



## Experimental design as a tool for studying trihalomethanes formation parameters during water chlorination



Larissa Bach<sup>a</sup>, Ellery R. Garbelini<sup>a</sup>, Sandra Stets<sup>a</sup>, Patricio Peralta-Zamora<sup>a,\*</sup>, Alexandre Emmel<sup>b</sup>

<sup>a</sup> Departamento de Química, Universidade Federal do Paraná, C.P. 19081, 81531-980, Curitiba, Brazil

<sup>b</sup> Centro Integrado de Tecnologia e Educação profissional, 81.310-010, Curitiba, Brazil

### ARTICLE INFO

#### Article history:

Received 27 March 2015

Accepted 3 July 2015

Available online 8 July 2015

#### Keywords:

Humic acid

Chlorination

Trihalomethanes

Factorial design

### ABSTRACT

Chlorination systems are widely used to ensure municipal drinking water's safety, providing defense against disease-causing organisms. However, previous studies indicated that, depending on the conditions of this treatment, a group of byproducts known as trihalomethanes (THMs), such as chloroform, may be formed and represent a considerable health risk. In this study, the effect of five variables (substrate and  $\text{ClO}^-$  concentration, presence of KBr, temperature, and pH) on THMs' formation during chlorination of aqueous solutions of humic acid is discussed using a factorial design. Results showed that in the absence of KBr, only traces of brominated THMs are produced, probably due to contamination of  $\text{ClO}^-$  by active bromine species. In the presence of KBr, the formation of chloroform is negligible, whereas within the group of brominated THMs, bromoform is produced in higher concentrations. Most relevant results are related to the existence of numerous higher-order effects, which shows the complexity of the involved reactions and also that THMs formation is not simply a function of substrate and  $\text{ClO}^-$  molar ratio but also depends on the number of reactive sites available for chlorination in the substrate.

© 2015 Published by Elsevier B.V.

### 1. Introduction

Toxic byproducts production during water disinfection by chlorination is known since the 1970s, when formation of haloforms by reaction between chlorine and natural organic matter contained in the raw water was first reported [1]. Since then, many disinfection byproducts have been identified and some of them are associated with public health risks through routes of ingestion, inhalation, and dermal absorption [2].

Over the last 40 years, many works have aimed to evaluate the effect of operational parameters on the formation of trihalomethanes (THMs) during the chlorination of water [3–7]. However, most of these studies are based on classical univariate experimental design and do not consider the interactions among all evaluated factors.

A multivariate optimization decreases the number of required experiments without loss of relevant information about the system. In particular, for factorial designs in which the number of variables are greater than four, a fractional factorial design is recommended in order to screen relevant factors and principal tendencies of each factor [8]. To perform a fractional factorial design, the number of experiments is  $2^{K-P} + C$ , where  $K$  is the number of variables,  $P$  indicates how fractionated the experimental design, is and  $C$  is the number of replicates at the central point [9].

In 2000, Judd and Black [10] studied the effect of selected variables on trihalomethanes formation in a model swimming pool, using a factorial design system. In that work, some two-order interactions were observed, which demonstrate the need to use multivariate analysis tools. Recently, Rodrigues et al. [11] has investigated the factors that affect trihalomethanes production during the chlorination of aqueous solutions of hydrophobic fulvic acids, using factorial analysis. According to them, the multivariate approach revealed to be very useful for a detailed evaluation of the disinfection process and THMs concentration prediction. Doederer et al. [2] evaluated the effect of operational parameters (reaction time, pH, and temperature) on disinfection byproducts (DBP) formation during disinfection of secondary effluent in the production of high-quality recycled water. The pH was the major influencing factor for most DBP formation, while temperature showed an influence that depends on the nature of the formed species.

Aquatic organic matter is the primary precursor of DBP [12]. However, due to the usual complexity of natural organic matter (NOM), many studies have involved the use of model substrates, including humic and fulvic acid, dihydroxyaromatic compounds, particularly meta-dihydroxybenzene structures (resorcinol),  $\beta$ -diketones, and carboxylic acids [13].

The main objective of present study was to examine, using factorial design, the effects of principal operational variables on trihalomethanes formation during chlorination of a model substrate aqueous solution. Humic acid was used as model substrate because of its high reactivity upon chlorine [14].

\* Corresponding author. Tel.: +55 41 3361 3297; fax: +55 41 3361 3186.  
E-mail address: [zamora@ufpr.br](mailto:zamora@ufpr.br) (P. Peralta-Zamora).

## 2. Experimental

### 2.1. Chemicals

Commercial humic acid (HA) was purchased from Sigma-Aldrich (Elementary analysis: 39.4% C; 4.5% H; 0.6% N).

THM  $2000 \mu\text{g mL}^{-1}$  standard solution in methanol was purchased from Supelco. Working solutions were daily prepared in ultrapure water (Milli-Q system).

