OCCURRENCE OF CHLORITE AND CHLORATE IN SWIMMING POOL WATER

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ABSTRACT
The disinfectants used in pool water can react with other chemicals in water, leading to the formation of disinfection by-products (DBP), among which are included chlorite (ClO_2^-), chlorate (ClO_3^-) and bromate (BRO_3^-). The concentrations of these products can vary as a result of the concentration of precursor compounds, the dose of disinfectant, disinfectant residual concentration, temperature and pH.

This work had as objectives to determine the concentration of ClO_2^- ion and ClO_3^- in water from swimming pools subject to various types of treatment (stabilized chlorine compounds, hypochlorite, sodium hypochlorite in combination with UV radiation, and bromine (this only in saltwater pools) and its relation to other parameters present in water. Ion chromatography was used to determine the ions ClO_2^- and ClO_3^-. Besides ions ClO_2^-, ClO_3^-, BrO_3^- and Br^- were also evaluated the following parameters: pH, chlorine (total, free and combined), chloride, bromine, conductivity at 20°C, total organic carbon (TOC), cyanuric acid, chloroform, bromodichloromethane, dibromochloromethane and bromoform.

We analyzed 54 samples of water of indoor pools of fresh water, 18 of which were treated with sodium dichloroisocyanurate (NaDCC), 18 with sodium hypochlorite (NaClO) and 18 with sodium hypochlorite and UV radiation (NaClO + UV). We also evaluated eight samples of seawater pools, 4 of which dealt with NaDCC 4 and treated with bromine.

ClO_2^- was not detected in any sample, compared to ClO_3^-, found in the majority of samples in concentrations above the provisional guideline value of the World Health Organization (0,7 μg L^{-1}), which could set a dangerous situation to public health. The values ranged between below the limit of quantification (25 μg L^{-1}) and 26,7 μg L^{-1}. The concentrations of ClO_3^- and BrO_3^- were consistently higher in samples treated with NaClO and NaClO + UV than in samples treated with NaDCC. In the case of swimming pools with salt water, there were higher concentrations of BrO_3^- in pools treated with NaDCC than in pools treated with bromine.

This continuation of the work will allow a better understanding of the behavior of these different types of DBP before treatment of water or pools of different users, contributing to a more appropriate management of health risks in indoor pools.

Keywords	swimming pool, disinfection by-products, chlorite, chlorate.

INTRODUCTION
Water disinfection is a part of the treatment process in which pathogenic microorganisms are eliminated by chemical (such as chlorination) or physical agents (for instance, ultraviolet radiation (UV)), aiming to reduce the risk of infection to an acceptable level (WHO, 2006).

Pool water needs to be disinfected and keep disinfectant power to protect bathers from getting infections produced by bacteria eventually present in water. The pool circulating water is disinfected during the treatment process, in which all disinfected mass water has a disinfectant residual, which contributes to inactivate biologic agents transferred from bathers to water. In order disinfection occurs with any oxidizing agent, its chemical demand in treatable water must be filled maintaining a residual effect so that there's a long lasting effect of disinfection (WHO, 2006).

The disinfectants used in pool water can react with other chemicals in water, leading to the formation of disinfection by-products (DBP), among which are included chlorite (ClO_2^-), chlorate (ClO_3^-) and bromate (BRO_3^-). The concentrations of these products can vary as a result of the concentration of precursor compounds, the dose of disinfectant, disinfectant residual concentration, temperature and pH.

Erdinger *et al.*, (1999) analyzed ClO_2^- and ClO_3^- concentrations in pool waters, verifying that, although o ClO_2^- hasn't been detected, ClO_3^- concentrations varied between 1 and 40 mg L^{-1}. ClO_3^- concentrations obtained from pool samples disinfected with chlorine ranged close to 1 mg L^{-1}, but the average concentration of ClO_3^- in water treated with sodium hypochlorite (NaClO) was 17 mg L^{-1}.

Michalski *et al.*, (2007) determined ClO_2^-, ClO_3^- and BrO_3^- concentrations in five samples of water pool disinfected with gas chlorine, chlorine dioxide and NaClO, and in two swimming pools disinfected with ozone. ClO_2^- wasn't detected in the pools treated with ozone and was present in concentrations ranging between 0.31 e 2.53 mg L^{-1} in the other samples. ClO_3^- values in all the samples varied from 2.14 to 31.93 mg L^{-1}. BrO_3^- was present only in samples treated with ozone.

This work had as objectives to determine the concentration of ClO_2^- and ClO_3^- ions in water from swimming pools subjected to various types of treatment (stabilized chlorine compounds, hypochlorite, sodium hypochlorite in combination with UV radiation, and bromine (this only in pools saltwater) and its relations to other parameters present in water.

