
**Title:** Incidence of Chlorination Byproducts (CBPs) in an Institutional Drinking Water Distribution Network, Islamabad, Pakistan using Response Surface methodology (RSM)

**Short Title:** Incidence of CBPs in Drinking Water Distribution Network, Islamabad using RSM

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Abstract

Trihalomethanes (THMs) are regulated disinfection byproducts (DBPs), analyzed in drinking water due to their toxicological health effects. However, few data exist regarding the content of emerging THMs in drinking water which are present at very low concentrations. This study aimed to monitor hazardous and emerging THMs from drinking water supply in a residential area via solid phase microextraction using gas chromatography. Response surface methodology was employed to evaluate the role of salt concentration, temperature, desorption and extraction times on THMs formation as a result of raw water prechlorination. Maximum THM detection was achieved at 3.25g Na$_2$SO$_4$ salt via 30 min extraction time at 80°C along with 8 min of desorption time. The quantification results revealed the presence of total THMs in all drinking water samples, while most of the sites (88%) exceeded the permissible limit set by USEPA. Among I-THM, chloriodomethane was found to be dominant as detected in 79% of samples.

Keywords: Disinfection by-products; Distribution network; Response surface methodology; Solid-phase microextraction; Water analysis.
1. Introduction

Chlorination of drinking water supplies is the most common practice of water disinfection in Pakistan, preventing the transmission of many waterborne diseases due to inadequate disinfection in water distribution networks (Amjad et al. 2013). Despite its role in disinfection, chlorine is also responsible for oxidizing natural organic matter (NOM) in water leading to the formation of various disinfection byproducts (DBPs) such as trihalomethanes (THMs) and haloacetic acids (HAAs) (Richardson et al. 2007).

Among them, The THMs such as chloroform (CF), bromodichloromethane (BDCM) and bromoform (BF) are of major concern due to their severe toxic and carcinogenic effects in humans (Richardson et al. 2007; USEPA 2003). Depending on the potential health risks, USEPA have set limits for total THMs (i.e. sum of chloroform, bromoform, bromodichloromethane, dibromochloromethane) at 80 µg/L in potable water (USEPA 2003).

Besides brominated and chlorinated THMs, iodinated THMs (I-THMs) may also be formed when iodide ion is present in water. New concerns regarding human health with respect to I-THMs were raised by Plewa et al. (2004), who reported I-THMs, particularly iodoform as more toxic than brominated and chlorinated THMs. The taste and odor threshold for iodoform is in the range of 0.02 - 5 µg/L, and when surpassed may prompt organoleptic issues and consumer complaints. Currently, there is no published standard analytical method for I-THMs in water (Allard et al. 2012). Therefore, there is a dire need to constantly monitor the levels of THMs and their precursors in drinking water supplies (Zia et al. 2005).

In Pakistan, very less work has been reported regarding identification of toxic DBPs in drinking water supplies. In a study by Amjad et al. (2013), average total THMs concentration (TTC) were found to be approximately 143 and 259 µg/L for Rawalpindi and Islamabad, respectively. Solid phase microextraction technique (SPME) is a rapid and sensitive technique for THMs determination. The sensitivity of the technique depends on a number of parameters that affect extraction of analytes from water, such as fiber type, sample volume, stirring, salt addition, extraction/desorption time and temperature (Bahri & Driss 2010). Conventional approach for process optimization is time consuming, requires a large number of experiments to be performed.
and expensive as well. According to Santos et al. (2011), extraction temperature was the most important factor in THMs extraction from soft drinks.

Therefore, it has been challenging to develop and optimize various variables and different conditions to estimate maximum THMs extraction from water. Recently, various statistical experimental designs have been used for this purpose in water distribution networks (Rosero et al. 2012). Response surface methodology (RSM) is a useful technique for designing experiments, building models, analyzing and optimizing effects of several independent variables. It also analyses the relationship between independent variables and resulted responses (Rasheed et al. 2016). RSM combined to central composite design (CCD) is an efficient tool to study the simultaneous effect of various variables, which influence the responses, with limited number of experiments by eliminating non-significant interactions of variables (Guimarães et al. 2008).