Sodium hypochlorite solution and potassium bromide were purchased from VETEC. NaClO ( $106.9 \text{ g L}^{-1}$ ) solution was standardized by iodometric method before use.

Other chemicals, e.g. NaOH, HCl, and sodium thiosulphate, were analytical grade.

### 2.2. Fractional factorial design

HA degradation and THM formation during chlorination was evaluated by a two-level fractional factorial design ( $2^{5-1}$ ), including a central point assayed in quintuplicate for experimental variance estimation. Variables and levels selection (Table 1) were carried out based on literature data [15–18]. The row entries for four first variables (HA, ClO<sup>-</sup>, KBr, and T) were equivalent to a full  $2^4$  factorial design, leading to 16 runs. For the fifth variable (pH) was defined a design generator I = 12345, resulting in a relation  $5 = 1234$  (resolution V).

The factorial design was processed based on two analytical responses: (1) the fluorescence signal associated to the presence of HA and (2) the THM concentration determined by HS-GC-ECD.

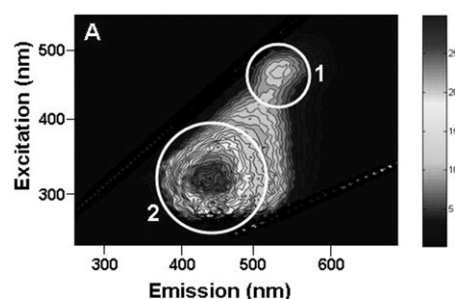
### 2.3. Chlorination procedure

Chlorination experiments were carried out following a  $2^{5-1}$  fraction factorial design, performing all possible high/low combinations of input factors (Table 1), in a total of twenty-one experiments, including the central point quintuplicate. Samples were prepared by diluting HA, adding potassium bromide stocks solution (just on required), and adjusting pH using HCl and NaOH solutions.

The temperature of the system was kept constant with a well-controlled water-bath (Lauda Brikmann, New Jersey, USA). After thermal equilibrium (20 min), the required volume of sodium hypochlorite solution was added. The reaction was carried out during 120 min and was stopped by adding sodium thiosulfate ( $2 \text{ mol L}^{-1}$ , 30  $\mu\text{L}$ ).

### 2.4. Fluorescence EEM measurements

Humic acid degradation was measured in a Hitachi F-4500 Spectrograph (Hitachi Co) in a standard 1 cm quartz cuvette, using a



**Fig. 1.** Contour plot of humic acid at pH 7: (A)  $20.0 \text{ mg L}^{-1}$ ; (B)  $10.0 \text{ mg L}^{-1}$ ; (C)  $5.0 \text{ mg L}^{-1}$ ; (D)  $3.0 \text{ mg L}^{-1}$ ; (E)  $1.0 \text{ mg L}^{-1}$ .

3D Emission-Excitation matrix. Spectra were recorded between 250 and 550 nm (excitation wavelength) and 200 and 600 nm (emission wavelength), with scanning speed of  $2400 \text{ nm min}^{-1}$  in 5 nm steps. 3-D spectra were plotted in Matlab® 7.0.1 software.

### 2.5. Gas chromatographic

THM were identified and determined by gas chromatography on an Agilent 6890 Gas Chromatograph equipped with headspace injection system, DB5 capillary column ( $30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \mu\text{m}$ ) and electron capture detector (ECD). The method was developed based on European Standard EN ISO 10301 [19], with initial oven temperature  $35 \text{ }^\circ\text{C}$  for 5 min, increase to  $150 \text{ }^\circ\text{C}$  in 2 min, increase to  $190 \text{ }^\circ\text{C}$  at a rate of  $20 \text{ }^\circ\text{C min}^{-1}$ , then maintained at  $190 \text{ }^\circ\text{C}$  during 3 min; injector temperature:  $250 \text{ }^\circ\text{C}$ ; detector temperature:  $300 \text{ }^\circ\text{C}$ ; syringe temperature:  $45 \text{ }^\circ\text{C}$ , using helium as carrier gas. Headspace extraction conditions were oven temperature:  $60 \text{ }^\circ\text{C}$ , stirring: 5 min, 250 rpm (10 s ON, 3 s OFF).

## 3. Results and discussion

### 3.1. Preliminary considerations

As already related by Valencia et al. (2013) [18], 3D-EEM fluorescence spectroscopy has been useful in the characterization of natural organic matter. Since EEM shows characteristic signals which represent its main chemical structure, then this tool can be used to assess the transformation process in the NOM structure during the chlorination.

