# Research Paper

# Incidence of chlorination by-products in an institutional drinking water distribution network, Islamabad, Pakistan, using response surface methodology

Romana Khan, Imran Hashmi, Habib Nasir, Sajida Rasheed and Luiza C. Campos

## ABSTRACT

Trihalomethanes (THMs) are regulated disinfection by-products (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 THM formation as a result of raw water prechlorination. Maximum THM detection was achieved at 3.25 g $Na_2SO_4$ 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 the United States Environmental Protection Agency (USEPA). Among I-THMs, chloroiodomethane was found to be dominant as detected in 79% of samples.

**Key words** | disinfection by-products, distribution network, response surface methodology, solid-phase microextraction, water analysis

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## 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 by-products (DBPs) such as trihalomethanes (THMs) and haloacetic acids (HAAs) (Richardson *et al.* 2007).

Among these by-products, THMs such as chloroform (CF), bromodichloromethane (BDCM) and bromoform (BF) are of major concern due to their severe toxic and carcinogenic effects in humans (USEPA 2003; Richardson *et al.* 2007). Depending on the potential health risks, the United States Environmental Protection Agency (USEPA) have set limits for total THMs (i.e. sum of chloroform, bromoform, bromodichloromethane and 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 ions are 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 0.02–5.00 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, there is a lack of reported work regarding identification of toxic DBPs in drinking water supplies. In a study by Amjad *et al.* (2013), average total THMs concentration (TTC) was 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). The conventional approach for process optimization is time consuming, requires a large number of experiments to be performed and is also expensive. According to Dos 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, and analyzing and optimizing effects of several independent variables. It also analyzes the relationship between independent variables and resulting responses (Rasheed *et al.* 2016). RSM combined with central composite design (CCD) is an efficient tool to study the simultaneous effect of various variables, which influence the responses, with a limited number of experiments by eliminating non-significant interactions of variables (Guimarães *et al.* 2008). Aguirre-González *et al.* (2011) optimized the extraction conditions for THMs from water samples in an RSM 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 by-products (CBPs), mainly THMs, in an institutional drinking water distribution network in Islamabad, Pakistan. Objectives of the study are: comparison of headspace (HS)-SPME method and liquid-liquid extraction (LLE) technique to achieve maximum THMs extraction from water; optimization of analytical conditions using RSM and CCD for THMs determination; and subsequently, application of the optimized method for THMs detection and quantification in drinking water distribution networks using gas chromatography.

## METHODS AND MATERIALS

### Chemicals and solvents

Standard analytes (iodoform, chloroiodomethane, chloroform, dibromochloromethane, bromodichloromethane and bromoform) and solvents were purchased from Sigma Aldrich (USA) and Merck (Germany), respectively, with 99% purity. The SPME fiber (75 µm Car-PDMS) was obtained from Supelco (USA).

### 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 a 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 end within the university (Table 1) were analyzed for physicochemical contamination (free chlorine, $UV_{254}$, pH, total dissolved solids (TDS), dissolved oxygen (DO), turbidity, electrical conductivity (EC), alkalinity, hardness, etc.) which showed that all the parameters were within USEPA and World Health Organization (WHO) limits. It was observed generally that free chlorine concentration at source was in the range 0.5–1.5 mg/L, whereas at consumer taps it ranged from 0.23 to 0.46 mg/L, which lies within the optimum range prescribed by WHO.

**Table 1** │ Details of sampling locations and their abbreviations

| Sampling locations | Abbreviations |
| --- | --- |
| Location # 1 | L1 |
| Location # 2 (before $Cl_2$) | L2B |
| Location # 2 (after $Cl_2$) | L2A |
| Location # 3 (U/G tank) | L3T |
| Location # 3 (tube well) | L3 W |
| Construction & Management | CNM |
| Material Recovery Centre | MRC |
| Tube well # 8 (before $Cl_2$) | TW8B |
| Tube well # 8 (after $Cl_2$) | TW8A |
| Medical Inspection Room | MI |
| Iqra Apartments | IA |
| Isra Apartments | Isra |
| Institute of Environmental Sciences & Engineering | IESE |
| Ghazali Hostels | GH |
| Rumi Hostels | RH |
| Attar Hostels | AH |
| Barrack 1 | B1 |
| School of Mechanical & Manufacturing Engineering | SMME |
| Main Office | MO |
| Admin. | Ad |
| Institute of Geographical Information Systems | IGIS |
| Concordia 1 | C1 |
| Fatima1 Hostels | FH |
| Zainab Hostels | ZH |

## Sampling and storage

Sampling was conducted from the main water reservoir and consumer taps from the National University of Sciences and Technology (NUST), 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 a chlorine quenching agent prior to sampling. Samples were analyzed as per standard methods (APHA 2012).

