



Factorial analysis of the trihalomethanes formation in water disinfection using chlorine

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Abstract

The factors that affect trihalomethane (THM) (chloroform, bromodichloromethane, chlorodibromomethane and bromoform) formation from the chlorination of aqueous solutions of hydrophobic fulvic acids (FA) were investigated in a prototype laboratorial simulation using factorial analysis. This strategy involved a fractional factorial design (16 plus 5 center experiments) of five factors (fulvic acids concentration, chlorine dose, temperature, pH and bromide concentration) and a Box Behnken design (12 plus 3 center experiments) for the detailed analysis of three factors (FA concentration, chlorine dose and temperature). The concentration of THM was determined by headspace analysis by GC–ECD. The most significant factors that affect the four THM productions were the following: chloroform—FA concentration and temperature; bromodichloromethane—FA concentration and chlorine dose; chlorodibromomethane—chlorine dose; and, bromoform—chlorine dose and bromide concentration. Moreover, linear models were obtained for the four THM concentrations in the disinfection solution as function of the FA concentration, chlorine dose and temperature, and it was observed that the complexity of the models (number of significant factors and interactions) increased with increasing bromine atoms in the THM. Also, this study shows that reducing the FA concentration the relative amount of bromated THM increases.
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1. Introduction

The disinfection of water is a universal practice in the drinking water treatment process used to reduce the risk of pathogenic infection. However, despite the vital relevance of this practice, several classes of disinfection by-products (DBP) have been identified in treated drinking water, which constitutes a threat to human health [1–6]. DBP constitute an important public health matter since some of them are carcinogenic and, more recently, epidemiologic studies indicate that can be also associate to reproductive and developmental problems [7–9].

Particular attention has been paid to trihalometanes (chloroform, bromodichloromethane, chlorodibromomethane and bromoform) and haloacetic acids, the two major groups of DBP

formed during the water chlorination. Indeed, among the disinfectants used, chlorine is the most common because it is effective, relatively inexpensive and allows a residual disinfection power, which is important to eliminate possible sources of contamination in the distribution system. Concern about health risks resulting from exposures to trihalomethane (THM) forced European Union to set out a new Drinking Water Quality Regulation that change the maximum levels of total THM in drinking water from 100 $\mu\text{g L}^{-1}$ to 80 $\mu\text{g L}^{-1}$ [4]. However, to comply with this directive the knowledge regarding the process of THM formation is crucial in order to adequate practices applied in municipal treatment utilities to supply safe and potable water.

Dissolved organic matter (DOM), including humic and fulvic acids (FA), have long been recognized as precursor of disinfection by-products during water treatment with chlorine [10–20]. Several studies have focused on the reaction of fulvic and humic acids with chlorine and the subsequent yield of THM, namely attempt to correlate some specific characteristics

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of organic matter, functionality and aromaticity with formation of THM [21,22]. Recently, it was discovered that different fractions of DOM react with chlorine originating different DBP [12,15,19,20]. In addition, bromide ion in raw water can also play an important role since it reacts with organic matter to form mainly brominated THM [3,4,6]. The operational parameters which influence the occurrence of THM are the chlorine dose, water temperature, pH and reaction time [21,22]. These results motivate an intense research in this area during the last years focusing in the development of mathematical models for predicting the formation of DBP [21,22]. Nevertheless, these models were mainly concerned with the prediction of total THM or chloroform production.

The objective of this study was to describe an experimental and data analysis methodology to detect the most important factors that affect the formation of the four THM during chlorine disinfection in a prototype laboratorial simulation. DOM fractions were extracted from the water of the Caldeirão dam (Guarda, Portugal) by a procedure recommended by the International Humic Substances Society and briefly consist in a reverse osmosis preconcentration step followed by XAD-8 extraction resin—this fraction is classified as hydrophobic FA [23,24]. Besides this sample of DOM, colloidal, transphilic and hydrophilic fractions will significantly influence THM formation [23,24].

The production of the four THM during disinfection is a complex process that depends on several factors that may involve interactions. In order to identify the most relevant factors and the way they influence the THM production a factorial analysis strategy was used [25–27]. Two experimental designs, based on a Fractional Factorial design of five factors (FA concentration, chlorine dose, temperature, pH and bromide ion concentration) and a Box Behnken design for the analysis of three factors (FA concentration, chlorine dose and temperature), were used to identify the most important factors in the four THM productions and in the calculation of the corresponding response surfaces. A Box Behnken design was selected because it enables to study precisely the effect of several factors and to obtain response surfaces with a relatively few experiments and with only three levels for the factors under analysis.

2. Experimental

2.1. FA sample and reagents

The FA sample was obtained from Caldeirão dam in Guarda, Portugal. The isolation process followed the procedure recommended by the International Humic Substances Society (IHSS). Briefly, a known volume of water was concentrated using a reverse osmosis system. This system comprises an electric pump, ionic exchange resins and a reverse osmosis membrane. The concentrated water collected after the osmosis process was filtered using a 0.45 μm Whatman cellulose acetate membranes and acidified to pH 2 with hydrogen chloride 6 M. Thereafter, sample was passed through a column containing XAD-8 resin and the FA adsorbed onto the resin was eluted with sodium

hydroxide 0.1 M and converted in acid form by treatment with strongly acidic-cation exchange resin.

