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

Romana Khan (corresponding author)
Imran Hashmi
Sajida Rasheed
Institute of Environmental Sciences and Engineering, School of Civil and Environmental Engineering,
National University of Sciences and Technology (NUST),
H-12 Sector, Islamabad, 44000, Pakistan
E-mail: *romanakhan333@gmail.com*; *romana@iese.nust.edu.pk*

Habib Nasir
School of Natural Sciences (SNS),
National University of Sciences and Technology (NUST),
H-12 Sector, Islamabad, 44000, Pakistan

Sajida Rasheed
Department of Biotechnology,
University of Kotli,
Azad Jammu and Kashmir, 11100, Pakistan

Luiza C. Campos
Department of Civil, Environmental and Geomatic Engineering,
University College London (UCL),
London, WC1E 6BT, UK

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

doi: 10.2166/washdev.2018.047

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).

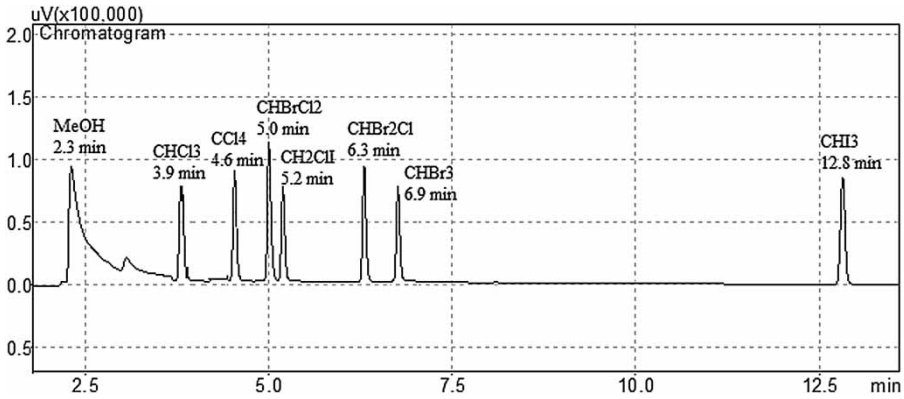

Figure 1 | Chromatogram of THMs mixture using SPME fiber.

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.

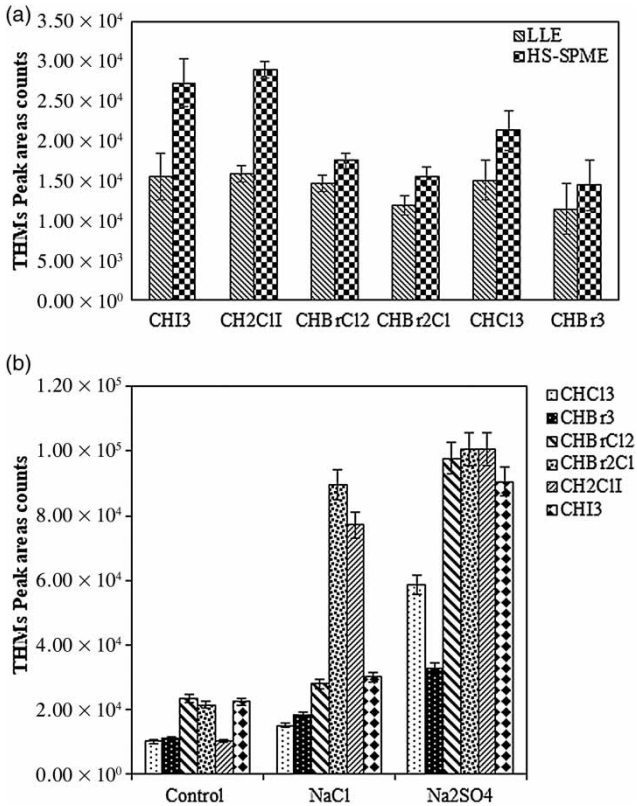

Figure 2 | Comparison studies for THMs extraction: (a) comparison of HS-SPME and LLE techniques; (b) comparison of various salts using HS-SPME (HS-SPME = headspace-solid phase microextraction; LLE = liquid-liquid extraction).

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

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

Extraction techniques	THMs				I-THMs	
	$CHCl_3$	$CHBr_3$	$CHBr_2Cl$	$CHBrCl_2$	CHI_3	CH_2ClI
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 (%)
$CHCl_3$	3.17×10^5	0.995	0.007	0.021	9.38	7.47
$CHBr_3$	2.39×10^5	0.966	0.010	0.030	10.68	10.6
$CHBr_2Cl$	1.43×10^5	0.998	0.060	0.183	6.73	9.81
$CHBrCl_2$	6.45×10^5	0.995	0.052	0.159	4.31	4.50
CHI_3	5.60×10^4	0.994	0.012	0.035	5.94	10.7
CH_2ClI	1.77×10^6	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

	Levels and ranges				
Coded variables	**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:

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

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.