## Standard solutions

A THM stock solution of 1,000 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 tetrachloride ($CCl_4$) solution was prepared in methanol (1,000 μg/L) to obtain a reproducible chromatogram (Figure 1).

## Instrumental conditions

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

## HS-SPME

Distilled water (30 mL) was placed in a glass vial, then THMs standard (10 μL), $Na_2SO_4$ salt and $CCl_4$ (internal standard) were added. The sample was stirred at 300 rpm and the SPME fiber was injected into the headspace at 50 °C. The fiber was retracted back and transferred without delay to the GC injection port at 220 °C (Allard *et al.* 2012).

## LLE

THMs standard (10 μL) was added to 35 mL distilled water followed by $Na_2SO_4$ salt and t-butyl methyl ether (MtBE) as extraction solvent. The vial was sonicated for 5 min, and 500 μL of the organic layer formed was transferred into a gas chromatography (GC) vial containing 10 μL of $CCl_4$ (internal standard). The extract was then injected into a GC column for analysis (Allard *et al.* 2012).

# RESULTS AND DISCUSSION

## 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 an increase in peak areas by using HS-SPME as compared with LLE (Figure 2).
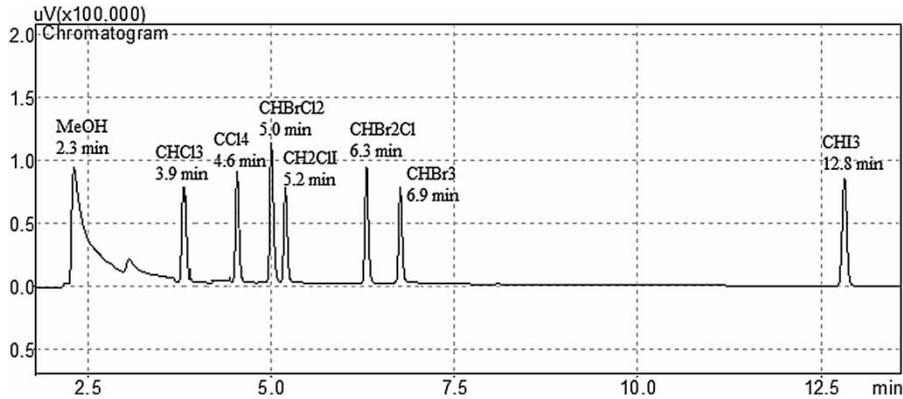
**Figure 1** │ Chromatogram of THMs mixture using SPME fiber.

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 as a reproducible, faster and more accurate technique for THMs analysis compared with 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.

## Salt selection for HS-SPME technique

Distilled water was fortified with THM (1,000 µg/L) and salted with 1 g of $Na_2SO_4$ and NaCl separately, whereas the control was without salt. The results showed that 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
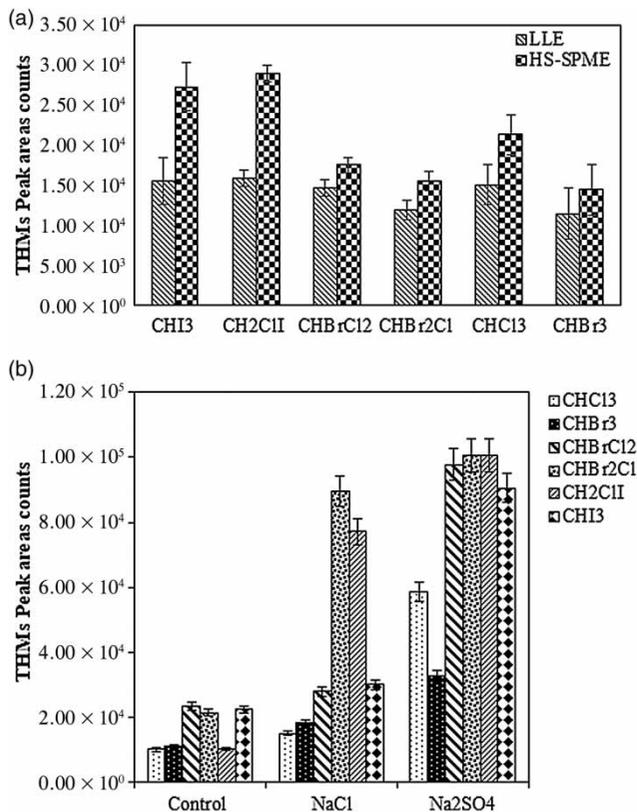