THM (CHCl_3 , chloroform; CHBrCl_2 , bromodichloromethane; CHBr_2Cl , dibromochloromethane; and CHBr_3 , bromoform) 200 $\mu\text{g mL}^{-1}$ standard solution in methanol (SUPELCO, Bellefonte, USA) was used for the preparation of the aqueous standard solutions in the $\mu\text{g L}^{-1}$ range (0.5–10 $\mu\text{g L}^{-1}$).

All reagents were of analytical quality but sodium hypochlorite used was a commercial solution (100 mg L^{-1}).

2.2. Laboratorial simulation of a water disinfection process

The disinfection of a water containing DOM followed the following steps: (a) put a reaction vessel of 250 ml volume, with an aqueous solution of FA (concentrations of 0.5, 2.7, and 5 mg L^{-1}), in a water bath at a constant temperature; (b) addition to the FA solution of a volume of sodium chloride to get a final concentration of 10 mg L^{-1} of chloride ion and a pre-determined volume of potassium bromide (final concentration of 0.1, 0.6, and 1.1 mg L^{-1}); (c) pH adjustment with hydrogen chloride and/or sodium hydroxide to a pre-determined value (pH 6.0, 7.0 and 8.0); (d) addition of a pre-determined amount of sodium hypochlorite to begin the disinfection reactions; (e) the sample is kept in a constant temperature water bath and 20.00 mL were removed at times zero (after sodium hypochlorite addition), 15 min and 60 min to perform the THM analysis (after the collection 30 μL of a solution 2 M sodium tiosulphate was added to eliminate the free chlorine); (f) free chlorine was analysed in all samples using a portable photometer kit (ELE International Limited, England).

2.3. THM GC analyses

Gas chromatographic analyses were performed with a Chrompack CP9003 GC gas chromatograph equipped with a ^{63}Ni electron capture detector and a split/splitless injector. The column used was a Chrompack CP-Sil 13CB (25 m \times 0.32 mm, 1.2 μm) fused-silica column [28]. Headspace analysis and GC-ECD parameters are shown in Table 1.

2.4. Data analysis

All calculations were done using peak areas obtained from the recorded chromatogram using Chrompack CP-Maitre I/II software (version 2.5).

Experimental design formulation and the corresponding analysis of the effects (ANOVA) and response surface calculations were done using The Unscramble v9.2 (CAMO PROCESS AS, Oslo, Norway).

3. Results and discussion

3.1. Preliminary analysis

To obtain information about the THM production process several disinfection simulations were programmed based on two

Table 1
GC–ECD parameters for THM determination

Parameter	Value
GC parameters	
Injector temperature operating in split/splitless mode (°C)	200
ECD Temperature (°C)	280
Volume of the overhead sample injected (mL)	1
Carrier gas	High purity helium (1 mL min ⁻¹)
Head space pressure of carrier gas (kPa)	175
Makeup gas	High purity nitrogen (50 mL min ⁻¹)
Oven program temperature	
Initial temperature (first 3 min) (°C)	60
Temperature raising up to 70 °C (°C min ⁻¹)	4
Constant temperature for 2 min (°C)	70
Temperature raising up to 100 °C (°C min ⁻¹)	4
Constant temperature for 5 min (°C)	100
Headspace analysis	
Volume of the sample (mL)	20
Volume of Na ₂ SO ₄ saturated solution added to the sample (mL)	1
Volume of the flask (mL)	40
Temperature (°C)	30
Time (min)	30

different experimental designs: (i) a screening analysis, based on a fractional factorial design, focus on the analysis of the five factors: FA concentration, chlorine dose, temperature, pH and bromide ion concentration; (ii) a Box Behnken design focus on the three factors that have natural variability (FA concentration and water temperature) and can be controlled in the water treatment station under investigation (chlorine dose).

Synthetic aqueous solutions were prepared containing predetermined concentrations of chloride and bromide ions (Table 2).

Table 2
Experimental designs, factors and corresponding levels under research

Factor ^a	Levels		
Fractional factorial design (16 plus 5 center experiments)			
FA concentration (FA) (mg L ⁻¹)	0.50	2.75	5.00
Bromide concentration (Br) (mg L ⁻¹)	0.10	0.55	1.00
Chlorine (Cl) (μL) ^b	5	17.5	30
pH	6.0	7.0	8.0
Temperature (T) (°C)	8.0	16.5	25.0
Box Behnken design (12 plus 3 center experiments)			
FA concentration (FA) (mg L ⁻¹)	0.50	2.75	5.00
Chlorine (Cl) (μL) ^b	5	17.5	30
Temperature (T) (°C)	8.0	16.5	25.0

^a A constant background concentration of 10 mg L⁻¹ chloride is present in all samples.

