Investigating relative contributions of various precursors’ ratio in TTHMs profiling in a proto-type distribution rig using central composite design (CCD)

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Abstract: - A rotatable full factorial (24 non center + 6 center points) in central composite design (CCD) was used to study relative contribution of total trihalomethanes (TTHMs) precursors i-e., HA/Br-, HA/Cl- and Cl-/Br- in formation and speciation of TTHMs mainly brominated species with pH and time in a proto-type distribution rig. The developed 2 factor interaction (2FI) model was significant (p < 0.0481) showing impact of both HA and Br- on TTHMs formation with pH together (r = 0.988, p < 0.007), chlorine dose (r= 0.97, p < 0.01) and time (r = 0.90, p < 0.12). Dibromochloromethane and bromoform formation is pH dependent provided sufficient Br- . Cl-/Br- ratio was observed as main combination in TTHMs formation and their speciation (r = 0.99, p < 0.0189), while HA/Br- (r =0.04, p < 0.26) and HA/Cl- (r = -0.89, p < 0.0169) has definite correlations either directly or indirectly while pH acts synergistically. The order of significance was Cl-/Br- < HA/Br- < HA/Cl- concluding that TTHMs formation is controlled by more than one factors and their combinations with positive or negative correlation. The pH region between 6.5-7.5 and HA: Br- ratio 4.3-6.00 seems satisfactory below the recommended ≤ 80 ppb. Their respective concentration may be altered/minimized by changing precursor’s individual concentration and possible combinations.

Key-Words: - Trihalomethanes, central composite design (CCD), distribution rig, precursors,

1 Introduction
Chlorination of drinking water containing natural organic matter (NOM) leads to the formation of chlorination by products (CBPs) [1, 2]. The CBPs are mainly formed by chlorination of activated aromatic rings, mostly contained in humic substances [3, 4] of which trihalomethanes (THMs) are the most prevalent and are therefore recognized as CBP surrogates [5]. They are collectively called TTHM4 comprising of chloroform (CHCl3), bromodichloromethane(CHCl2Br), dibromochloromethane (CHCIBr2), and bromoform (CHBr3) respectively. Several studies are reported about the carcinogenic and non-carcinogenic health effects of THMs [6, 7]. Due to the hazardous health effects, the concentration of THMs in water supplies is monitored on regular basis in several countries guideline values for CHCl3, CHCl2Br, CHCIBr2 and CHBr3 are 200, 60, 100 and 100 µg /L respectively [3]. This has led to the monitoring of their presence in drinking water for regulatory compliance, health risk assessment, epidemiological evaluation and water quality control purposes so measures may be taken to minimize or eliminate their presence whenever concentration approaches levels of concern. Due to the complexity of the reactions between TTHMs precursors and their relative importance, there was a need to simulate the distribution system in a scale-up scale, continuous system and to systemically study these factors by CCD individually and the relative HA/Br-, HA/Cl- and Cl-/Br- ratio in defining the formation and profiling of TTHMs within the scaled-up proto-type distribution network.
2 Methodology

2.1 Experimental design (Response surface methodology (RSM) using central composite design (CCD))

The main objective is to optimize the response surface that is influenced by various process parameters. It also quantifies the relationship between the controllable input parameters and the obtained response surfaces [8, 9]. Design-Expert software (trial version 9, Stat-Ease, Inc., MN) was used for the design of experiments (DoE) because there were several independent variables and the main interest and aim was their combined effect on the dependent variable for the selection of the experimental points at which the response should be evaluated and optimized [10]. A central composite design in DoE consisting of a full factorial design with 30 experiments was selected to simultaneously optimize the levels of these variables to attain the best system performance. (Table 1).