Gonzalez et al. (2011) optimized the extraction conditions for THMs from water samples using response surface methodology's study using a composite $2^5$ factorial design. It was found that the extraction temperature and desorption times are the most influential conditions in the process.

The present study was designed to investigate the incidence of Chlorination Byproducts (CBPs) mainly THMs in an institutional drinking water distribution network, Islamabad, Pakistan. Following are the study objectives:

- Comparison of HS-SPME method and LLE technique to achieve maximum THMs extraction from water.
- Optimization of analytical conditions using response surface methodology (RSM) and central composite design (CCD) for THMs determination.
- Subsequently, application of the optimized method for THMs detection and quantification in drinking water distribution network using Gas Chromatography.

2. Methods and Material

2.1. Chemicals and Solvents

Standard analytes (Iodoform, Chloroiodomethane, Chloroform, Dibromochloromethane, Bromodichloromethane and Bromoform) and solvents were purchased from Sigma Aldrich (USA) and Merck (Germany) with 99% purity respectively. Whereas, SPME (75 μm Car-PDMS)
fiber was obtained from Supelco (USA).

2.2. Chlorination process of treated water at treatment plant

The water treatment plant within the institution mainly consisted of underground tanks for water storage, from here water is pumped to overhead reservoirs for further distribution to all the filtration plants throughout the campus. Prior to distribution water is treated with chlorine on regular basis and its concentration is also monitored regularly to ensure safe water quality to consumers.

The samples collected from the drinking water source and consumer’s end within the university (Table 1) were analyzed for physicochemical (free chlorine, UV$_{254}$, pH, TDS, DO, Turbidity, EC, alkalinity, hardness etc) contamination which showed that all the parameters were within the USEPA and WHO limits. It was observed generally, that free chlorine concentration at source ranged between 0.5 - 1.5 mg/L, whereas at consumer’s tap ranged between 0.23 to 0.46 mg/L, which lies within the optimum range prescribed by WHO.

<table>
<thead>
<tr>
<th>Sampling Locations</th>
<th>Abbreviations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Location # 1</td>
<td>L1</td>
</tr>
<tr>
<td>Location # 2 (Before Cl$_2$)</td>
<td>L2B</td>
</tr>
<tr>
<td>Location # 2 (After Cl$_2$)</td>
<td>L2A</td>
</tr>
<tr>
<td>Location # 3 (U/G Tank)</td>
<td>L3T</td>
</tr>
<tr>
<td>Location # 3 (Tubewell)</td>
<td>L3W</td>
</tr>
<tr>
<td>Construction &amp; Management</td>
<td>CNM</td>
</tr>
<tr>
<td>Material Recovery Centre</td>
<td>MRC</td>
</tr>
<tr>
<td>Tube Well # 8 (Before Cl$_2$)</td>
<td>TW8B</td>
</tr>
<tr>
<td>Tube Well # 8 (After Cl$_2$)</td>
<td>TW8A</td>
</tr>
<tr>
<td>Medical Inspection Room</td>
<td>MI</td>
</tr>
<tr>
<td>Iqra Apartments</td>
<td>IA</td>
</tr>
<tr>
<td>Isra Apartments</td>
<td>Isra</td>
</tr>
<tr>
<td>Institute of Environmental Sciences &amp; Engineering</td>
<td>IESE</td>
</tr>
<tr>
<td>Ghazali Hostels</td>
<td>GH</td>
</tr>
<tr>
<td>Rumi Hostels</td>
<td>RH</td>
</tr>
<tr>
<td>Attar Hostels</td>
<td>AH</td>
</tr>
<tr>
<td>Barrack 1</td>
<td>B1</td>
</tr>
<tr>
<td>School of Mechanical &amp; Manufacturing Engineering</td>
<td>SMME</td>
</tr>
<tr>
<td>Main Office</td>
<td>MO</td>
</tr>
<tr>
<td>Admin</td>
<td>Ad</td>
</tr>
<tr>
<td>Institute of Geographical Information Systems</td>
<td>IGIS</td>
</tr>
<tr>
<td>Concordia 1</td>
<td>C1</td>
</tr>
<tr>
<td>Fatima1 Hostels</td>
<td>FH</td>
</tr>
<tr>
<td>Zainab Hostels</td>
<td>ZH</td>
</tr>
</tbody>
</table>
2.3. Sampling and storage

Sampling was conducted from main water reservoir and consumer’s tap from NUST University, H-12 campus premises. Samples were collected from each site in duplicate (Table 1). Freshly prepared ascorbic acid solution (0.142 M) was added to each 40 mL vial as chlorine quenching agent prior to sampling. Samples were analyzed as per Standard Methods (APHA 2012).