^b This factor corresponds to the volume of sodium hypochlorite solution (20 mg L⁻¹) added (corresponding to a concentration of 0.4, 1.4 and 2.4 mg L⁻¹) originating a final free chlorine concentration (after disinfection) between 0.02 and 0.91 mg L⁻¹.

The concentrations were based on the normal values of these substances in natural waters and on information about the composition of the water of the Caldeirão Dam. The temperature range used in this study (from 8 °C to 25 °C) corresponds to the annual water temperature amplitude that is observed in this region.

The amount of sodium hypochlorite used to simulate the disinfection process was subject to a preliminary study to adjust its quantity to an excess quantity in order to allow for a residual amount of free chlorine in the samples after disinfection. The minimum amount of sodium hypochlorite was found to be 5 μL (corresponding to a total concentration of 0.4 mg L⁻¹) which originated a free chlorine residual of at least 0.02 mg L⁻¹. Higher levels for the amount of sodium hypochlorite used for disinfection were generated accordingly (Table 2). With these quantities of sodium hypochlorite the residual amount of free chlorine observed after disinfection (a few minutes after addition of sodium hypochlorite) was between 0.02 and 0.91 mg L⁻¹. These values did not decrease markedly after 90 min of subsequent reaction.

The analysis of THM in the designed samples showed a quite variable concentration of the four THM:CHCl₃ varies its concentration between 0.2 and 7.6 μg L⁻¹; CHBrCl₂ varies its concentration between 1.7 and 7.3 μg L⁻¹; CHBr₂Cl varies its concentration between 0.1 and 6.1 μg L⁻¹; and CHBr₃ varies its concentration between 1.2 and 19 μg L⁻¹. The concentration of the four THM in each sample did not change during the 90 min that followed the addition of sodium hypochlorite. This result agrees with the constancy of the free chlorine in the samples in the same period of time and suggests that the disinfection reactions are quite rapid, resulting in the formation of THM in the few minutes after sodium hypochlorite addition.

3.2. Fractional factorial design

Table 2 shows the five factors and levels used in the experimental designs. In this first analysis the five factors were studied and a fractional factorial design was used (16 plus 5 center experiments).

Table 3 shows the analysis of the effects of the five parameters on the four THM productions using the fractional factorial design experiments (experimental error estimated from replicated centre samples). From the analysis of this table the following conclusions can be drawn:

Table 3
Qualitative analysis of the effects of the five parameters on the four THM productions using the fractional factorial design experiments (experimental error estimated from replicated centre samples)^a

Factor	CHCl ₃	CHBrCl ₂	CHBr ₂ Cl	CHBr ₃
FA concentration	+	++	+++	++
Bromide concentration	--	NS	++	+++
Chlorine	+	++	+++	+++
pH	+	NS	++	NS
Temperature	---	NS	++	+

^a NS, not significant; the number of (+) and (-) signs indicates the degree of significance.

Table 4
ANOVA for the analysis of the effects of the CHCl_3 production response obtained using a Box Behnken designs^a

Effect	SS	d.f.	MS	<i>F</i>	<i>p</i> -value	β	S.E. _{β}
Model	31.135	9	3.459	3.063	0.1152		
Error	5.647	5	1.129				
Adjusted total	37.781	15	2.627				
Factor							
Intercept	36.715	1	36.715	32.510	0.0023	3.498	0.614
FA	23.134	1	23.134	20.485	0.0062	0.756	0.167
Cl	2.249	1	2.249	1.992	0.2173	0.042	0.030
<i>T</i>	2.926	1	2.926	2.591	0.1684	0.071	0.044
FA × Cl	0.187	1	0.187	0.165	0.7012	0.123	0.304
FA × <i>T</i>	0.701	1	0.701	0.621	0.4663	0.239	0.304
Cl × <i>T</i>	0.395	1	0.395	0.350	0.5798	0.180	0.304
FA × FA	0.068	1	0.068	0.061	0.8154	−0.078	0.316
Cl × Cl	0.421	1	0.421	0.372	0.5684	−0.193	0.316
<i>T</i> × <i>T</i>	1.202	1	1.202	1.064	0.3496	−0.326	0.316
Model check							
Main	28.310	3	9.437				
Int	1.284	3	0.428	0.379	0.7730		
Int + Squ	1.541	3	0.514	0.455	0.7254		
Squ	1.541	3	0.514	0.455	0.7254		
Error	5.647	5	1.129				
Lack of Fit	5.612	3	1.871	109.125	0.0091		
Lack of Fit	0.034	2	0.017				
Pure error	5.647	5	1.129				

^a SS, sum of squares; d.f., degrees of freedom; MS, mean squares; *F*, Fisher ratio; *p*-value, probability of getting the *F*-ratio under the null hypothesis; β , regression coefficient from a multiple linear regression analysis; S.E. _{β} , standard error of β .

