Original Research

Occurrence of Chlorite, Chlorate and Bromate in Disinfected Swimming Pool Water

R. Michalski*, B. Mathews

Institute of Environmental Engineering of Polish Academy of Science, 34 Sklodowska-Curie Str., 41-819 Zabrze, Poland

Received: June 29, 2006
Accepted: November 10, 2006

Abstract

Swimming pool water treatment in general includes flocculation, sand filtration and subsequent disinfection. Chlorite, chlorate and bromate are disinfection by-products of swimming pool water treated by chlorine species or ozone. They are responsible for adverse effects on human health and their analyses in swimming pool water are necessary.

The simply and fast suppressed ion chromatography simultaneous separation and conductivity determination of chlorite, chlorate, bromate, fluoride, chloride, nitrate, bromide, phosphate and sulfate in disinfected swimming pool water has been described. The separation was performed on an anion-exchange column with 1.0 mM Na_2CO_3 + 3.2 mM $NaHCO_3$ as eluent, and determination by suppressed conductivity detection.

Chlorite has been found in 5 analyzed samples, chlorate in all of them, and bromate in the 2 samples originated from ozonated swimming pool water. Ions were analyzed in the wide concentrations range from 0.05 mg L^{-1} (bromate) up to 300 mg L^{-1} (chloride, sulfate). Linearity of disinfection by-products was checked up to 2.0 mg/L (chlorite), 30 mg L^{-1} (chlorate) and 0.5 mg L^{-1} (bromate) with a 50 µL injection loop (r^2= 0.9966 – 0.9985), respectively. Fluoride, chloride, nitrate, bromide, phosphate, and sulfate did not interfere with target anions.

The detection limits of ClO_2^-, ClO_3^- and BrO_3^- were on the levels: 0.19 mg L^{-1}, 0.69 mg L^{-1} and 0.006 mg L^{-1}, respectively. The mean recoveries of target anions for spiked samples were 85% – 110% and coefficient of variation of analyzed anions do not exceed 4.72%. The concentrations of inorganic disinfection by-products differ from 0.31 mg L^{-1} up to 31.92 mg L^{-1}.

Keywords: chlorite; chlorate; bromate; ion chromatography; swimming pool water

Introduction

Swimming pool water needs to be disinfected to keep swimmers from infections caused by microbial pathogens. Traditionally, sodium hypochlorite, chlorine dioxide or gaseous chlorine has been widely used for this purpose.

Unfortunately, the uses of these compounds have been reported to produce various halogenated organic compounds, since organic materials of various forms (perspiration, urine, mucus, skin particles, hair, lotion, etc.) are released into swimming pool water by swimmers [1]. In addition, most pool waters are supplied with chlorinated surface water already contaminated with disinfection by-products. In this connection extensive research for alternative disinfection methods such as ozonation has been developed.

The main hazardous inorganic oxyhalide disinfection by-products are: bromate, chlorite and chlorate. The ozonation of water containing bromide can cause the formation of bromate [2]. Chlorite is formed when chlo-

*Corresponding author; e-mail: michalski@ipis.zabrze.pl

rine dioxide is used [3], whereas chlorate is formed when chlorine, chlorine dioxide, hypochlorite or chloramine is used to disinfect raw water [4]. Chlorine dioxide oxidizes the organic matter under the formation of chlorite, which can be oxidized to chlorate by ozone or hypochlorite if a combination of chlorine dioxide and these disinfectants is used.

Chlorite, chlorate and in particular bromate have potential harmful effects for human beings. The International Agency for Research on Cancer (IARC) has concluded that chlorite is not classifiable as to its carcinogenicity to humans, though it may cause hemolytic anemia and allergic dermatitis [5].

Although the database for chlorate is less extensive than that for chlorite, it is known that the primary concern with chlorate is oxidative damage to red blood cells, and more toxic than free chlorate ions are their metabolites [6].

Next, bromate has been identified as an animal and possible human carcinogen [7]. IARC classified bromate into group B-2 as the agent is possibly carcinogenic to humans [8]. The United States Environmental Protection Agency [9], as well as the Commission of the European Communities [10], have recently issued new rules that require public water supplies to control previously unregulated microorganisms and cancer-causing disinfection by-products in final treatment of drinking water. Maximum Contaminant Level (MCL) for bromate is 10 $\mu g\ L^{-1}$. Chlorite MCL is regulated only in the US EPA guidelines and is on the level of 1000 $\mu g\ L^{-1}$.