2.4. Standard solutions

A THM stock solution of 1000 µg/L was prepared in methanol as per EPA Method 551.1 (USEPA 1995). Working standard solutions were prepared to obtain linear calibration curves and detection limits. For spiking THMs standard solution, carbon tetra chloride (CCl₄) solution was prepared in methanol (1000 µg/L) to get a reproducible chromatogram (Fig. 1).

![Chromatogram of THMs mixture using SPME fiber](Fig1.TIFF)

2.5. Instrumental conditions

THMs analysis was conducted using Shimadzu 2010 gas chromatography system with fused silica capillary column (30m x 0.32mm x 1µm) equipped with an electron capture detector. Initially, oven temperature was 50°C, which increased at a rate of 15°C/min to 200°C. The constant flow of Helium, carrier gas, was maintained at 4 mL/min.

2.6. HS-SPME

Distilled water (30 mL) was placed in a glass vial, THMs standard (10 µL), Na₂SO₄ salt and CCl₄ (internal standard) was added to it. The sample was stirred at 300 rpm and SPME fiber was injected into the headspace at 50°C. Fiber was retracted back and transferred without delay to the GC injection port at 220°C (Allard et al. 2012).

2.7. Liquid-liquid extraction (LLE)
THMs standard (10 µL) was added to 35 mL distilled water followed by Na$_2$SO$_4$ salt and MtBE as extraction solvent. The vial was sonicated for 5 min. 500 µL of the organic layer formed was transferred into a GC vial containing 10 µL of CCl$_4$ (internal standard). The extract was then injected in a GC column for analysis (Allard et al. 2012).

3. Results and Discussion

3.1. Comparison of HS-SPME and LLE techniques

Conventional LLE-GC-ECD and HS-SPME-GC-ECD techniques were compared using unpaired t-test in order to achieve maximum response. The results indicated increase in peak areas by using HS-SPME as compared to LLE (Fig. 2).

![Fig2.TIFF](attachment://Fig2.png)

Comparison studies for THMs extraction (a) Comparison of HS-SPME and LLE techniques (b) Comparison of various salts using HS-SPME
(Note: HS-SPME = Headspace-solid phase micro extraction; LLE = Liquid-liquid extraction)
The recovery efficiencies were also calculated for these methods to evaluate the method performance for THMs. According to USEPA percent recoveries must fall in the range of 70 to 120 for THMs. The HS-SPME gave acceptable recovery values for all THMs (Table 2). As a result, HS-SPME is proposed to be a reproducible, faster and accurate technique for THMs analysis as compared to LLE. Cancho et al. (1999) determined the recovery values close to 100% by spiking the water samples at a concentration of 10, 1.5 and 0.5 mg/L with I-THMs.

Table 2 Comparison of recoveries for THMs and I-THMs by using HS-SPME and LLE methods

<table>
<thead>
<tr>
<th>Extraction Techniques</th>
<th>THMs</th>
<th>I-THMs</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CHCl₂</td>
<td>CHBr₃</td>
</tr>
<tr>
<td>HS-SPME/GC/ECD</td>
<td></td>
<td></td>
</tr>
<tr>
<td>recovery % (1000 µg/L)</td>
<td>99.3</td>
<td>69.3</td>
</tr>
<tr>
<td>S.D ^a</td>
<td>0.20</td>
<td>0.10</td>
</tr>
<tr>
<td>R.S.D ^b %</td>
<td>20.8</td>
<td>22.1</td>
</tr>
<tr>
<td>LLE/GC/ECD</td>
<td></td>
<td></td>
</tr>
<tr>
<td>% recovery (1000 µg/L)</td>
<td>95.0</td>
<td>69.4</td>
</tr>
<tr>
<td>S.D</td>
<td>0.25</td>
<td>0.11</td>
</tr>
<tr>
<td>R.S.D %</td>
<td>26.3</td>
<td>24.1</td>
</tr>
</tbody>
</table>