Table 5
ANOVA for the analysis of the effects of the CHBrCl_2 production response obtained using a Box Behnken designs^a

Effect	SS	d.f.	MS	<i>F</i>	<i>p</i> -value	β	S.E. _{β}
Model	42.785	9	4.754	3.294	0.1012		
Error	7.215	5	1.443				
Adjusted total	50.000	14	3.571				
Factor							
Intercept	59.668	1	59.668	41.350	0.0014	4.460	0.694
FA	21.716	1	21.716	15.049	0.0116	0.732	0.189
Cl	7.122	1	7.122	4.935	0.0770	0.075	0.034
<i>T</i>	1.352	1	1.352	0.937	0.3775	0.048	0.050
FA × Cl	0.681	1	0.681	0.472	0.5226	0.236	0.343
FA × <i>T</i>	1.223	1	1.223	0.848	0.3995	−0.316	0.343
Cl × <i>T</i>	0.236	1	0.236	0.164	0.7026	0.139	0.343
FA × FA	0.012	1	0.012	0.082	0.9312	0.032	0.357
Cl × Cl	8.036	1	8.036	5.569	0.0648	−0.843	0.357
<i>T</i> × <i>T</i>	1.734	1	1.734	1.202	0.3229	0.392	0.357
Model check							
Main	30.190	3	10.063				
Int	2.140	3	0.713	0.494	0.7017		
Int + Squ	10.454	3	3.485	2.415	0.1823		
Squ	10.454	3	3.485	2.415	0.1823		
Error	7.215	5	1.443				
Lack of fit	7.197	3	2.399	268.804	0.0037		
Lack of fit	0.018	2	0.009				
Pure error	7.215	5	1.443				

^a See footnote of Table 4.

Table 6
ANOVA for the analysis of the effects of the CHBr₂Cl production response obtained using a Box Behnken designs^a

Effect	SS	d.f.	MS	F	p-value	β	S.E. _{β}
Model	39.198	9	4.355	5.013	0.0453		
Error	4.344	5	0.869				
Adjusted total	43.542	15	3.110				
Factor							
Intercept	47.897	1	47.897	55.125	0.0007	3.996	0.538
FA	5.811	1	5.811	6.688	0.0491	0.379	0.146
Cl	11.107	1	11.107	12.784	0.0160	0.094	0.026
T	5.591	1	5.591	6.435	0.0521	0.098	0.039
FA × Cl	0.404	1	0.404	0.466	0.5254	0.182	0.266
FA × T	0.229	1	0.229	0.264	0.6296	-0.137	0.266
Cl × T	0.784	1	0.784	0.902	0.3857	0.253	0.266
FA × FA	4.929	1	4.929	5.673	0.0630	-0.660	0.277
Cl × Cl	11.298	1	11.298	13.003	0.0154	-1.000	0.277
T × T	0.007	1	0.007	0.008	0.9339	-0.024	0.277
Model check							
Main	22.509	3	7.503				
Int	1.418	3	0.473	0.544	0.6732		
Int + Squ	15.271	3	5.090	5.859	0.0431		
Squ	15.271	3	5.090	5.859	0.0431		
Error	4.344	5	0.869				
Lack of fit	4.222	3	1.407	22.054	0.0419		
Lack of fit	0.122	2	0.061				
Pure error	4.344	5	0.869				

^a See footnote of Table 4.

- (i) The FA concentrations contribute to the increase of the total THM production. This result was expected because FA is the reactant that originates THM [1,14–20].
- (ii) The higher concentration of bromide in the disinfection solution the higher the amount of bromated THM and

smaller is the concentration of chloroform. Considering the chemical processes behind THM production, this result was expected because the higher bromide concentration the production of bromated THM is increased [3,4,6] and, consequently, that of chloroform is reduced.

Table 7
ANOVA for the analysis of the effects of the CHBr₃ production response obtained using a Box Behnken designs^a

Effect	SS	d.f.	MS	F	p-value	β	S.E. _{β}
Model	23.976	9	2.664	3.255	0.1034		
Error	4.092	5	0.818				
Adjusted total	28.068	15	2.005				
Factor							
Intercept	49.696	1	49.696	60.721	0.0006	4.070	0.522
FA	2.406	1	2.406	2.940	0.1471	-0.244	0.142
Cl	2.975	1	2.975	3.634	0.1149	0.049	0.026
T	4.595	1	4.595	5.615	0.0640	0.089	0.038
FA × Cl	0.006	1	0.006	0.007	0.9370	0.021	0.258
FA × T	4.608	1	4.608	5.631	0.0637	-0.613	0.258
Cl × T	0.176	1	0.176	0.215	0.6625	0.120	0.258
FA × FA	2.385	1	2.385	2.914	0.1485	-0.459	0.269
Cl × Cl	7.159	1	7.159	8.747	0.0316	-0.796	0.269
T × T	0.038	1	0.038	0.046	0.8380	-0.058	0.269
Model check							
Main	9.976	3	3.225				
Int	4.790	3	1.598	1.951	0.2398		
Int + Squ	9.210	3	3.070	3.751	0.0944		
Squ	9.210	3	3.070	3.751	0.0944		
Error	4.092	5	0.818				
Lack of fit	4.037	3	1.347	48.922	0.0201		
Lack of fit	0.055	2	0.028				
Pure error	4.092	5	0.818				

^a See footnote of Table 4.