The World Health Organization has published the guideline value of 700 $\mu g\ L^{-1}$ for chlorite and chlorate in drinking water [6]. However, WHO recommends minimizing the level of chlorate as long as there is no reliable toxicological data.

This is a reason why chlorite, chlorate and bromate should be regularly monitored not only in drinking water, but also in swimming pool water.

The determination of common inorganic anions and cations usually was carried out using chemical wet methods such as: gravimetry, titration, photometry, turbidimetry and colorimetry. Many of these methods suffer from interferences and limited sensitivity; they can be labour intensive and are often difficult to automate.

Recently the commonly used analytical method for the determination of inorganic anions and cations is ion chromatography, which has almost replaced most of the wet chemical methods used in water and waste water analyses [11].

There are several ion chromatographic standards for inorganic anion determination, including disinfection by-products such as: chlorite, chlorate and bromate recommended by ISO [12, 13], US EPA [14-17] and by ion chromatography manufactures such as Dionex [18, 19] and Metrohm [20].

These methods are designed for the determination of inorganic disinfection by-products mainly in samples with simply matrix, such as drinking water. Swimming pool water is a complex matrix due to the high content of chloride and sulfate, whose concentration can exceed 1000 mg L^{-1}. Outdoor and indoor swimming pools are popular places of human rest and activity. In this connection their monitoring is necessary.

This work describes an isocratic suppressed ion chromatography method for the simultaneous determination of: F^-, ClO_2^-, BrO_3^-, Cl^-, Br^-, ClO_3^-, NO_3^-, PO_4^{3-} and SO_4^{2-} in several indoor swimming pools water treated by chlorine species or ozone. The occurrence of inorganic by-products depending on disinfection agents used is investigated.

Experimental Procedures

Instrumentation

Ion chromatographic separations were performed on Metrohm ion chromatography system (Herisau Metrohm AG, Switzerland) consisting of: 818 IC Pump, 837 IC Eluent Degasser, 830 IC Interface, 820 IC Separation Center, Rheodyne injection valve, Metrodata 2.3 software, autosampler (838 Advanced Sample Processor), MSM suppressor, conductivity detector (819 IC) and 50 µL sample injection loop.

Reagents and Procedures

Analytical grade of Na_2CO_3 and $NaHCO_3$ used for eluent preparation and 95% H_2SO_4 as a regenerant solution were obtained from Fluka (Fluka, Steinheim, Switzerland). Standard solutions of inorganic anions were prepared by dissolving a suitable amount of salt in deonized water.

Analytical grades of KF, NaCl, $NaClO_2$, $NaClO_3$, $KBrO_3$, $NaNO_3$, KBr, K_3PO_4 and Na_2SO_4 were purchased from Fluka (Fluka, Steinheim, Switzerland). Water used in the experiments was purified using Millipore equipment (Millipore, Bedford, MA, USA) and had an electrical conductivity < 0.05 $\mu S\ cm^{-1}$.

All standard solutions were stored in a refrigerator at 2°C to 8°C. Calibration solutions of analyzed inorganic anions were prepared by diluting the stock standard solution to the required concentration just before use.

Method Optimization

Because of the high ratio of the concentration of chloride and sulfate to other anions, analytical conditions must be chosen carefully in order to simultaneous separation and detection of 9 anions in one run.

An anion-exchange column from Metrohm (Metrosep A Supp 5-250 x 4.0 mm I.D) in connection with Transgenomic Cetac 300 precolumn (100 x 7.8 mm I.D.) was used. Within the confines of method optimalization, two eluent concentrations (1.7 mM Na_2CO_3 + 1.5 mM

$NaHCO_3$ and 1.0 mM Na_2CO_3 + 3.2 mM $NaHCO_3$), and two eluent flow rates (0.7 mL min^{-1} or 1.0 mL min^{-1}) were tested. The best chromatographic performances proved for 1.0 mM Na_2CO_3 + 3.2 mM $NaHCO_3$ eluent with 0.7 mL min^{-1} flow rate.

Calibration and Method Validation

Validation based on ISO guidelines [21] was carried out in the ion chromatography method with responses for peak areas collected and evaluated. 10 calibration solutions of analyzed inorganic anions prepared in deonized water were injected into the eluent stream. The concentration ranges have been chosen according to the expected concentrations of analyzed anions in swimming pool waters. All calibration solutions were analyzed in triplicate under optimized chromatographic conditions.

