In Polish]
15. HADDAD P.R. Comparison of ion chromatography and capillary electrophoresis for the determination of inorganic anions. J. Chromatogr. **770**, 281, **1997**.
16. MAGNUSON M.L. Determination of bromate at parts-per-trillion levels by gas chromatography mass spectrometry with negative chemical ionization. Anal. Chim. Acta. **377**, 53, **1998**.
17. JACKSON P.E. Ion chromatography in environmental analysis: [in] Encyclopedia of analytical chemistry. Wiley&Sons. Chichester, **2000**.
18. MARCHETTO A., MOSELLO R., TARTARI G.A., MUNTAU H., BIANCHI M., GEISS H., SERRINI G., LANZA G.S. Precision of ion chromatographic analyses compared with that of other analytical techniques through intercomparison exercises. J. Chromatogr. **706**, 13, **1995**.
19. ISO 15061. Water quality - Determination of dissolved bromate – Method by liquid chromatography of ions. **2001**.
20. ISO 10304-4. Water Quality - Determination of dissolved anions by liquid chromatography of ions – Part 4: Determination of chlorate, chloride and chlorite in water with low contamination. **1997**.
21. HAUTMAN D.P., MUNCH D.J., FREBIS Ch., WAGNER H.P., PEPICH B.V. Review of the methods of the US Environmental Protection Agency for the bromate determination and validation of Method 317.0 for desinfection by-product anions and low-level bromate. J.Chromatogr. **920**, 221, **2001**.
22. KAISER E., RIVIELLO J., REY M., STATLER J., HEBERLING S. Determination of trace level ions by high-volume direct-injection ion chromatography. J. Chromatogr. **739**, 71, **1996**.
23. CREED J.T., MAGNUSON M.L., MATTHEW L., BROCKHOFF C.A. Determination of bromate in the presence of brominated haloacetic acids by ion chromatography with inductively coupled plasma mass spectrometric detection. Environ. Sci. Technol. **31**, 2059, **1997**.
24. WAGNER H.P., PEPICH B.V., HAUTMAN D.P., MUNCH D.J. Performance evaluation of a method for the determina-

tion of bromate in drinking water by ion chromatography (EPA Method 317.0) and validation of EPA Method 324.0. J. Chromatogr. **884**, 201, **2000**.

25. JACKSON P.E. Determination of inorganic ions in drinking water by ion chromatography. Trend. Anal. Chem., **20**, 320, **2001**.
26. JACKSON L.K., JOYCE R.J., LAIKHTMAN M., JACKSON P.E. Determination of trace level bromate in drinking water by direct injection ion chromatography. J. Chromatogr. **829**, 187, **1998**.
27. MICHALSKI R., OLSINSKA U. The determination of bromates in water by means of ion chromatography. Acta Chrom. **6**, 127, **1996**.
28. COLOMBINI S., POLESELLO S., VALSECCHI S., CAVALLI S. Matrix effects in the determination of bromate in drinking water by ion chromatography. J. Chromatogr. **847**, 279, **1999**.
29. WEINBERG H. Pre-concentration techniques for bromate analysis in ozonated waters. J.Chromatogr. **671**, 141, **1994**.
30. JOYCE R.J., DHILLON H.S. Trace level determination of bromate in ozonated drinking water using ion chromatography. J.Chromatogr. **671**, 165, **1994**.
31. HAUTMANN D.P., BOLYYARD M. Analysis of oxyhalide disinfection by-products and other anions of interest in drinking water by ion chromatography. J.Chromatogr. **602**, 65, **1992**.
32. LIU Y.J., MOU S.F. Simultaneous determination of trace level bromate and chlorinated haloacetic acids in bottled drinking water by ion chromatography. Microchem. J. **75**, 79, **2003**.
33. LIU Y.J., MOU S.F., HERBERLING S.S. Determination of trace level bromate and perchlorate in drinking water by ion chromatography with an evaporative preconcentration technique. J. Chromatogr. **956**, 85, **2002**.
34. ISOZAKI A., SHIMAMURA H., TAKEDA S., NAGASHIMA H., OKUTANI T. Determination of trace amounts of bromate ion by ion chromatography with a graphitized carbon column. Bunseki Kagaku. **48**, 891, **1999**.
35. HUANG Y.A., MOU S.F., YAN Y.J. Determination of bromate in drinking water at the low µg/L level by column switching ion chromatography. J. Liq. Chromatogr. & Relat. Tech. **22**, 2235, **1999**.
36. TIAN F., XIE J.L. Determination of chlorine dioxide, chlorine, chlorite and chlorate in water by ion chromatography. Chin. J. Anal. Chem. **32**, 522, **2004**.
37. SACHER F., MATASCHI A., BRAUCH H-J. Analysis and occurence of bromate in raw water and drinking water. Acta Hydrochim. Hydrobiol. **23**, 26, **1995**.
38. JACKSON P.E., WEIGERT C., POHL Ch., SAINI C. A. Determination of inorganic anions in environmental waters with a hydroxide-selective column. J. Chromatogr. **884**, 175, **2000**.