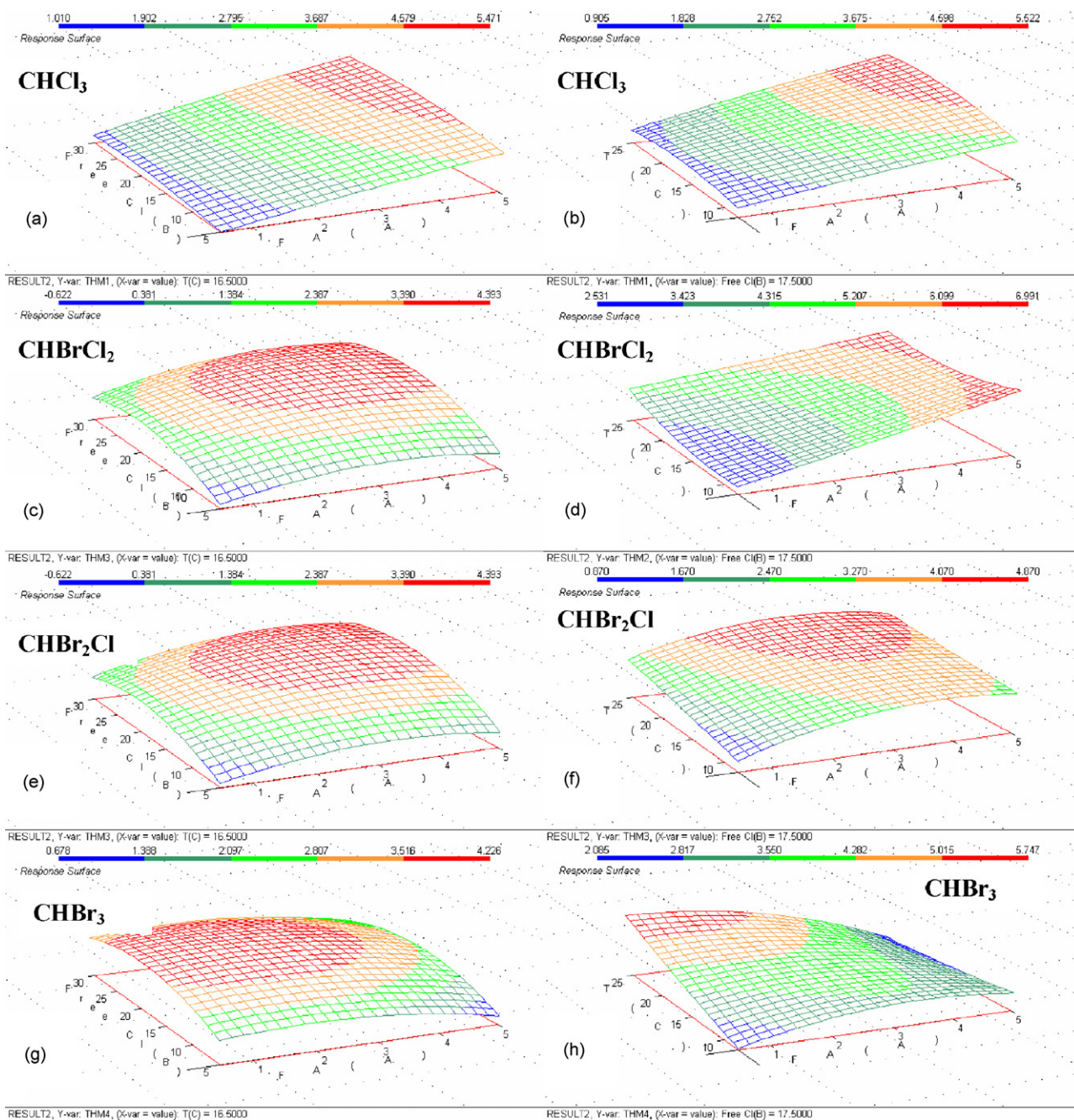


Fig. 1. Response surfaces for the four THM productions based on the Box Behnken design experiments: Cl vs. FA (a, c, e, g); T vs. FA (b, d, f, h).

- (iii) The higher the amount of chlorine used in the disinfection the higher the amount of THM. This result is similar to that of FA because this factor and chlorine are the two main reagents in total THM production and agrees with literature results [1,21,22].
- (iv) Although the pH of the solution has no clear trend in the amount of THM production there is some tendency to increase with the pH, which agrees with literature results [1,21,22].
- (v) Increasing the temperature provokes a decrease in the concentration of chloroform but an increase in the concentration of the bromated THM. A global increase of the THM pro-

duction with the temperature would be expected but, due to the volatility of chloroform this THM escapes from the disinfected solution before analysis [1,21,22]. However, the amount of the less volatile bromated THM increases.