The calibration curve covering the concentration range was obtained and the linear relationship between peak area and concentration were experimentally verified. Linearity of disinfection by-products was checked up to 2.0 mg L^{-1} (chlorite), 30 mg L^{-1} (chlorate) and 0.5 mg L^{-1} (bromate). Common inorganic anions (fluoride, chloride, nitrate, bromide, phosphate, and sulfate) did not interfere with target anions.

The accuracy of the method was evaluated from recovery assays, preparing samples spiked with Reference Standard Solution (AccuIon™, NIST, USA). The Limit of Detection (LOD) and the Limit of Quantification (LOQ) were calculated as six and ten times, respectively, the ratio between the standard deviation of the regression and the slope of the calibration line. Selected method validation parameters are listed in Table 1.

Results

Determination of Chlorite, Chlorate, Bromate and Six Common Inorganic Anions in Swimming Pool Water

The target anions were determined in water samples taken from 7 indoor swimming pools. In the pools under investigation, disinfection of the water was carried out either by gaseous chlorine, chlorine dioxide or hypochlorite solution (5 swimming pools) or with ozone (2 swimming pools). After sampling, samples were kept in the dark at +4°C and were analyzed within 48 hours.

Two samples – one from swimming pool water disinfected with chlorine dioxide and one by ozone – were chosen for recovery study. The analyses were carried out by spiking the samples with ClO_2^-, ClO_3^- and BrO_3^- in concentrations of 0.2 or 5.0 mg L^{-1}, respectively. The results are listed in Table 2. An example of chromatogram obtained for sample no.3 spiked with 0.2 mg L^{-1} of chlorite, bromate and chlorate is shown in Fig. 1.

Table 1. Method validation parameters.

Parameter	ClO_2^-	ClO_3^-	BrO_3^-	F^-	Cl^-	Br^-	NO_3^-	PO_4^{3-}	SO_4^{2-}
Concentration range [mg L^{-1}]	0.2-2.0	3-30	0.05-0.5	0.2-2.0	30-300	0.2-2.0	2-20	0.2-2.0	30-300
Standard deviation [mg L^{-1}]	0.08	0.31	0.003	0.04	0.69	0.06	0.28	0.43	0.44
Coefficient of variation [%]	3.09	3.12	4.72	1.37	2.53	2.04	2.62	2.73	1.60
Limit of detection [mg L^{-1}]	0.19	0.69	0.006	0.08	1.57	0.12	0.65	0.97	0.99
Limit of quantification [mg L^{-1}]	0.57	2.07	0.018	0.24	4.71	0.36	1.95	2.91	2.97
Regression coefficient (r^2)	0.9966	0.9985	0.9967	0.9997	0.9989	0.9983	0.9990	0.9993	0.9996

Table 2. Recoveries of chlorite, chlorate and bromate from spiked samples, (n=3).

Sample No	Added [mg L^{-1}]	ClO_2^-		ClO_3^-		BrO_3^-	
		Found [mg L^{-1}]	Recovery [%]	Found [mg L^{-1}]	Recovery [%]	Found [mg L^{-1}]	Recovery [%]
3	0.20	+ 0.18	90	+ 0.21	105	+ 0.22	110
	5.00	+ 4.56	91	+ 4.83	97	+ 5.27	105
7	0.20	+ 0.21	105	+ 0.18	90	+ 0.17	85
	5.00	+ 4.70	94	+ 5.31	106	+ 4.92	98