**Figure 2** │ Comparison studies for THMs extraction: (a) comparison of HS-SPME and LLE techniques; (b) comparison of various salts using HS-SPME (HS-SPME = headspace-solid phase microextraction; LLE = liquid-liquid extraction).

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

| Extraction techniques | THMs | | | | I-THMs | |
|---|---|---|---|---|---|---|
| | CHCl₃ | CHBr₃ | CHBr₂Cl | CHBrCl₂ | CHI₃ | CH₂ClI |
| HS-SPME/GC/ECD | | | | | | |
| % Recovery (1,000 µg/L) | 99.3 | 69.3 | 98.3 | 85.9 | 73.7 | 83.6 |
| SD | 0.20 | 0.10 | 0.16 | 0.21 | 0.22 | 0.24 |
| RSD (%) | 20.8 | 22.1 | 16.3 | 24.0 | 30.5 | 28.9 |
| LLE/GC/ECD | | | | | | |
| % Recovery (1,000 µg/L) | 95.0 | 69.4 | 91.1 | 71.5 | 69.8 | 79.9 |
| SD | 0.25 | 0.11 | 0.21 | 0.20 | 0.17 | 0.20 |
| RSD (%) | 26.3 | 24.1 | 23.1 | 28.0 | 26.9 | 25.0 |

SD = standard deviation; RSD = relative standard deviation.

Figure 2, $Na_2SO_4$ was observed to have a considerable effect on the THMs extraction as compared with NaCl and control. Therefore, use of $Na_2SO_4$ for THMs analysis was preferred over NaCl due to fewer impurities (USEPA 1995).

## Testing method performance

Accuracy of the HS-SPME technique was evaluated by plotting calibration curves. An acceptable linear range with regression coefficients ($R^2$) 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 $R^2$ 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 $CHI_3$ and 68 ng/L for $CHCl_3$. Repeatability and reproducibility values were found to be less than 11%. The results demonstrated that the proposed HS-SPME technique is appropriate for measuring THMs at µg/L levels in drinking water.

## Optimization of HS-SPME technique using RSM

Design of experiments and statistical analysis were conducted using software package *DESIGN-EXPERT* (trial version 9, Stat-Ease, Inc., MN). The full factorial CCD 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.

## Effect of extraction temperature and extraction time

Interaction between extraction temperature and extraction time was observed in a 3D response surface revealing synergetic effects of both variables for THMs (Figure 3(a)). 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 (Dos Santos *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, an 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 Figure 3(a), 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). Acceptable equilibrium was attained for all THMs at 30 min in the present study.

## 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 Figure 3(b). It is evident that addition of more salt resulted in

**Table 3** | Demonstration of method performance for THMs determination

| Analytes | Linearity range (µg/L) | Correlation coefficient ($R^2$) | LOD (µg/L) | LOQ (µg/L) | Repeatability (*n* = 5) RSD (%) | Reproducibility (*n* = 9) RSD (%) |
|---|---|---|---|---|---|---|
| $CHCl_3$ | $3.17 \times 10^5$ | 0.995 | 0.007 | 0.021 | 9.38 | 7.47 |
| $CHBr_3$ | $2.39 \times 10^5$ | 0.966 | 0.010 | 0.030 | 10.68 | 10.6 |
| $CHBr_2Cl$ | $1.43 \times 10^5$ | 0.998 | 0.060 | 0.183 | 6.73 | 9.81 |
| $CHBrCl_2$ | $6.45 \times 10^5$ | 0.995 | 0.052 | 0.159 | 4.31 | 4.50 |
| $CHI_3$ | $5.60 \times 10^4$ | 0.994 | 0.012 | 0.035 | 5.94 | 10.7 |
| $CH_2ClI$ | $1.77 \times 10^6$ | 0.938 | 0.001 | 0.003 | 4.68 | 4.32 |

LOD = limit of detection; LOQ = limit of quantification; RSD = relative standard deviation.