**Table 1**  
Experimental design, factors, and corresponding levels under study.

Experiments	Humic acid (HA)	Hypochlorite (ClO <sup>-</sup> )	Potassium bromide (KBr)	Temperature (T, °C)	pH
1	-1 ( $1.0 \text{ mg L}^{-1}$ )	-1 ( $1.0 \text{ mg L}^{-1}$ )	-1 (0.0)	-1 ( $10 \text{ }^\circ\text{C}$ )	+1 (8)
2	+1 ( $5.0 \text{ mg L}^{-1}$ )	-1 ( $1.0 \text{ mg L}^{-1}$ )	-1 (0.0)	-1 ( $10 \text{ }^\circ\text{C}$ )	-1 (6)
3	-1 ( $1.0 \text{ mg L}^{-1}$ )	+1 ( $5.0 \text{ mg L}^{-1}$ )	-1 (0.0)	-1 ( $10 \text{ }^\circ\text{C}$ )	-1 (6)
4	+1 ( $5.0 \text{ mg L}^{-1}$ )	+1 ( $5.0 \text{ mg L}^{-1}$ )	-1 (0.0)	-1 ( $10 \text{ }^\circ\text{C}$ )	+1 (8)
5	-1 ( $1.0 \text{ mg L}^{-1}$ )	-1 ( $1.0 \text{ mg L}^{-1}$ )	+1 ( $1.0 \text{ mg L}^{-1}$ )	-1 ( $10 \text{ }^\circ\text{C}$ )	-1 (6)
6	+1 ( $5.0 \text{ mg L}^{-1}$ )	-1 ( $1.0 \text{ mg L}^{-1}$ )	+1 ( $1.0 \text{ mg L}^{-1}$ )	-1 ( $10 \text{ }^\circ\text{C}$ )	+1 (8)
7	-1 ( $1.0 \text{ mg L}^{-1}$ )	+1 ( $5.0 \text{ mg L}^{-1}$ )	+1 ( $1.0 \text{ mg L}^{-1}$ )	-1 ( $10 \text{ }^\circ\text{C}$ )	+1 (8)
8	+1 ( $5.0 \text{ mg L}^{-1}$ )	+1 ( $5.0 \text{ mg L}^{-1}$ )	+1 ( $1.0 \text{ mg L}^{-1}$ )	-1 ( $10 \text{ }^\circ\text{C}$ )	-1 (6)
9	-1 ( $1.0 \text{ mg L}^{-1}$ )	-1 ( $1.0 \text{ mg L}^{-1}$ )	-1 (0.0)	+1 ( $30 \text{ }^\circ\text{C}$ )	-1 (6)
10	+1 ( $5.0 \text{ mg L}^{-1}$ )	-1 ( $1.0 \text{ mg L}^{-1}$ )	-1 (0.0)	+1 ( $30 \text{ }^\circ\text{C}$ )	+1 (8)
11	-1 ( $1.0 \text{ mg L}^{-1}$ )	+1 ( $5.0 \text{ mg L}^{-1}$ )	-1 (0.0)	+1 ( $30 \text{ }^\circ\text{C}$ )	+1 (8)
12	+1 ( $5.0 \text{ mg L}^{-1}$ )	+1 ( $5.0 \text{ mg L}^{-1}$ )	-1 (0.0)	+1 ( $30 \text{ }^\circ\text{C}$ )	-1 (6)
13	-1 ( $1.0 \text{ mg L}^{-1}$ )	-1 ( $1.0 \text{ mg L}^{-1}$ )	+1 ( $1.0 \text{ mg L}^{-1}$ )	+1 ( $30 \text{ }^\circ\text{C}$ )	+1 (8)
14	+1 ( $5.0 \text{ mg L}^{-1}$ )	-1 ( $1.0 \text{ mg L}^{-1}$ )	+1 ( $1.0 \text{ mg L}^{-1}$ )	+1 ( $30 \text{ }^\circ\text{C}$ )	-1 (6)
15	-1 ( $1.0 \text{ mg L}^{-1}$ )	+1 ( $5.0 \text{ mg L}^{-1}$ )	+1 ( $1.0 \text{ mg L}^{-1}$ )	+1 ( $30 \text{ }^\circ\text{C}$ )	-1 (6)
16	+1 ( $5.0 \text{ mg L}^{-1}$ )	+1 ( $5.0 \text{ mg L}^{-1}$ )	+1 ( $1.0 \text{ mg L}^{-1}$ )	+1 ( $30 \text{ }^\circ\text{C}$ )	+1 (8)
17–21	0 ( $2.5 \text{ mg L}^{-1}$ )	0 ( $2.5 \text{ mg L}^{-1}$ )	0 ( $0.5 \text{ mg L}^{-1}$ )	0 ( $20 \text{ }^\circ\text{C}$ )	0 (7)

Download English Version:

<https://daneshyari.com/en/article/1227666>

Download Persian Version:

<https://daneshyari.com/article/1227666>

[Daneshyari.com](https://daneshyari.com)