a. S.D = standard deviation; b. R.S.D = relative standard deviation

3.2. Salt selection for HS-SPME technique

Distilled water was fortified each with THM (1000 µg/L) and salted with 1 g of Na₂SO₄ and NaCl separately whereas, the control was without salt. The results showed an increase in salt concentration resulted in high THMs extraction. It can be related to the fact that the salt addition amplified the ionic potency of the solution and resulted in dispersion of analytes into the headspace (Takamatsu & Ohe 2003). As shown in Fig. 2, Na₂SO₄ was observed to have a considerable effect on the THMs extraction as compared to NaCl and control. Therefore, use of Na₂SO₄ for THMs analysis was preferred over NaCl due to less impurities (USEPA 1995).

3.3. Testing method performance

Accuracy of HS-SPME technique was evaluated by plotting calibration curves. An acceptable linear range with regression coefficients (R²) higher than 0.93 was obtained for all THMs, which correlated with the findings of Stack et al. (2000) who indicated 0.9920 to 0.9959 R² value at THMs concentration ranging from 10 to 160 mg/L. The validity of HS-SPME technique was estimated in terms of limit of quantification (LOQ) and limit of detection (LOD) (Table 3). The
LOQs ranged between 4 ng/L for CHI\textsubscript{3} and 68 ng/L for CHCl\textsubscript{3} respectively. Repeatability and reproducibility values were found less than 11%. The results demonstrated that proposed HS-SPME technique is appropriate for measuring THMs at µg/L levels in drinking water.

Table 3 Demonstration of method performance for THMs determination

<table>
<thead>
<tr>
<th>Analytes</th>
<th>Linearity range (µg/L)</th>
<th>Correlation coefficient (R\textsuperscript{2})</th>
<th>LOD \textsuperscript{a} (µg/L)</th>
<th>LOQ \textsuperscript{b} (µg/L)</th>
<th>Repeatability (n=5) RSD %</th>
<th>Reproducibility (n=9) RSD %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHCl\textsubscript{3}</td>
<td>3.17E+05</td>
<td>0.995</td>
<td>0.007</td>
<td>0.021</td>
<td>9.38</td>
<td>7.47</td>
</tr>
<tr>
<td>CHBr\textsubscript{3}</td>
<td>2.39E+05</td>
<td>0.966</td>
<td>0.010</td>
<td>0.030</td>
<td>10.68</td>
<td>10.6</td>
</tr>
<tr>
<td>CHBr\textsubscript{2}Cl</td>
<td>1.43E+05</td>
<td>0.998</td>
<td>0.060</td>
<td>0.183</td>
<td>6.73</td>
<td>9.81</td>
</tr>
<tr>
<td>CHBr\textsubscript{2}Cl</td>
<td>6.45E+05</td>
<td>0.995</td>
<td>0.052</td>
<td>0.159</td>
<td>4.31</td>
<td>4.50</td>
</tr>
<tr>
<td>CHI\textsubscript{3}</td>
<td>5.60E+04</td>
<td>0.994</td>
<td>0.012</td>
<td>0.035</td>
<td>5.94</td>
<td>10.7</td>
</tr>
<tr>
<td>CH\textsubscript{2}ClI</td>
<td>1.77E+06</td>
<td>0.938</td>
<td>0.001</td>
<td>0.003</td>
<td>4.68</td>
<td>4.32</td>
</tr>
</tbody>
</table>

\textsuperscript{a.} LOD = Limit of detection; \textsuperscript{b.} LOQ = Limit of quantification; \textsuperscript{c.} R.S.D = Relative standard deviation

3.4. Optimization of HS-SPME technique using response surface methodology (RSM)

Design of experiments and statistical analysis were conducted using software package Design-Expert (trial version 9, Stat-Ease, Inc., MN). The full factorial central composite design with 30 experiments was applied to optimize the level of effective variables such as; salt amount, extraction temperature, extraction and desorption time for visualizing the significant THMs extraction conditions. Table 4 lists the ranges and levels of applied parameters by RSM-CCD.