2.2 Distribution rig

A scaled-up distribution network (proto-type rig) was established consisting of HDPE pipe of 220 meters in two concentric loop connected to a main water reservoir with a flow meter to regulate the flow in the network (Fig. 1). Nine sampling ports were provided, 22.5 meter apart, to collect the samples at various time/distance intervals. De-chlorinated tap water was used as a medium to introduce various combinations of humic acid (HA) and Br- for the profiling of TTHMs and various factors affecting the process. Commercial humic acid was used as the precursor material for THMs. Stock solution of the HA was prepared and used as per requirement. Commercial sodium hypochlorite (10.5 %) was freshly prepared and different dilutions were applied as per experimental requirement. Samples were taken at various time intervals. The residual chlorine was quenched by adding 0.01 N sodium thiosulphate (Na2S2O3) to cease further reaction. Free chlorine was measured by Spectroquant Picco colorimeter according to standard methods [11].

2.3 THMs Analysis

THMs extraction was performed using liquid-liquid extraction (LLE). For extraction, in 6 mL of the water sample, 0.45 g of salt, sodium sulphate (anhydrous) was added and mixed vigorously for 30 seconds. Then 1 mL MtBE was added and mixed on vortex mixer for 90 seconds and left undisturbed for two minutes. This salt addition, called salting out, enhances the separation of the organic layer from water layer. One microliter (µl) of the organic layer containing TTHMs was applied to Gas chromatography (GC) (Model Claurus 500) with column Car/PMDS for detection provided with mass spectroscopy (MS). GC/MS analysis for TTHMS are illustrated Fig. 2.

3 Results and Discussions

The two factors interaction (2 FI) model was applied as best fit as per suggestion of the software based on significant results (p < 0.0481) as reported in Table 4.

3.1 Effect of HA/Br- on speciation of TTHMs

The concentration of TTHMs at pH 9 was approximately 6 times when observed at pH 5 as also reported by [12]. It is evident that TTHMs concentration is high at low HA/Br- concentration due to high availability of Br- ions which results in a shift towards brominated species and an overall increase in TTHMs concentration [13, 14]. Another reason may be attributed that initially the chlorinated species were formed which were later attacked by Br- to form brominated species in sufficient Br- presence, also suggested by several researchers [15]. This trends reverses as TTHMs formation is high at low HA/Br- ratio, but with high pH. It seems that pH has a synergistic effect as the reaction proceeds at a greater speed at high pH (Fig. 3). As pH increases above neutral point, the concentration of the TTHMs increases exponentially reflecting a positive effect of pH on this reaction. Similar results were also reported by [6, 16, 17].

With an increase in pH, from acidic to basic, high amount of TTHMs is formed within initial hours of reaction, comprising mainly of brominated species. Among these, BF is almost double the concentration of DBCM which means that multi-brominated species formation is pH dependent provided sufficient Br- in the system. But if Br- are absent or insufficient, then chlorinated species will be the only products resulting in an overall decrease in TTHMs species. Similar results were found by
many workers [18]. Analysing the 3D graph for chlorine vs pH and time separately, the formation of

Table 1. Independent variables and their low and high levels values by CCD

<table>
<thead>
<tr>
<th>Variables</th>
<th>Lowest</th>
<th>Low</th>
<th>Centre</th>
<th>High</th>
<th>Highest</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time (Hours)</td>
<td>A</td>
<td>0</td>
<td>4</td>
<td>16</td>
<td>24</td>
</tr>
<tr>
<td>pH</td>
<td>B</td>
<td>5</td>
<td>6</td>
<td>7</td>
<td>8</td>
</tr>
<tr>
<td>HA/Br-</td>
<td>C</td>
<td>1.5</td>
<td>3.33</td>
<td>4.44</td>
<td>6.66</td>
</tr>
<tr>
<td>Applied chlorine</td>
<td>D</td>
<td>1</td>
<td>3</td>
<td>5</td>
<td>7</td>
</tr>
<tr>
<td>Cl:Br-</td>
<td>E</td>
<td>0.6</td>
<td>2</td>
<td>3.3</td>
<td>4.6</td>
</tr>
<tr>
<td>HA:Cl-</td>
<td>F</td>
<td>0.6</td>
<td>1.4</td>
<td>1.6</td>
<td>2.1</td>
</tr>
</tbody>
</table>

Fig. 1, Lay-out of the prototype distribution network (rig)