3.3. Response surface analysis of the production of the four THM

In order to obtain more rigorous information about the production of THM in the water treatment station in the Caldeirão Dam, a Box Behnken design was performed for the factors FA, Cl and T (Table 2). The range of these factors is similar to that

Table 8
ANOVA for the analysis of the effects of the total THM production response obtained using a Box Behnken designs^a

Effect	SS	d.f.	MS	<i>F</i>	<i>p</i> -value	β	S.E. _{β}
Model	366.933	9	40.770	4.817	0.0491		
Error	42.317	5	8.463				
Adjusted total	409.250	15	29.232				
Factor							
Intercept	770.288	1	770.288	91.013	0.0002	16.024	1.680
FA	106.697	1	106.697	12.607	0.0164	1.623	0.457
Cl	85.116	1	85.116	10.057	0.0248	0.261	0.082
<i>T</i>	54.488	1	54.488	6.438	0.0521	0.307	0.121
FA × Cl	3.875	1	3.875	0.458	0.5287	0.562	0.831
FA × <i>T</i>	8.373	1	8.373	0.989	0.3656	−0.827	0.831
Cl × <i>T</i>	5.854	1	5.854	0.692	0.4435	0.691	0.831
FA × FA	15.343	1	15.343	1.813	0.2360	−1.165	0.865
Cl × Cl	90.634	1	90.634	10.709	0.0221	−2.831	0.865
<i>T</i> × <i>T</i>	0.112	1	0.112	0.013	0.9130	0.099	0.865
Model check							
Main	246.301	3	82.100				
Int	18.102	3	6.034	0.713	0.5850		
Int + Squ	102.530	3	34.177	4.038	0.0835		
Squ	102.530	3	34.177	4.038	0.0835		
Error	42.317	5	8.463				
Lack of fit	42.135	3	14.045	153.971	0.0065		
Lack of fit	0.182	2	0.091				
Pure error	42.317	5	8.463				

^a See footnote of Table 4.

used in the previous design because these are the values usually found in real systems. The concentration of the bromide ion was kept constant to a relatively low value (0.10 mg L^{−1}) because the water system under investigation is a dam located in a mountain in the interior of Portugal where there are no geological source of bromide ions. Also, the pH was kept at a constant value (pH 7.0) because it is the normal operational value used in the water station treatment plant.

Tables 4–7 present the ANOVA of the effects of the individual THM productions. These tables also include the beta-regressions coefficients and corresponding standard deviations resulting from the fitting of the THM productions to a linear model. Taking into consideration only the variables that have beta-regression coefficients higher than the correspondent standard deviations the following models were obtained:

$$\text{CHCl}_3 (\mu\text{g L}^{-1}) = 3.5 + 0.8 \text{FA} + 0.02 \text{Cl} \\ + 0.07 T - 0.3 T^2$$

$$\text{CHBrCl}_2 (\mu\text{g L}^{-1}) = 4.5 + 0.7 \text{FA} + 0.04 \text{Cl} \\ - 0.8 \text{Cl}^2 + 0.4 T^2$$

$$\text{CHBr}_2\text{Cl} (\mu\text{g L}^{-1}) = 4.0 + 0.4 \text{FA} + 0.05 \text{Cl} + 0.1 T \\ - 0.7 \text{FA}^2 - 1.0 \text{Cl}^2$$

$$\text{CHBr}_3 (\mu\text{g L}^{-1}) = 4.0 - 0.2 \text{FA} + 0.03 \text{Cl} + 0.09 T \\ - 0.6 \text{FA} \times T - 0.5 \text{FA}^2 - 0.8 \text{Cl}^2$$

The factors FA and Cl are present in the four equations but the corresponding coefficient show different trends: FA coefficient decreases its magnitude from 0.8 for CHCl₃ to −0.2 for CHBr₃; Cl coefficient holds approximately constant. This result shows that the concentration of FA and the amount of chlorine affect the production of the four THM. Moreover, increasing the concentration of FA provokes an increase on the production of the less bromated THM but a decrease on the production of the more bromated THM, particularly bromoform. Also, the analysis of these models (and Tables 4–7) shows that only for the production of CHBr₃ (bromoform) an interaction term is significant (between FA and *T*) and, consequently for the other THM, the factors can be studied and optimized independently one at a time. Also, the observation of these four models shows that their complexity (number of significant factors and interactions) increases with increasing bromine atoms in the THM.

A global analysis of Tables 4–7 shows a significant lack of fit suggesting a model miss-adjustment. Nevertheless, this result may be due to the relative high precision of the THM concentration measurements [27]. Even though, if a model miss-adjustment exists, the information about the effects on the THM productions is still valid. Also, a comparative analysis of the models obtained for the four THM shows an increase model complexity, i.e., more significant factors and interactions, as the number of bromines increase in THM.