"+" - additional amount of analyzed anion

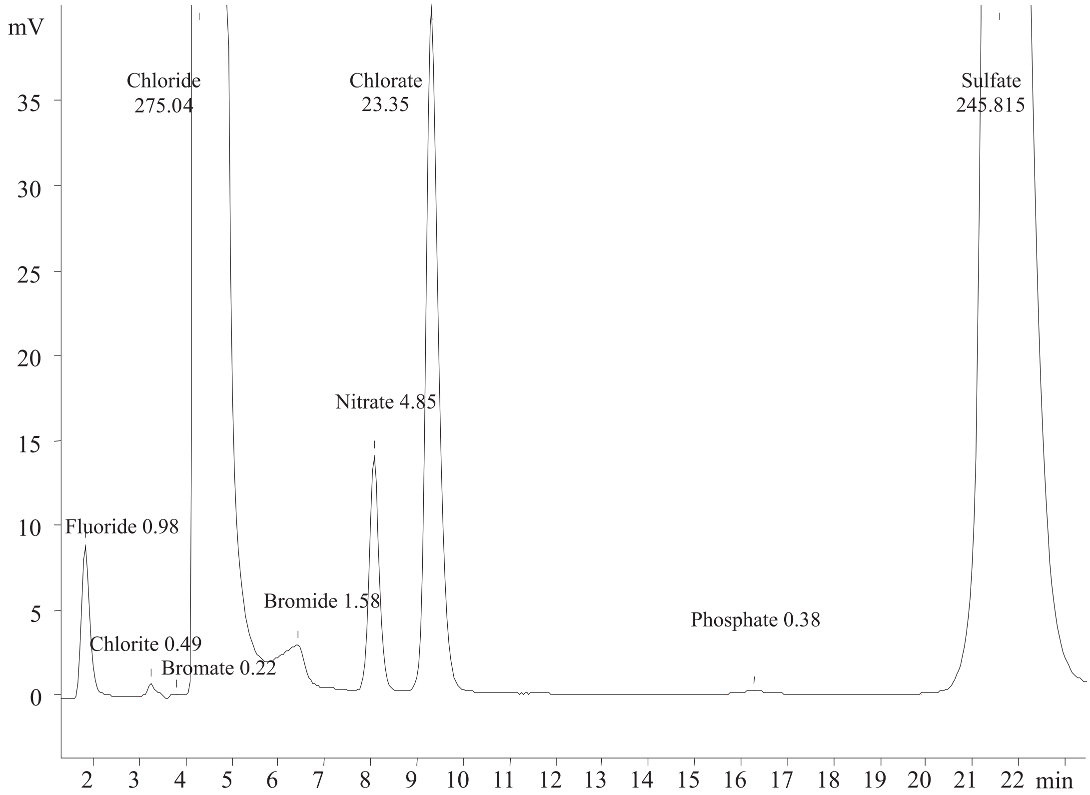

Fig. 1. Chromatogram of sample No. 3 spiked with 0.2 mg L^{-1} of chlorite, bromate and chlorate, respectively.

Table 3. Quantitative results for 9 inorganic anions in water samples from swimming pools [mg L^{-1}] (n=3).

Sample	Disinfection agent	ClO_2^-	ClO_3^-	BrO_3^-	F^-	Cl^-	Br^-	NO_3^-	PO_4^{3-}	SO_4^{2-}
1	ClO_2	0.51 ± 0.02	22.23 ± 0.85	< LOD	0.28 ± 0.01	213.71 ± 15.36	1.13 ± 0.04	4.17 ± 0.15	0.18 ± 0.03	145.58 ± 9.64
2	NaClO	2.53 ± 0.09	31.92 ± 1.02	< LOD	0.38 ± 0.02	396.11 ± 17.54	0.60 ± 0.02	5.53 ± 0.18	2.28 ± 0.06	185.97 ± 10.14
3	ClO_2	0.31 ± 0.02	23.14 ± 0.87	< LOD	0.98 ± 0.9	275.04 ± 14.21	1.58 ± 0.06	4.85 ± 0.15	0.38 ± 0.07	245.81 ± 12.06
4	ClO_2	0.71 ± 0.03	21.73 ± 0.97	< LOD	0.33 ± 0.02	415.27 ± 19.93	0.53 ± 0.04	5.71 ± 0.17	1.53 ± 0.05	266.96 ± 12.67
5	NaClO	1.60 ± 0.06	29.23 ± 1.12	< LOD	0.23 ± 0.02	213.71 ± 16.05	0.44 ± 0.03	9.25 ± 0.22	0.18 ± 0.03	145.58 ± 9.35
6	O_3	< LOD	3.21 ± 0.11	0.08 ± 0.01	2.43 ± 0.02	135.56 ± 12.67	0.09 ± 0.01	16.25 ± 0.83	1.82 ± 0.04	105.48 ± 10.17
7	O_3	< LOD	2.14 ± 0.09	0.511 ± 0.02	0.72 ± 0.05	116.23 ± 11.73	< LOD	26.34 ± 1.09	2.28 ± 0.07	98.34 ± 8.03

All samples taken from swimming pools were filtered through 0.45 µm membrane filter, and were injected into the ion chromatograph directly. Each sample was run in triplicate. The concentrations of analyzed anions including standard deviation are given in Table 3.