Figure 2. The MS chromatograph of THM4 compounds under SIR mode: (upper values = retention time, lower values = peak area)
Table 2. Analysis of Variance (ANOVA) for TTHMs formation with varied variables

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of Squares</th>
<th>df</th>
<th>Mean square</th>
<th>F value</th>
<th>P value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>214</td>
<td>10</td>
<td>21.40</td>
<td>2.40</td>
<td>0.0481</td>
</tr>
<tr>
<td>A-Time</td>
<td>0.89</td>
<td>1</td>
<td>0.89</td>
<td>0.10</td>
<td>0.7548</td>
</tr>
<tr>
<td>B-pH</td>
<td>23.38</td>
<td>1</td>
<td>23.38</td>
<td>2.62</td>
<td>0.1218</td>
</tr>
<tr>
<td>C-HA/Br-</td>
<td>11.98</td>
<td>1</td>
<td>11.98</td>
<td>1.34</td>
<td>0.2606</td>
</tr>
<tr>
<td>D-Chl</td>
<td>72.40</td>
<td>1</td>
<td>72.40</td>
<td>8.12</td>
<td>0.0102</td>
</tr>
<tr>
<td>AB</td>
<td>2.70</td>
<td>1</td>
<td>2.70</td>
<td>0.30</td>
<td>0.5881</td>
</tr>
<tr>
<td>AC</td>
<td>1.27</td>
<td>1</td>
<td>1.27</td>
<td>0.14</td>
<td>0.7095</td>
</tr>
<tr>
<td>AD</td>
<td>0.89</td>
<td>1</td>
<td>0.89</td>
<td>0.10</td>
<td>0.7551</td>
</tr>
<tr>
<td>BC</td>
<td>81.40</td>
<td>1</td>
<td>81.40</td>
<td>9.13</td>
<td>0.0070</td>
</tr>
<tr>
<td>BD</td>
<td>6.46</td>
<td>1</td>
<td>6.46</td>
<td>0.72</td>
<td>0.4015</td>
</tr>
<tr>
<td>CD</td>
<td>12.61</td>
<td>1</td>
<td>12.61</td>
<td>1.42</td>
<td>0.2488</td>
</tr>
<tr>
<td>Residual</td>
<td>169.31</td>
<td>19</td>
<td>8.91</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Lack of fit</td>
<td>167.90</td>
<td>14</td>
<td>11.99</td>
<td>42.58</td>
<td>0.0003</td>
</tr>
<tr>
<td>Pure error</td>
<td>1.41</td>
<td>5</td>
<td>0.28</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Corrected total</td>
<td>383.31</td>
<td>29</td>
<td>Mean</td>
<td>2.61</td>
<td></td>
</tr>
<tr>
<td>SD</td>
<td>2.99</td>
<td></td>
<td>Press</td>
<td></td>
<td>7.87</td>
</tr>
<tr>
<td>CV</td>
<td>114.42</td>
<td></td>
<td>Adeq. Precision</td>
<td></td>
<td>7.208</td>
</tr>
<tr>
<td>R2</td>
<td>0.5583</td>
<td></td>
<td></td>
<td>Adj R2</td>
<td>0.3258</td>
</tr>
<tr>
<td>Pred. R2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-1.0540</td>
</tr>
</tbody>
</table>
TTHMs seems dependent on applied chlorine as TTHMs are formed at all applied chlorine doses (Fig. 4 and 5). THMs formation increased as a function of chlorine consumption. In a similar study, a low but significant relationship occurred between TTHM and applied chlorine dosage [19]. There is a reciprocal effect on chlorine residuals which decreases with time as more and more THMs are formed.