Fig. 1 shows the response surface of THM production as function of the three factors. One common characteristic feature of these response surfaces is the displacement of the maximum of THM production (from CHCl₃, chloroform, up to CHBr₃, bromoform) towards lower FA concentration. This result shows

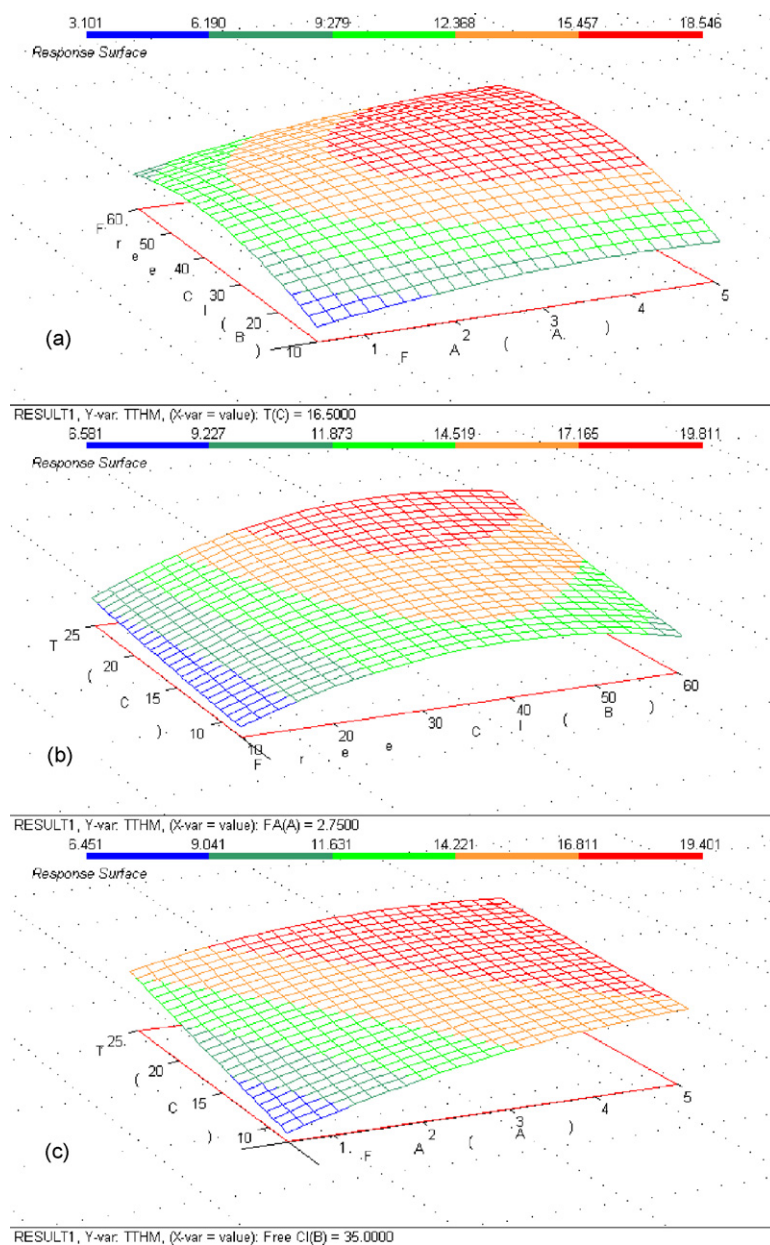


Fig. 2. Response surfaces for the total THM production based on the Box Behnken design experiments: Cl vs. FA (a); T vs. Cl (b); T vs. FA (c).

that reducing the amount of FA concentration the relative amount of bromated THM increases.

3.4. Response surface analysis of the production of the total THM

Although the previous information is important for the comprehension of the factors that affect the individual THM, current EU regulation considers the sum of all the four THM and, consequently, the effect of the factors FA, Cl and T on the total THM production was analysed. Table 8 presents the ANOVA of the effects of the total THM production and Fig. 2 shows the response surface of the total THM production as function of the three factors. Taking into consideration only the variables that

have beta-regression coefficients higher than the correspondent standard deviations the following model was obtained:

$$\text{Total THM } (\mu\text{gL}^{-1}) = 16.0 + 1.6\text{FA} + 0.1\text{Cl} + 0.3\text{T} \\ - 0.8\text{FA} \times \text{T} - 1.2\text{FA}^2 - 2.8\text{Cl}^2$$

The analysis of Table 8 and Fig. 2 show that the amount of FA is the most important factor and the higher the concentration the higher the total THM production. A marked quadratic dependence of the total THM production on the amount of free chlorine is observed with a Cl value at the maximum of the response surface at about 20 μL . Although less significant, the temperature also affects the total THM production originating higher productions as it is increased.

4. Conclusions

The factorial analysis of the disinfection process revealed to be a particularly useful approach for its detailed understanding. Indeed, the obtained information confirmed previous information about chlorine disinfection that exists in the literature, and allowed to obtain further information about the underlying models for the four THM productions.

The information obtained about the effect of the concentration of FA (DOM) is quite important. The higher the FA concentration the higher the amount of less bromated THM are produced and the lower the amount of bromated THM. This result is relevant in risk assessment analysis because the four THM have different toxicities. Indeed, under a set of water and process conditions, the risk should be minimized, i.e. the concentration of the less toxic species should be minimized.