**Table 4** | Levels and range of independent variables

| Coded variables | Levels and ranges | | | | |
| --- | --- | --- | --- | --- | --- |
| | Lowest (−α) | Low (−1) | Center (0) | High (+1) | Highest (+α) |
| Salt (g) | −1.25 | 1 | 3.25 | 5.5 | 7.75 |
| Extraction time (min) | −7.5 | 5 | 17.5 | 30 | 42.5 |
| Extraction temp (°C) | 5 | 30 | 55 | 80 | 105 |
| Desorption time (min) | −4 | 2 | 8 | 14 | 20 |

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). Longer extraction time synergistically led to higher THMs extraction; desorption time of 8 min was sufficient to desorb analytes in the GC port (see Figure 5). Similar behavior for high molecular weight compounds has been reported previously (Cancho *et al.* 1999; San *et al.* 2007).

## Response surface modelling

Response surface modelling was performed to develop the relationship between the process variables and the THMs response. The significance of the model was assessed by applying analysis of variance (ANOVA), and finally the best fitted model equation was obtained as:

$$
\begin{aligned}
THMs \left(\frac{\mu g}{L}\right) = \ & 111.21 + 12.93A + 0.26B + 25.04C \\
& + 10.17D + 37.93AB - 6.92AC \\
& + 9.85AD - 33.82BC + 32.25BD \\
& - 1.7CD
\end{aligned}
\tag{1}
$$

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

$$
\begin{aligned}
THMs \left(\frac{\mu g}{L}\right) = \ & +111.21 + 12.93A + 25.04C + 10.17D \\
& + 37.93AB + 9.85AD - 33.82BC \\
& + 32.25BD
\end{aligned}
\tag{2}
$$
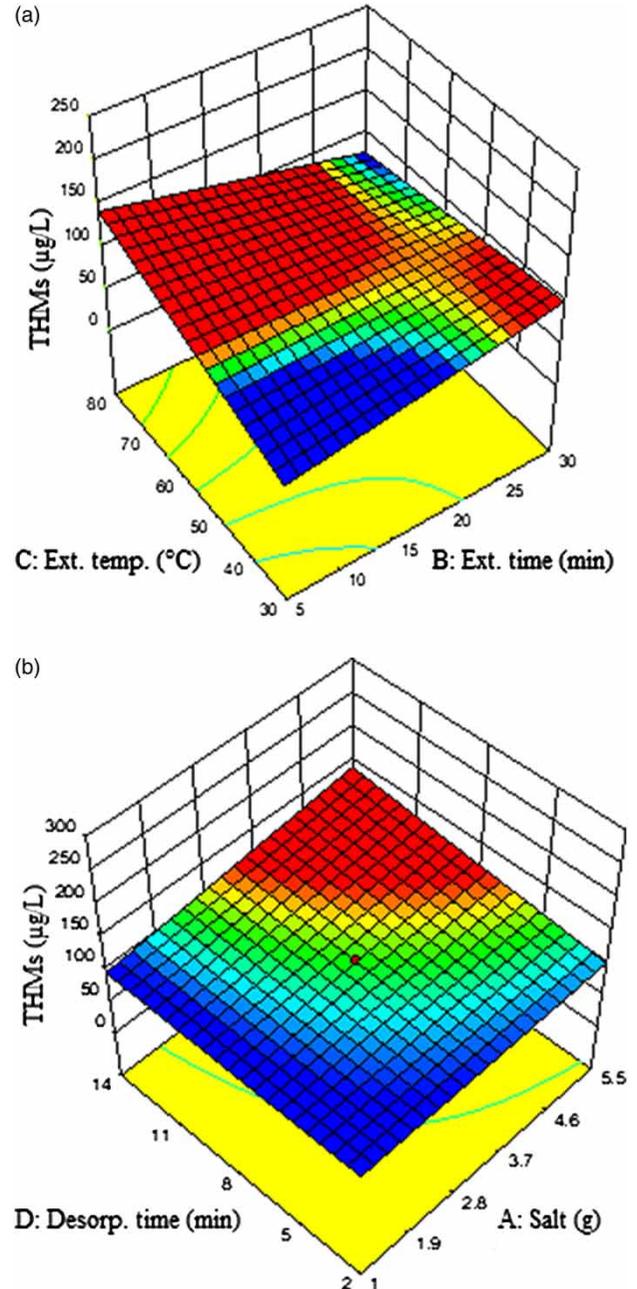