Table 4 Levels and range of independent variables

<table>
<thead>
<tr>
<th>Coded variables</th>
<th>Lowest (-α)</th>
<th>Low (-1)</th>
<th>Centre (0)</th>
<th>High (+1)</th>
<th>Highest (+α)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salt (g)</td>
<td>-1.25</td>
<td>1</td>
<td>3.25</td>
<td>5.5</td>
<td>7.75</td>
</tr>
<tr>
<td>Extraction time (min)</td>
<td>-7.5</td>
<td>5</td>
<td>17.5</td>
<td>30</td>
<td>42.5</td>
</tr>
<tr>
<td>Extraction temp (ºC)</td>
<td>5</td>
<td>30</td>
<td>55</td>
<td>80</td>
<td>105</td>
</tr>
<tr>
<td>Desorption time (min)</td>
<td>-4</td>
<td>2</td>
<td>8</td>
<td>14</td>
<td>20</td>
</tr>
</tbody>
</table>

3.5. Effect of extraction temperature and extraction time

Interaction between extraction temperature and extraction time was observed in a 3D response surface revealing synergetic effect of both variables for THMs (Fig. 3a). This can be attributed to the fact that increasing the extraction temperature increases the diffusion of the analytes to the fiber surface. Consequently, the time necessary to reach the equilibrium of partition between the sample and extractor phase is reduced (Santos \textit{et al.} 2011). In addition, here diffusion coefficients in both water and headspace are higher thus diffusion of volatile analytes from aqueous phase to headspace is enhanced. Therefore, with increase in temperature during adsorption period,
increased THMs extraction rate was observed. Similar results were also reported by Deok-Hee et al. (2003).

While observing the effect of extraction time on THMs extraction in Fig 3a, an increase in THMs extraction (Z-axis) was observed with increased extraction time (B: y-axis: extraction time). The highest extraction was observed at 30 min. Here extraction time was evaluated as an important parameter that influences partition of analytes as HS-SPME is an equilibrium process that involves separation of analytes from aqueous phase to headspace and eventually into the fiber (Pawliszyn 1997). In addition, acceptable equilibrium was attained for all THMs at 30 min in the present study.

3.6. Effect of desorption time and salt addition

The impact of desorption time (D: x-axis: desorption time) and salt on the THMs extraction was evaluated in Fig. 3b. It is evident that addition of more salt resulted in higher THMs extraction. This could be attributed to the fact that the salt addition increases the ionic strength of matrix and decreases the solubility of analytes so that more analytes are dispersed into the headspace, thereby, contributing to enhanced adsorption on the fiber (Takamatsu & Ohe 2003). Meanwhile, longer extraction time synergistically lead to higher THMs extraction. While desorption times 8 min was sufficient to desorb analytes in GC port (Fig. 5). Similar behavior for high molecular weight compounds has been reported earlier (Cancho 1999; San 2007).
Response surface modelling was done to develop relationship between the process variables and the THMs response. The significance of the model was assessed by applying ANOVA, and finally the best fitted model equation was obtained as:

\[ THMs \left( \frac{ug}{L} \right) = 111.21 + 12.93A + 0.26B + 25.04C + 10.17D + 37.93AB - 6.92AC + 9.85AD - 33.82BC + 32.25BD - 1.7CD \] (1)

Based upon the ANOVA results and p values given in response Table 5, the Eq. (1) reduces to Eq. (2) with only those factors which are statistically significant in the formation of THMs in drinking water.

\[ THMs \left( \frac{ug}{L} \right) = +111.21 + 12.93A + 25.04C + 10.17D + 37.93AB + 9.85AD - 33.82BC + 32.25BD \] (2)

The coded equation is useful to evaluate the relative impact of the factors by comparing the factor coefficients and to make predictions about the THMs response. Furthermore, this mathematical model may be used to predict performance of each studied factor as well as the mutual interactions.