The factor temperature, which is an environmental factor, has also an interesting effect on THM production. Apparently it increases the speed of THM production. However, it also decreases their solubility, particularly of the most volatile (less bromated THM). In the summer, when the water temperature is relatively high (above 20 °C), the simple aeration of the water after chlorination would reduce the amount of the most volatile THM (and other volatile organochloride species). Independently of the time of the year, this operation would always reduce the amount of THM in the distributed water.

The amount of free chlorine used in disinfection should be reduced to a minimum because the production of THM is positively correlated to that amount. However, residual free chlorine must be present in the water after chlorination to account for any contamination in the water distribution network.

Raw water having relatively high amounts of bromide, for example groundwater near coastal sea areas or desalted water, will originate relatively high amounts of bromated THM species. In this case, water pre-processing to selectively remove bromide ions would be advisable.

Nevertheless, the models found in this work will not represent a real situation because only one fraction of DOM was analysed. Also, the validation of an overall model should be made by performing experiments in a water treatment station under controlled conditions. This work is currently in progress.

References

- [1] R. Garcia-Villanova, C. Garcia, J. Gomez, M. Garcia, R. Ardanuy, *Water Res.* 31 (1997) 1299.
- [2] R. Garcia-Villanova, C. Garcia, J. Gomez, M. Garcia, R. Ardanuy, *Water Res.* 31 (1997) 1405.
- [3] S.D. Richardson, A.D. Thruston, T.V. Caughran, P.H. Chen, T.W. Collete, K.M. Schenck, B.W. Lykins, C.R. Acha, V. Glezer, *Water Air Soil Pollut.* 123 (2000) 95.
- [4] T.K. Nissinen, I.T. Miettinen, P.J. Martikainen, T. Vartiainen, *Chemosphere* 48 (2002) 9.
- [5] S.D. Richardson, *Trends Anal. Chem.* 22 (2003) 666.
- [6] A. Astel, M. Biziuk, A. Przyjazny, J. Namiesnik, *Water Res.* 40 (2006) 1706.
- [7] M.J. Nieuwenhuijsen, M.B. Toledano, N.E. Eaton, P. Elliott, *Occup. Environ. Med.* 57 (2000) 73.
- [8] L. Attias, A. Contu, A. Massiglia, P. Valente, G.A. Zapponi, *Sci. Total Environ.* 171 (1995) 61.
- [9] W.H. Glaze, J.B. Andelman, R.J. Bull, R.B. Conolly, C.D. Hertz, R.D. Hood, R.A. Pegram, *Environ. Health Perspect.* 110 (2002) 1013.
- [10] B. Legube, J.P. Croue, M. Doré, *Sci. Total Environ.* 47 (1985) 217.
- [11] C.E. Rostad, B.S. Martin, L.B. Barber, J.A. Leehneer, S.R. Daniel, *Environ. Sci. Technol.* 34 (2000) 2703.
- [12] J.A. Leehneer, C.E. Rostad, L.B. Barber, R.S. Schroeder, R. Anders, M.L. Davisson, *Environ. Sci. Technol.* 35 (2001) 3869.
- [13] G.V. Korshin, W.W. Wu, M.M. Benjamin, O. Hemingway, *Water Res.* 36 (2002) 3273.
- [14] D. Nikolaou, S.K. Golfinopoulos, T.D. Lekkas, M.N. Kostopoulou, *Environ. Monitor. Assess.* 93 (2004) 301.
- [15] J.A. Leenheer, *Water Sci. Technol.: Water Supply* 4 (2004) 1.
- [16] P. Westerhoff, P. Chao, H. Mash, *Water Res.* 38 (2004) 1502.
- [17] C. Uyguner, C. Hellriegel, W. Otto, C. Larive, *Anal. Bioanal. Chem.* 378 (2004) 1579.
- [18] J. van Leeuwen, R. Daly, M. Holmes, *Desalination* 176 (2005) 81.
- [19] H.C. Kim, M.J. Yu, *Water Res.* 39 (2005) 4779.
- [20] Z.Y. Zhao, J.D. Gu, X.J. Fan, H.B. Li, *J. Haz. Mat.* B314 (2006) 60.
- [21] J. Sohn, G. Amy, J. Cho, Y. Lee, Y. Yoon, *Water Res.* 38 (2004) 2461.
- [22] S. Radiq, M.J. Rodriguez, *Sci. Total Environ.* 321 (2004) 21.
- [23] J.A. Leehneer, J.P. Croué, *Environ. Sci. Technol.* 37 (2003) 18A.
- [24] S. Hiradate, T. Yonezawa, H. Takesako, *Geoderma* 132 (2006) 196.
- [25] J.C.G. Esteves da Silva, J. Dias, J. Magalhaes, *Anal. Chim. Acta* 450 (2001) 175.
- [26] P.B.M. Pinheiro, J.C.G. Esteves da Silva, *Anal. Bioanal. Chem.* 382 (2005) 341.
- [27] S.N. Deming, S.L. Morgan, *Experimental Design: A Chemometric Approach*, Elsevier, Amsterdam, 1997.
- [28] J. Kuivinen, H. Johnsson, *Water Res.* 33 (1999) 1201.