To represent the above mentioned factors effects in various combination, a Pareto chart of effects was created and based upon the comparative importance of the factors. A 2 FI effect and ANOVA was performed to determine the significance of the variables and their interactions. The independent variables A, B, C, D are given in Table 1. The minimal effect was presented in the upper portion and then progress to the maximal effect. In addition, it directly shows that the most important factors determining TTHMs were B(pH), C (HA:Br- ) and D (Chl) along with the product of BC(pH*HA:Br-), CD (HA:Br-*Chl) and BD (pH* Chl) as this is a 2FI mechanism (Fig. 6). The other contributing factor are also shown based upon the relative degree of significance which are summarized as equation 1 (Eq. 1) mentioned below:

\[
\text{TTHMs (mg/L)} = 2.608 - 0.1931 A +0.986 B - 0.706.60 C +1.7368 D - 0.44 AB +0.282.19 AC - 0.236 AD - 2.26 BC +0.63544 BD – 0.887 CD
\]

Eq. 1
Based upon the ANOVA results and p values given in Interaction/response table (Table 3), the Equation (1) reduces to Equation (2) with only those factors which are statistically significant in the formation and speciation of TTHMs in a distribution network.

\[
\text{TTHMs (mg/L)} = 2.608 + 0.986 \, B - 0.7066 \, C + 1.7368 \, D - 0.44 \, AB - 2.26 \, BC + 0.63544 \, BD - 0.887 \, CD
\]

Eq. 2

Fig. 6. Pareto chart of standardized effects of independent variables and their interactions obtained from CCD

Table 3: Interaction/Response table showing various combinations of factors along p values

3.1.2 Validation of the model
The normal probability plots of the residuals and the plots of the actual versus the predicted response in Fig.7 (a) and (b) respectively revealed that the residuals generally fall on a straight line showing that experimental data is in full agreement with the predicted values. It also implies that the errors are distributed normally.
4 Relative contribution of HA/Br\(^-\), Cl\(^-\)/Br\(^-\) and HA/Cl\(^-\) ratio on TTHMs speciation

To observe the effect of HA/Br\(^-\), Cl\(^-\)/Br\(^-\) and HA/Cl\(^-\) ratio and to find out the key player species or combination of any species, various combinations were also analysed.

4.1 Effect of HA/Br\(^-\)

HA/Br\(^-\) ratios were analysed carefully on neutral pH 7 to avoid any synergistic effect associated with pH as TTHMs formation is pH dependent as mentioned earlier. By carefully observing various combinations of HA/Br\(^-\) ratio, it is evident that there is a weak positive correlation (r = 0.0416, p < 0.26) between the two species in speciation of TTHMs in the system (Fig. 8). The TTHMs formation is high at low HA/Br\(^-\) ratio and vice versa. Hong et al., [3] explained this trend that at low HA/Br\(^-\), means high Br\(^-\) content in the system, the rate of hydrolysis of the trihalo intermediates to form the corresponding THMs is reported to increase with increasing bromine content.

4.2 Effect of Cl\(^-\)/Br\(^-\)

Beside HA/Br\(^-\), another combination of Cl\(^-\)/Br\(^-\) was observed in determining the THMs speciation. TTHMs concentration showed a positive correlation with HA applied (r = 0.998, p < 0.0184) due to more organic carbon available for the substitution of chloride from HOC\(_\text{l}\) species (Fig. 9). Increasing the chlorine dose but keeping Br\(^-\) concentration constant, reveals that initially the high concentration of chlorinated species are formed which are then
incorporated/replaced by the Br- present in the system resulting in high brominated species.

Figure 9: Relative proportion of individual THMs species at different Cl:Br- ratio

The increased amount of Br- shifts the reaction towards the bromination and results in an increase in brominated species, so there is an overall high concentration of TTHMs. Same results were also mentioned by [19]. For bromine, all species (i.e., Br\(^2\), HOBr) are important in defining the brominated species. During chlorination, bromide quickly oxidized by bromine to form hypobromous acid (HOBr), which is a more powerful halogenating agent than hypochlorous acid (HOCl) [3].