The coefficient for \( AB \) was found to be 37.92, higher than the factor \( C, BC \) and \( BD \). Thus, the
Table 5 Response of contributing factors along p values

<table>
<thead>
<tr>
<th>Response</th>
<th>Intercept</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>AB</th>
<th>AC</th>
<th>AD</th>
<th>BC</th>
<th>BD</th>
<th>CD</th>
</tr>
</thead>
<tbody>
<tr>
<td>THMs</td>
<td>111.21</td>
<td>*12.9</td>
<td>*0.25</td>
<td>**25.04</td>
<td>*10.2</td>
<td>*37.9</td>
<td>*-6.92</td>
<td>*9.85</td>
<td>**-33.8</td>
<td>**32.2</td>
<td>*-1.70</td>
</tr>
<tr>
<td>P values</td>
<td>*0.20</td>
<td>*0.98</td>
<td>**0.02</td>
<td>*0.31</td>
<td>*0.005</td>
<td>*0.57</td>
<td>*0.42</td>
<td>**0.01</td>
<td>**0.01</td>
<td>*0.88</td>
<td></td>
</tr>
</tbody>
</table>

*Significant effect (p<0.01); **Less significant (p = 0.01< = p<0.05); *Least significant (p>0.1).

Note: A = salt concentration; B = extraction time; C = extraction temperature; D = desorption time.

The order of significance is listed as, \( AB > BC, BD > AC, AD, CD \). The standardized effects of these factors and their interactions on the THMs extraction were investigated by the Pareto chart analysis. It is evident from Fig. 4 that the factors \( AB \) (salt-extraction time) are the most influential factors affecting THMs extraction (p<0.01) by HS-SPME technique, followed by \( C \) (extraction temperature), \( BC \) (extraction time-extraction temperature) and \( BD \) (extraction time-desorption time).

Fig4.TIFF Pareto chart of standardized effects of factors and their interactions on THMs extraction in water.

3.8. Optimization modelling for THMs extraction

Process optimization is an important step in determining values of factors for which response is at a maximum (Rasheed et al. 2016). Based on the variables selected (Table 4), numerical optimization was performed by the RSM-CCD to achieve one or more points in factors domain that would maximize the THMs extraction. The desirability value (D) closer to 1 is considered to be significant by the RSM software. It was observed that maximum extraction efficiency was
obtained when temperature was maintained at 80°C with extraction time of 30 min and 3.25 g salt at 8 min of desorption time at a D value of 1.0 (Fig. 5).

3.9. *THMs monitoring from drinking water samples by the optimized HS-SPME technique*

The HS-SPME technique optimized by the RSM software was then employed for determination of THMs from the water samples of an educational institution in Islamabad, Pakistan. Samples were collected and analyzed as per standard protocol. The concentration of total and iodinated THMs is shown in Fig. 6 (a) and (b) respectively. For TTHMs, among all sites, sites L2A, L3A, CNM, MRC, TW8A and SMME had high concentration of TTHMs as shown in Fig. 6 (a). The respective chromatographic peaks for TTHMs and I-THMs can be observed in Fig. 7a and 7b respectively. Fig. 7 shows clearly identifiable chromatographic peaks from sites L2A and MRC. The large peak signal of chloroform showed high content of chlorine present at these sites to react with organic matter which resulted in high THMs yield at site L2A and MRC. This high concentration of TTHMs could be attributed to the presence of high UV$_{254}$ absorbance, TDS and residual chlorine. Some 88% sites exceeded the standard values while highest concentration was observed to be 455.9 µg/L at site L2A. UV$_{254}$ absorbance is the indicator of NOM in water, which is one of the most significant precursors of THMs development (Chang *et al.* 2001; Singer 1999). At all the sampling sites, chloroform was detected in the highest ratio (Fig. 6a), with maximum concentration of 233.4 µg/L observed at site L3A. While I-THMs were detected in approximately...
85% of the samples as shown in Fig. 6b. Chloroiodomethane was the dominant specie, found in 79% of the tested samples with highest mean value of 101.1 µg/L at MRC, while on remaining 8 sites, it exceeded the threshold values of 0.2 - 5 µg/L. However, iodoform was detected in lowest concentration ranging from 0.012 - 0.433 µg/L in 45% of the samples, whereas in other sites it was within the threshold values.