Discussion of Results

According to obtained results, the following can be concluded:

1. The health hazard risk for swimmers concerned with inorganic disinfection by-products (bromate, chlorite and chlorate) present in swimming pool water is common and significant. In this connection their analyses are necessary and swimmers should be informed about water quality.
2. The performance characteristics of the method were established by determining the following validation parameters: precision and accuracy, linearity, limit of detection and limit of quantification (Table 1). These data show that ion chromatography is convenient, sensitive,

reproducible, and can be used in the routine monitoring of chlorite, chlorate, and bromate, as well as other common inorganic anions in swimming pool water.
3. Application of highly selective and high capacity anion-exchange column allows for simultaneously isocratic separation and determination of 9 inorganic anions in 25 minutes in the presence of high content of chloride and sulfate. The only sample treatment was filtration.
4. The results of recovery test (Table 2) show that recovery of target anions is on the acceptable levels for environmental purposes (85-110%).
5. Chlorite has been found in 5 samples, chlorate in all of them, and bromate only in the 2 samples originated from ozonated swimming pool. Nevertheless its concentration was much higher than the imposed limit for drinking water, though swimmers only ingest the pool water occasionally.
6. Higher concentrations of chlorate were found to be associated with those pools using hypochlorite solution as a disinfectant agent. In contrast, lower chlorate and chlorite concentration were found in pools treated with chlorine dioxide. It is in good agreement with literature data [4, 22].
7. At present, the efforts of high chlorate concentrations in analyzed samples are unclear. It is therefore strongly recommended that measures should be taken to reduce chlorate level in swimming pool water.
8. In further study the stability of the inorganic disinfection by-products and changes of their concentrations depending on climate should be checked.
9. In order to keep the harmful chlorite, chlorate and bromate by-products in disinfected swimming pools at minimum levels, some actions, such as frequent water change and circulation of pool water through an appropriate filtering system, need to be taken.

References

1. KIM H., SHIM J., LEE S. Formation of disinfection by-products in chlorinated swimming pool water. Chemosphere. **46,** 123, **2002**.
2. GUNTEN U.V., OLIVERAS Y. Advanced oxidation of bromide-containing waters: Bromate formation mechanisms. Environ. Sci. Technol. **32**, 63, **1998**.
3. VESCHETTI E., CITTADINI B., MARESCA D., CITTI, G., OTTAVIANI M. Inorganic by-products in waters disinfected with chlorine dioxide. Microchem. J. **79**, 165, **2005**.
4. ERDINGER L., KIRSCH F., SONNTAG H. G. Chlorate as an inorganic disinfection by product in swimming pools. Zentral. Hyg. Umwelt. **202**, 61, **1999**.
5. SASSEVILLE D., GEOFFRION G., LOWRY R.N. Allergic contact dermatitis from chlorinated swimming pool water. Cont. Dermat. **41**, 347, **1999**.
6. WHO Guidelines for drinking-water quality, 3rd edition, chapter 12, pp. 326–328
7. KUROKAWA Y., MAEKAA A., TAKAHASAHI M. Toxicity and carcinogenicity of potassium bromate. A new renal carcinogen, Environ. Health Perspect. **87**, 309, **1990**.
8. 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**.
9. US EPA, National Primary Drinking Water Regulations, EPA 816-F-016 June **2003**.
10. Council directive concerning the quality of water intended for human consumption. Directive 98/83/CE. Commission of the EU, Brussels, **1998**.
11. MICHALSKI R. Ion Chromatography as a Reference Method for the Determination of Inorganic Ions in Water and Wastewater. Crit. Rev. Anal. Chem. **36(2)**, 107, **2006**.
12. 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.
13. ISO 15061: **2001**. Water Quality – Determination of dissolved bromate – Method by liquid chromatography of ions.
14. US EPA Method 300.1: **1997**: The Determination of inorganic anions in water by ion chromatography.
15. US EPA Method 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.
16. US EPA Method 321.8: **1997**: Determination of bromate ions in waters using ion chromatography with inductively coupled plasma mass spectrometry.
17. US EPA 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 bromate analysis.
18. Dionex Application Note 81:**1996** Determination of oxyhalides and other anions by ion chromatography using a borate-based eluent.
19. Dionex Application Note 149:**2003** 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.
20. Metrohm Application Note 74: **2004**. Determination of chlorite and bromate besides standard anions in tap water without sample pre-treatment according to EPA 317.0.
21. International Organization for Standardization, Guide to the Expression of Uncertainty in Measurement (GUM), ISO, Geneva, **1993**.
22. WANG P., LI S. F. Y., LEE H. K. Measurement of nitrate and chlorate in swimming pool water by capillary zone electrophoresis. Talanta, **45/4**, 657, **1998**.