**Figure 3** | 3D response surface showing response of THMs as a function of (a) extraction temperature and extraction time and (b) desorption time and salt.

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.

**Table 5** | Response of contributing factors along with *p* values

| Response | Intercept | A | B | C | D | AB | AC | AD | BC | BD | CD |
|---|---|---|---|---|---|---|---|---|---|---|---|
| THMs | 111.21 | 12.9 | 0.25 | 25.04 | 10.2 | 37.9 | −6.92 | 9.85 | −33.8 | 32.2 | −1.70 |
| *p* values | | 0.20 | 0.98 | 0.02 | 0.31 | 0.005 | 0.57 | 0.42 | 0.01 | 0.01 | 0.88 |

A = salt concentration; B = extraction time; C = extraction temperature; D = desorption time. Significant effect ($p < 0.01$); less significant ($p = 0.01$–$0.05$); least significant ($p > 0.1$).
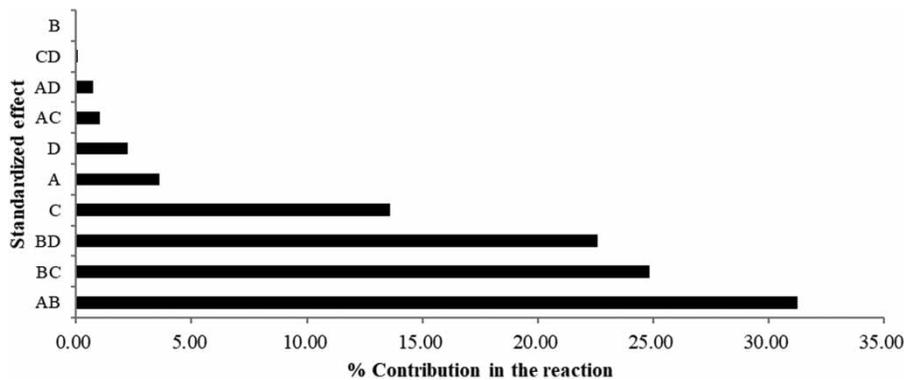


**Figure 4** | Pareto chart of standardized effects of factors and their interactions on THMs extraction in water.
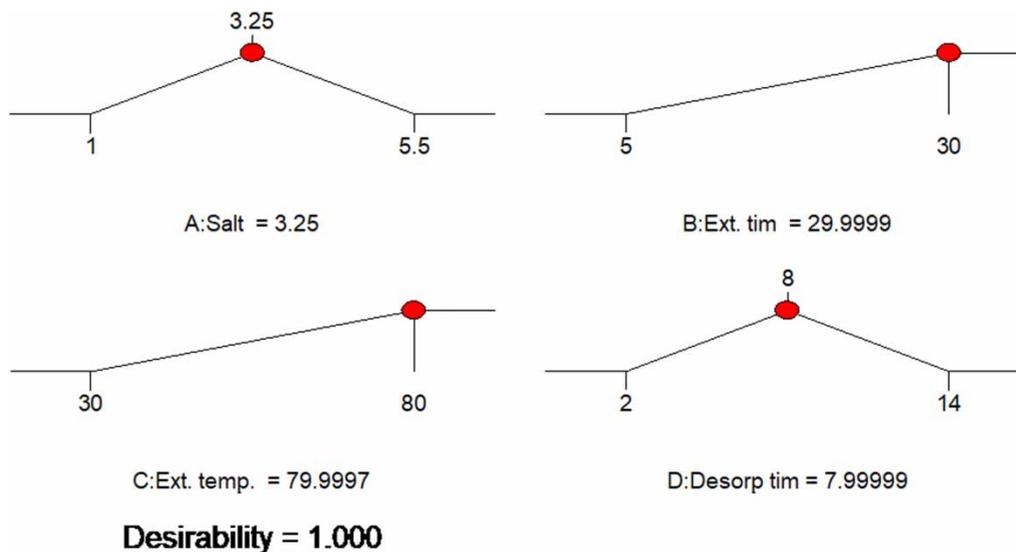