METHODS AND MATERIALS

The object of the study was the water of swimming pools in the metropolitan area of Oporto, subject to different types of water treatment and of different typologies (adults and children; leisure, sports and therapeutic). Sampling procedures were executed according to a norm of the General Directorate of Health (Circular Normativa nº 14/DA, de 21-08-2009) and the *Standard Methods for the Examination of Water and Wastewater* (APHA, 2004), and were performed by environmental health technicians working in local public health units. After the collection, all samples were taken under refrigeration conditions to the laboratory of the National Institute of Health (Instituto Nacional de Saúde Dr. Ricardo Jorge), in Oporto, where all the analytic procedures were made.

Chromatography based on EPA Method 300.1 reference standard - *Determination of inorganic anions in drinking water by ion chromatography* – was used to determine ions ClO_2^- and ClO_3^-. Besides ClO_2^-, ClO_3–, BrO_3^- and Br^-, the following parameters were also evaluated: pH, chlorine (total, free and combined), chloride, bromine, conductivity at 20°C, total organic carbon (TOC), isocyanuric acid, chloroform, bromodichloromethane, dibromochloromethane and bromoform.

The range of analytic determinations was 25 to 150 µg L^{-1}, with a quantifying limit of 25 µg L^{-1} and a detection limit of 7.6 µg L^{-1}. Precision and accuracy were inferior to 4 %. We obtained recovery averages of 97 % to ClO_2^- and of 98 % to ClO_3^-. Calculated uncertainty estimate was less than 10 %, either to ClO_2^-, or to ClO_3^-.

An internal quality control program was established to validate results in each work session, being checked the following requirements: linearity, sensitivity, retention time of control pattern, control of the response of the control pattern (independently of the calibration curb), control of blanks, control of samples duplicates, and control of the quantification limit independently of the calibration curb and recovery essay.

The water quality control parameters were analyzed according to the disinfection method that was used in the swimming pool. Each group of measurements was tested for normality, using the test of Shapiro-Wilk (Royston, 1982); the test of Levene (Fox, 1997) was used to test the homogeneity of variances between different groups of water treatment. Kruskal-Wallis test was also used to determine differences between water treatment types. Besides these, Wilcoxon test analyzed inter-group differences, and Spearman correlations inter-variable differences (for each water treatment type). A possible effect of ClO_3^- or BrO_3^- on chlorine concentrations was analyzed using linear regression, considering DBP (separately or combined) explanatory variables.

All statistics were done using CANOCO 4.5 and Primer 5 for similarity tests. For the rest of the statistical analysis was used R software.

RESULTS

We analyzed 54 samples of water from indoor pools, 18 of which were treated with sodium dichlor-oisocyanurate (NaDCC), 18 with sodium hypochlorite (NaClO) and 18 with sodium hypochlorite and UV radiation (NaClO + UV). We also evaluated eight samples of sea water pools, 4 of which disinfected with NaDCC and 4 with bromine.

ClO_2– was not detected in any sample, compared to ClO_3^-, found in the majority of samples in concentrations above the provisional guideline value of the World Health Organization (0,7 μg L^{-1}), which could pose a hazardous situation to public health. The values ranged between below the limit of quantification (25 μg L^{-1}) and 26,7 μg L^{-1}.

The concentrations of ClO_3^- and BrO_3^- were consistently higher in samples treated with NaClO and NaClO + UV than in samples treated with NaDCC. In the case of swimming pools with salt water, there were higher concentrations of BrO_3– in pools treated with NaDCC than in pools treated with bromine.

According to Kruskal-Wallis test, the averages of TOC, BrO_3^-, ClO_3^-, conductivity and chloride observed for the three different water treatment procedures presented statistical differences (α=0.05). Wilcoxon test showed that, for all water treatments, TOC values were also statistically different ($p < 0.05$).

There were also confirmed statistical differences in the results for ClO_3^- and BrO_3^- in relation to water treatments (ClO_3^-: p = 0.044 between NaDCC and NaClO, and p = 0.000 between NaDCC and NaClO.UV; BrO_3^-: p = 0.011 between NaDCC and NaClO, and p = 0.000 between NaDCC and NaClO.UV). For conductivity, statistical differences existed when comparing water treated with NaDCC and NaClO.UV (p = 0.007), and comparing NaClO and NaClO.UV (p = 0.001). In relation to chloride, we've only found statistical differences between water treatment with NaClO and NaClO.UV (p = 0.002).

Although it wasn't included in the study objectives, it was possible to conclude, in a cost analysis perspective, that it would be necessary to make 4931 laboratory essays to cover the investment costs, that is, only from that number of tests on the laboratory can obtain economic sustainability in relation to the methods used to determine ClO_2^- and ClO_3^- in water.

DISCUSSION AND CONCLUSIONS

The present work and its further development is expected to contribute to understand the behavior of the different types of DBP in relation with different types of pool water treatments or different swimming pool users, allowing to a more appropriate risk management in indoor pools.

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