39. LIU Y.J., MOU S.F. Determination of bromate and chlorinated haloacetic acids in bottled drinking water with chromatographic methods. Chemosphere. **55**, 1253, **2004**.
40. SALHI E., VON GUNTEN U. Simultaneous determination of bromide, bromate and nitrite in low µg/l levels by ion chromatography without sample treatment. Wat. Res. **33**, 3239, **1999**.
41. NOWACK B., VON GUNTEN U. Determination of chlorate at low µg/l levels by ion-chromatography with post column reaction. J. Chromatogr. **849**, 209, **1999**.
42. WEINBERG H., YAMADA H. Post-column chromatography derivatization for the determination of oxyhalides at sub-ppb levels in drinking water. Anal. Chem. **70**, 1, **1998**.
43. VALSECCHI S., ISERNIA A., POLESELLO S., CAVALLI S. Ion chromatography determination of trace level bromate by large volume injection with conductivity and spectrometric detection after post column derivatisation. J. Chromatogr. **864**, 263, **1999**.
44. WAGNER H.P., PEPICH B.V. HAUTMAN D.P., MUNCH D.J. Analysis of 500-ng/l levels of bromate in drinking water by direct-injection suppressed ion chromatography coupled with a single pneumatically delivered post-column reagent. J. Chromatogr. **850**, 119, **1999**.
45. INOUE Y., SAKAI T., KUMAGAI H., HANAOKA Y. High selective determination of bromate in ozonized water by using ion chromatography with postcolumn derivatization equipped with reagent preparation device. Anal. Chem. Acta. **346**, 299, **1997**.
46. MICHALSKI R. Toxicity of bromate ions in drinking water and its determination using ion chromatography with post column derivatisation. Pol. J. Environ. Stud. **12**, 727, **2003**.
47. ACHILLI M., ROMELE L. Ion chromatographic determination of bromate in drinking water by post-column reaction with fuchsin. J. Chromatogr. **847**, 271, **1999**.
48. WEINBERG H., YAMADA H., JOYCE R. J. New, sensitive and selective method for determining sub-µg/l levels of bromate in drinking water. J. Chromatogr. **804**, 137, **1998**.
49. YAMANAKA M., SAKAI T., KUMAGAI H., INOUE Y. Specific determination of bromate and iodate in ozonized water by ion chromatography with postcolumn derivatization and inductively-coupled plasma mass spectrometry. J. Chromatogr. **789**, 259, **1997**.
50. ECHIGO S., MINEAR R.A., YAMADA H., JACKSON P.E. Comparison of three post-column reaction methods for the analysis of bromate and nitrite in drinking water. J. Chromatogr. **920**, 205, **2001**.
51. DELCOMYN C.A., WEINBERG H.S., SINGER P.C. Use of ion chromatography with post-column reaction for the measurement of tribromide to evaluate bromate levels in drinking water. J. Chromatogr. **920**, 213, **2001**.
52. SCHMINKE G., SEUBERT A. Simultaneous determination of inorganic desinfection by-products and the seven standard anions by ion chromatography. J. Chromatogr. **890**, 295, **2000**.
53. WALTERS B.D., GORDON G., BUBNIS B. A ion chromatographic method for measuring <5 µg/L bromate ion in drinking water. Anal. Chem., **69**, 4275, **1997**.
54. WAGNER H.P., PEPICH B.V., HAUTMAN D.P., MUNCH D.J. Elimination the chlorite interference in US Environmental Protection Agency Method 317.0 permits analysis of trace bromate levels in drinking water matrices. J. Chromatogr. **884**, 309, **2000**.
55. INGRAND V., GUINAMANT J.L., BRUCHET A., BROSSE C, NOIJ T.H.M., BRANDT A., SACHER F., McLEOD C., ELWAER A.R., CROUE J.P. QUEVAUVIL-

LER P. Determination of bromate in drinking water: development of laboratory and field methods. Trend. Anal. Chem. **21**, 1, **2002**.

56. BIESAGA M., KWIATKOWSKA M., TROJANOWICZ M. Separation of chlorine-containing anions by ion chromatography and capillary electrophoresis. J. Chromatogr. **777**, 375, **1997**.
57. DIVJAK B., NOVIC M., GOESSLER W. Determination of bromide, bromate and other anions with ion chromatography and an inductively coupled plasma mass spectrometer as element-specific detector. J. Chromatogr. **862**, 39, **1999**.
58. DIEMER J., HEUAMNN K.G. Bromide-bromate speciation by NTI-IDMS and ICP-MS coupled with ion exchange chromatography. Fres. J. Anal. Chem. **357**, 72, **1997**.
59. CREED J.T., MAGNUSON M.L., PFAFF J.D., BROCKHOFF C. Determination of bromate in drinking waters by ion chromatography with inductively coupled plasma mass spectrometric detection. J. Chromatogr. **753**, 261, **1996**.