**Figure 5** | Ramp function for maximum THMs extraction.

The coefficient for *AB* was found to be 37.92, higher than for factors *C, BC* and *BD*. Thus, 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 Pareto chart analysis. It is evident from Figure 4 that the factors *AB* (salt–extraction time) are the most influential factors affecting THMs extraction ($p < 0.01$) by the HS-SPME technique, followed by *C* (extraction temperature), *BC* (extraction time–extraction temperature) and *BD* (extraction time–desorption time).
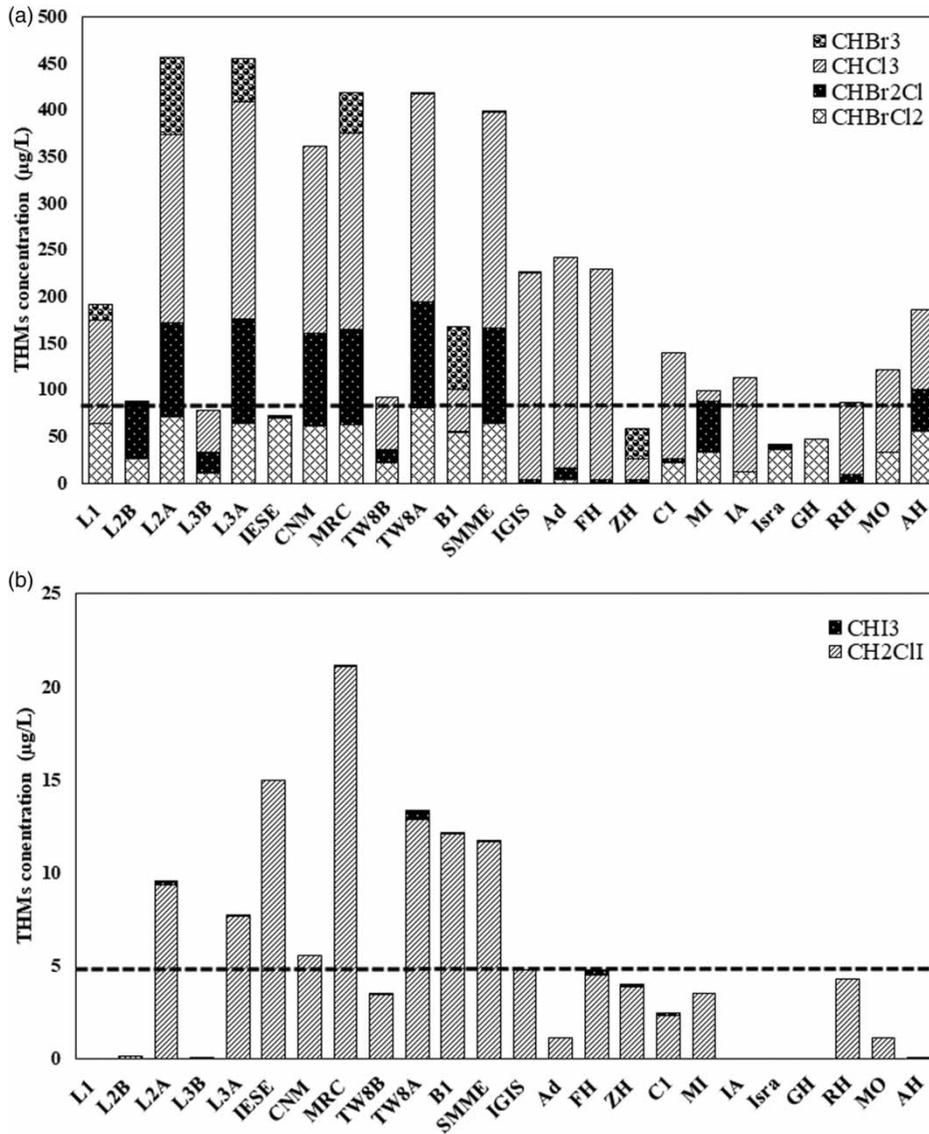
**Figure 6** │ Mean THMs concentration in drinking water samples using optimized HS-SPME technique: (a) mean TTHMs; (b) mean I-THMs. TTHMS = total THMs; I-THMS = iodinated THMs.