Fig.6.TIFF Mean THMs concentration in drinking water samples using optimized HS-SPME technique
(a) Mean TTHMs (b) Mean I-THMs
(Note: TTHMS = Total THMs; I-THMS = Iodinated THMs)
Another reason could be attributed to the close occurrence of sampling sites to the chlorination source as more residual chlorine was available to react with the precursor UV$_{254}$ absorbance, yielding high concentration of TTHMs and I-THMs. Similar findings were also reported by Bergamaschi et al. (1999) and Karanfil et al. (2002).

![Chromatograms of drinking water collected from sampling sites (a) L2A (b) MRC](Note: L2A = Location 2 after chlorination; MRC = Material Recovery Centre)

3.10. Correlations between THMs and residual chlorine and UV$_{254}$

A correlation between THMs concentration, residual Cl$_2$ and UV$_{254}$ absorbance was assessed by regression analysis, keeping in view the findings of Chang et al. (2001) and (Singer 1999) as mentioned above.

The results showed a strong positive linear correlation between residual Cl$_2$ and UV$_{254}$ concentration with THMs formation with $R^2 = 0.80$ (Fig. 8). These results are in accordance with literature (Chowdhury et al. 2007). Hence it proves that the potential reason for THMs contamination in drinking water was the presence of NOM and residual Cl$_2$. 
4. Conclusions

The present study was designed to quantify THMs in drinking water through an optimized HS-SPME technique by using GC. The outcomes of this research work are as follows:

(1) The physical and chemical parameters (pH, EC, temperature, UV$_{254}$ absorbance, residual Cl$_2$, TDS, turbidity, DO etc.) of drinking water samples meet the permissible limits recommended by WHO.

(2) The HS-SPME and LLE techniques were compared to achieve the maximum THMs response. The results showed significant (p < 0.1) increase in peak areas for HS-SPME, which is an excellent alternative extraction technique comparable to LLE.

(3) HS-SPME technique was optimized using RSM-CCD for THMs determination. Optimum conditions for THMs extraction were 30 min extraction time at 80°C with addition of 3.25g Na$_2$SO$_4$ salt and 8 min of desorption time.

(4) The optimized method was used to determine THMs in an institutional drinking water samples which revealed THMs presence in 90% of the samples, with 30% exceeding the U.S.EPA limit, indicating the possibility of adverse public health risks suggested by various researchers such as cancer, adverse reproductive disorders, taste/odor problems, organoleptic issues and consumer complaints. As THMs are more common in the public water systems,
therefore they are a threat to any water supply that uses chlorine, thus a large population may
be affected by this contamination, ultimately putting pressure on population dynamics.

(5) Results revealed a strong correlation of THMs formation with UV$_{254}$ concentration ($R^2 = 0.8$)
and residual Cl$_2$ ($R^2 = 0.8$).

(6) The validity of the optimized HS-SPME technique was further investigated by linear range,
detection limits, precision and recovery efficiency for each analyte. The results verified that
this technique is suitable and applicable for drinking water analysis.

Keeping in view the need and significance of the current study, following are some of the future
recommendations for undertaking further research in this field.

1. Epidemiological and genotoxicity studies of THMs exposure to human cells/blood may be
carried out to identify toxic levels using comet assay or various other techniques.

2. Different methods of C-DBPs mainly THMs removal and control may also be investigated in
detail to minimize the THMs formation in drinking water sources as they are potential human
carcinogens.

Furthermore, few mitigation measures to control DBPs formation and ultimately providing safe
drinking water to the consumers are stated below:

- Granular activated carbon (GAC) adsorption may be used to remove NOM, the major
  precursor of DBPs.
- Multiple other drinking water treatment processes, including pre-ozonation, conventional
treatments (coagulation/sedimentation, pre/post-sand filtration), ozone biological activated
  and carbon advanced treatment, may also be investigated depending upon the available
  resources and need of the particular area.
- New approaches may be developed to effectively control THMs formation, in chlorinated
drinking water by targeting intermediate aromatic halogenated DBPs.

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