60. NOWACK M., SEUBERT A. Ultra-trace determination of bromate in drinking water by means of microbore column ion chromatography and on-line coupling with inductively coupled plasma mass spectrometry. Anal. Chim. Acta. **359**, 193, **1998**.
61. PANTSAR-KALLIO M., MANNINEN P.K.G. Speciation of halogenides and oxyhalogens by ion chromatography-inductively coupled plasma mass spectrometry. Anal. Chim. Acta. **360**, 161, **1998**.
62. CHARLES L., PEPIN D. Electrospray ion chromatography - tandem mass spectrometry of bromate at sub-ppb levels in water. J. Chromatogr. **804**, 105, **1998**.
63. AHRER W., BUCHBERGER W. Analysis of low-molecular-mass inorganic and organic anions by ion-chromatography – atmospheric pressure ionisation mass spectrometry. J. Chromatogr. **854**, 257, **1999**.
64. CHARLES L., PEPIN D., CASETTA B. Electrospray ion chromatography - tandem mass spectrometry of bromate at sub-ppb levels in water. Anal. Chem. **68**, 2554, **1996**.
65. GUO Z.X., CAI Q.T., YI Ch., YANG Z.G. Determination of bromate and bromoacetic acids in water by ion chromatography-inductively coupled plasma mass spectrometry. J. Anal. Atom. Spectrom. **18**, 1396, **2003**.
66. FERNANDEZ R.G., ALONSO J.I.G., SANZ-MEDEL A. Coupling of ICP-MS with ion chromatography after conductivity suppression for the determination of anions in natural and waste waters. J. Anal. Atom. Spectrom. **16**, 1035, **2001**.
67. SEUBERT A., SCHMINKE G., NOWACK M., AHRER W., BUCHBERGER W. Comparison of on-line coupling of ion-chromatography with atmosphere pressure ionisation mass spectrometry and with inductively coupled plasma mass spectrometry as tools for the ultra-trace analysis of bromate in surface water samples. J. Chromatogr. **884**, 191, **2000**.
68. BETTLER K. M., CHIB H. B. Determination of inorganic chlorine compounds in water by ion chromatography. J. Assoc. Off. Anal. Chem. Int. **78**, 878, **1995**.
69. KOSCIELNA H., Determination of bromate (V) in drinking water. A review. Chem.Anal. **49**, 445, **2004**.
70. WEINBERG H., DELCOMYN C.A., UNNAM V. Bromate in chlorinated drinking waters: Occurrence and implications for future regulation. Environ. Sci. Technolog. **37**, 3104, **2003**.
71. CHIU G., EUBANKS E.D. Rapid determination of bromide ions in sea water by spectrometric method. Microchim. Acta. **11**, 145, **1989**.
72. LAUBLI M., PROOST R., SEIFERT N., UNGER S., WILLE A. Bromate in drinking water - Which method to use in ion chromatography. LC GC. **6**, 17, **2003**.
73. MONTES-BAYON M., DeNICOLA K., CARUSO J.A. Liquid chromatography - inductively coupled plasma mass spectrometry (Review). J.Chromatogr. **1000**, 457, **2003**.
74. BOHME U., SCHMIDT W., DIETRICH P.G., MATSCHI A., SACHER F., BRAUCH H.J. Trace analysis of bromate and bromide with ion chromatography on coated reversed phase materials. Fres. J. Anal. Chem. **357**, 629, **1997**.
75. WARNER C.R., DANIELS D.H., JOE F.L., DIACHENKO G.W. Measurement of bromate in bottled water by high-performance liquid chromatography with post-column flow reactor detection. Food Addit. Contamin. **13**, 633, **1996**.
76. ELWAER A.R., McLEOD M.C., THOMPSON K.C. On-line separation and determination of bromate in drinking water using flow injection ICP mass spectrometry. Anal. Chem. **72**, 5725, **2000**.
77. FARRELL S., JOA J.F., PACEY G.E. Spectrophotometric determination of bromate ions using phenothiazines. Anal. Chim. Acta. **313**, 121, **1995**.
78. WANG K., LIU H., HUANG J., CHEN X., HU Z. Determination of bromate in bread additives and flours by flow injection analysis. Food Chem. **70**, 509, **2000**.
79. SILVA J.C.G.E., DIAS J.R.M., MAGALHAES J.M.C.S. Factorial analysis of a chemiluminescence system for bromate detection in water. Anal. Chim. Acta. **540**, 175, **2001**.
80. Laboratory and field methods for the determination of bromate in drinking water, EC contract SMT4-CT96-2134, EUR report, European Commission, No.1960, ISBN 92-828-9401-0, Brussels, **2000**.
81. THOMPSON K.C., GUINAMANT J.L., INGRAND V., ELWAER A.R., McLEOD C.W., SCHMITZ F., SWAEF G., QUEVAUVILLER P. Interlaboratory trial to determine the analytical state-of-the-art of bromate determination in drinking water. J. Environ. Monit. **2**, 416, **2000**.