## 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 the factors domain that would maximize the THMs extraction. A 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 an extraction time of 30 min and 3.25 g salt at 8 min of desorption time at a *D* value of 1.0 (Figure 5).

## 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 concentrations of total and iodinated THMs are shown in Figure 6(a) and 6(b), respectively. For TTHMs (total trihalomethanes) among all sites, sites L2A, L3A, CNM, MRC, TW8A and SMME had high concentration of TTHMs as shown in Figure 6(a). The respective chromatographic peaks for TTHMs and I-THMs can be observed in Figure 7(a) and 7(b), respectively. Figure 7 shows clearly identifiable chromatographic peaks from sites L2A and MRC. The large peak signal of chloroform showed a high content of chlorine present at these sites available to react with organic matter, which resulted in high THMs yield at sites 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% of sites exceeded the standard values, while the 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 (Singer 1999; Chang *et al.* 2001). At all the sampling sites, chloroform was detected in the highest ratio (Figure 6(a)), 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 Figure 6(b). Chloroiodomethane was the dominant species, found in 79% of the tested samples with highest mean value of 101.1 μg/L at MRC, while on the remaining eight sites, levels 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.

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 concentrations of TTHMs
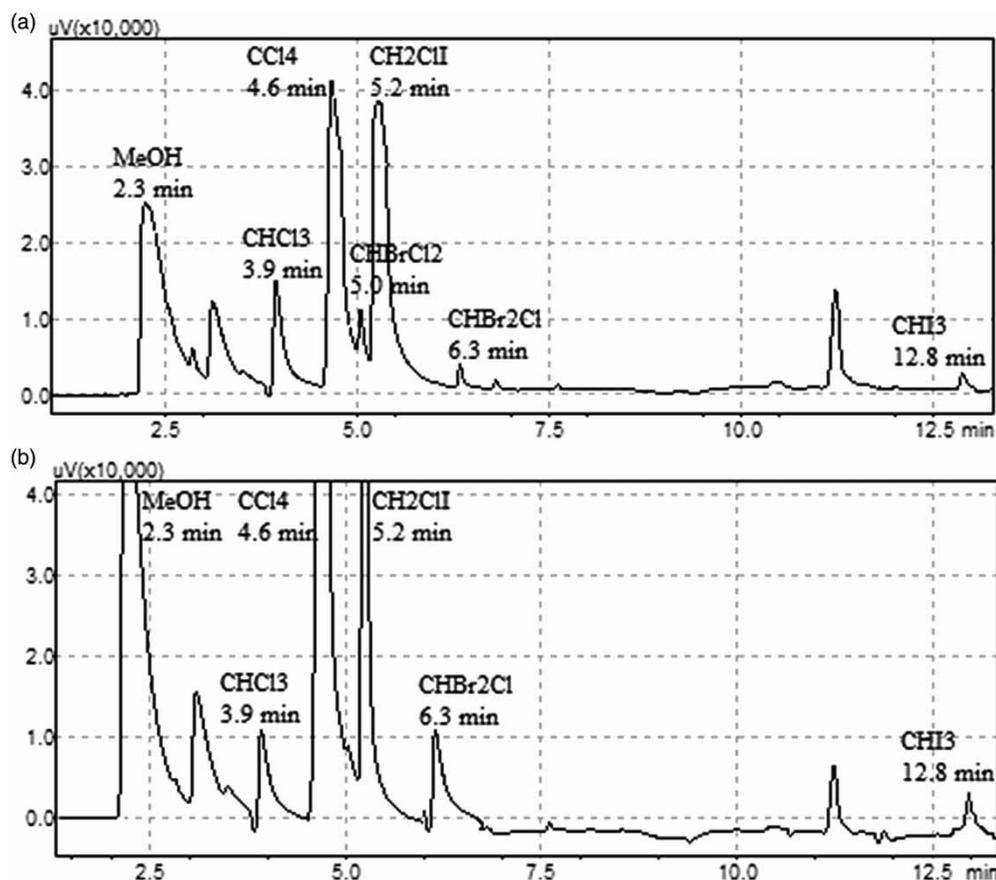


**Figure 7** | Chromatograms of drinking water collected from sampling sites (a) L2A, location 2 after chlorination; and (b) MRC, Material Recovery Centre.

and I-THMs. Similar findings were also reported by Berga-maschi *et al.* (1999) and Karanfil *et al.* (2002).