4.3 Effect of HA/Cl\(^-\)

Another combination of HA/Cl\(^-\) was analysed to observe its effect on TTHMs formation at constant Cl/Br ratio to avoid Br\(^-\) as a limiting factor. Looking at the various ratios of HA/Cl\(^-\), it is observed that increasing the HA/Cl\(^-\) ratio first increase TTHMs formation due to more and more HA presence in the system. But after an initial increase, a gradual decrease in observed TTHMs concentration. A negative correlation was observed between HA and Cl\(^-\) ratio was observed (r = -0.89; p< 0.0169) (Fig. 10). This negative correlation shows that an increase in HA/Cl\(^-\) ratio, decrease the TTHMs formation and vise versa. The reason can be attributed to the fact that when there occurs an increase in HA/Cl\(^-\) ratio, i-e., high HA concentration but low Cl\(^-\) concentration, the Cl\(^-\) concentration acts as a limiting factor, and which definitely results in low TTHMs irrespective of the high concentration of HA as precursor. To represent the above mentioned factors‘ and their combinations’ effects, another pareto chart of effects was created and based upon the comparative importance of the interacting factors specially various combinations of precursors described above.

Figure 10: Relative concentration of THMs species at various HA:Cl\(^-\) ratio at a constant Br\(^-\) ion concentration

The overall interaction and their proportion can be visualized easily as independent factor as well as in combinations, particularly when pH is taken into consideration as 2FI mechanism in dotted line pH*Cl\(^-\):Br\(^-\) being more influential in speciation of TTHMs in proto-type DS (Fig. 11).

5 Multiple response optimizations

The expert design software (Version 9) was used to optimize the operational conditions. The numerical optimization process involves combining the goals into an overall desirability function (D), an objective function that ranges from zero outside of the limits to one at the goal [12].

5.1 Numerical Optimization

It finds one point or more in the factors domain that would maximize this objective function. The value closer to 1 is considered to be best. The present objective was to minimize the TTHMs (≤ 80ug/L) with maximum precursor’s concentrations in sudden mishaps like HA/Br-, Cl\(_2\), pH and time. The concentration of HA/Br- is 5.97, pH=7.54, Cl\(_2\)= 7.00 and time is almost 9.5 hours, the maximum time from the treatment plant to the end consumers (Figure 12).
5.2 Graphical optimization

It is obvious that the graphical optimization allows visual selection of the optimum conditions according to certain criterion resulting in the graphical called overlay plots. The yellow/shaded areas other than grey on the overlay plots show that the criterion is met in this region. These type of plots are extremely practical for quick technical use. The amount of all four TTHMs species was selected ≤20 ppb each, altogether ≤80 ppb (Fig. 13). The region of pH between 6.5-7.5 and HA:Br-ratio between 4.2-5.00 seems safe with respect to the formation of TTHMs above the recommended level of WHO.

![Image of Pareto chart and ramp function](image-url)

Fig. 11, Pareto chart of standardized effects of independent variables and their interactions obtained from CCD

Fig. 12, Ramp function for maximum precursor's values and TTHMs ≤80 ppb as a response
Fig. 13, Overlay plot shows the region of optimal conditions of HA:Br- and pH for TTHMs formation ≤ 80 ppb

6 Conclusions
This study depicts that CCD and RSM may efficiently be applied for the modeling and optimization of the contribution of THMs precursors and associated factors on the formation and speciation of TTHMs in a proto-type distribution network. The following conclusion may be drawn:

TTHMs precursor species work in various combinations i.e., HA:Br-, HA:Cl- and Cl-:Br- in their speciation; Cl-/Br- being the most influential with \( r = 0.99, p < 0.0189 \). The order of significance is Cl-/Br- < HA/Br- < HA/Cl- with \( p < 0.0189, 0.26 \) and 0.0169 respectively. The pH of medium acts as a synergistically, while the brominated species formation was pH dependent provided sufficient Br- in the system. Increasing HA/Cl- ratio, the Cl- concentration acts as a limiting factor, resulting in a decrease in TTHMs concentration irrespective of the high concentration of HA as precursor. Increasing the chlorine dose but keeping Br- concentration constant, reveals that first the high concentration of chlorinated species were formed which were then incorporated/replaced by the Br- present in the system resulting in high brominated species with time. The graphical optimization over lay plots shows pH region between 6.5-7.5 and HA:Br- ratio between 4.3-6.00 seems safe with respect to the formation of TTHMs below the recommended level of WHO.

References