### 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 $R^2 = 0.80$ for both (Figure 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$_2$.

### 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.

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.

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.

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 3.25 g Na$_2$SO$_4$ salt and 8 min of desorption time.

The optimized method was used to determine THMs in institutional drinking water samples, which revealed THMs presence in 90% of the samples, with 30% exceeding the USEPA limit, indicating the possibility of adverse public health risks such as cancer, reproductive disorders, taste/odor problems, organoleptic issues and consumer complaints. As THMs are more common in the public water systems, they are a threat to any water supply that uses
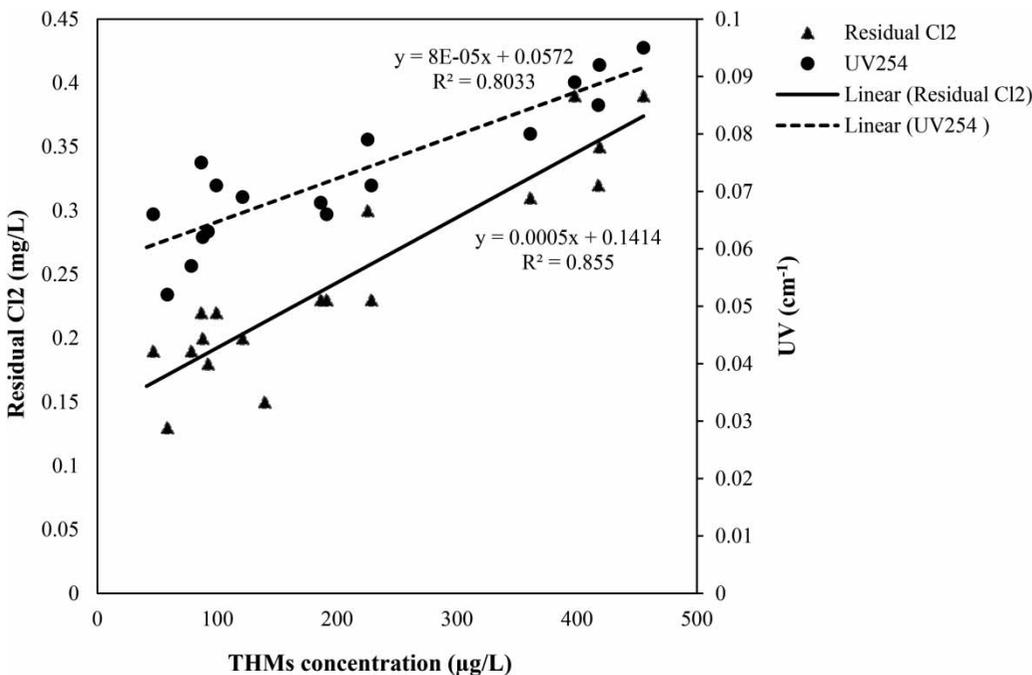


**Figure 8** | Linear correlations of THMs with UV$_{254}$ and residual Cl$_2$.

chlorine; thus, a large population may be affected by this contamination, ultimately putting pressure on population dynamics.

Results revealed a strong correlation of THMs formation with $UV_{254}$ concentration ($R^2 = 0.8$) and residual $Cl_2$ ($R^2 = 0.8$).

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, there follow some 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 chlorinated disinfection by-products (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, a few mitigation measures to control DBPs formation and ultimately provide safe drinking water to consumers are: granular activated carbon (GAC) adsorption may be used to remove NOM, the major precursor of DBPs; multiple alternative 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; and finally, new approaches may be developed to effectively control THMs formation in chlorinated drinking water by targeting intermediate aromatic halogenated DBPs.

## ACKNOWLEDGEMENTS

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