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

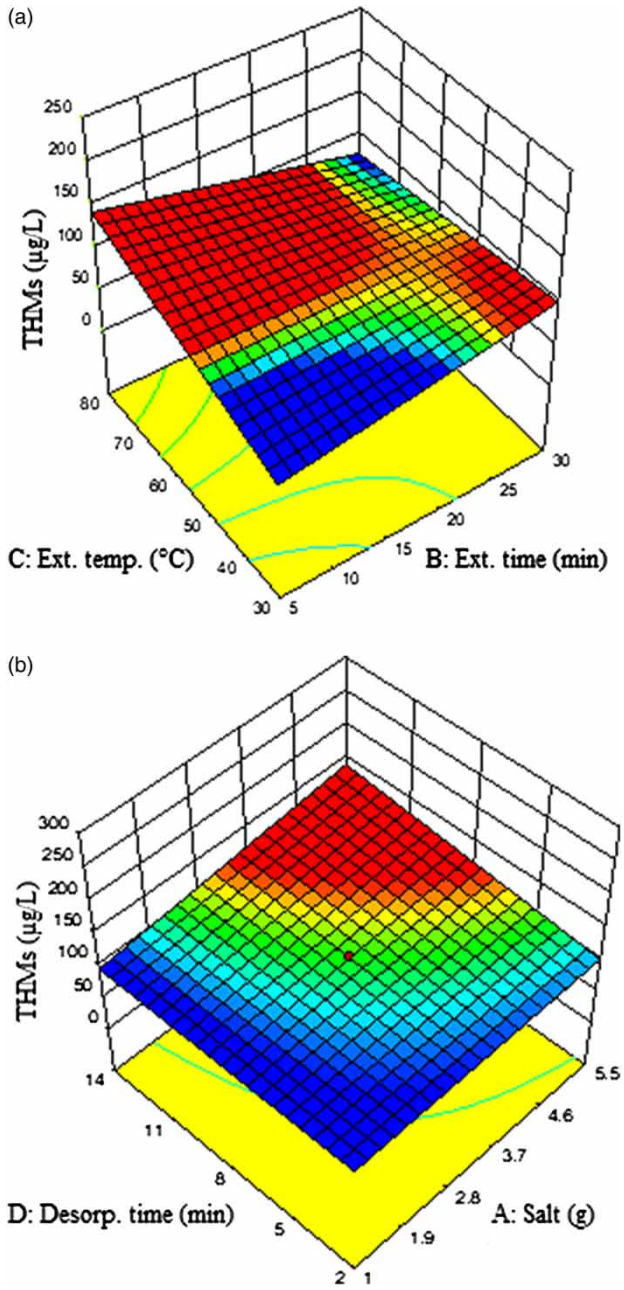

Figure 3 | 3D response surface showing response of THMs as a function of (a) extraction temperature and extraction time and (b) desorption time and salt.

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 ($p > 0.1$).

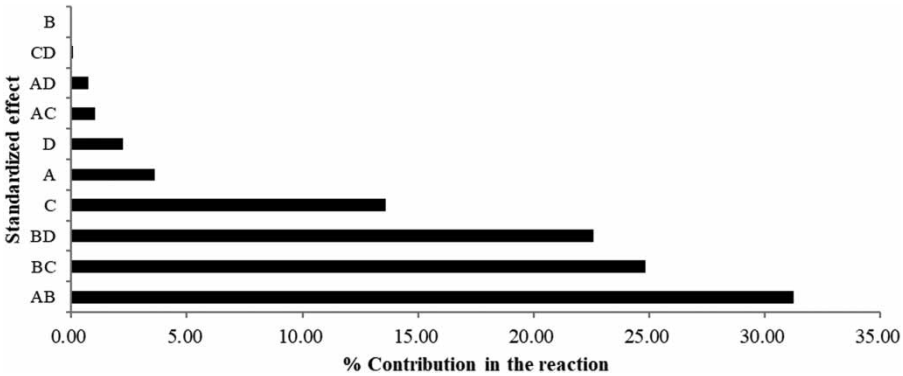

Figure 4 | Pareto chart of standardized effects of factors and their interactions on THMs extraction in water.

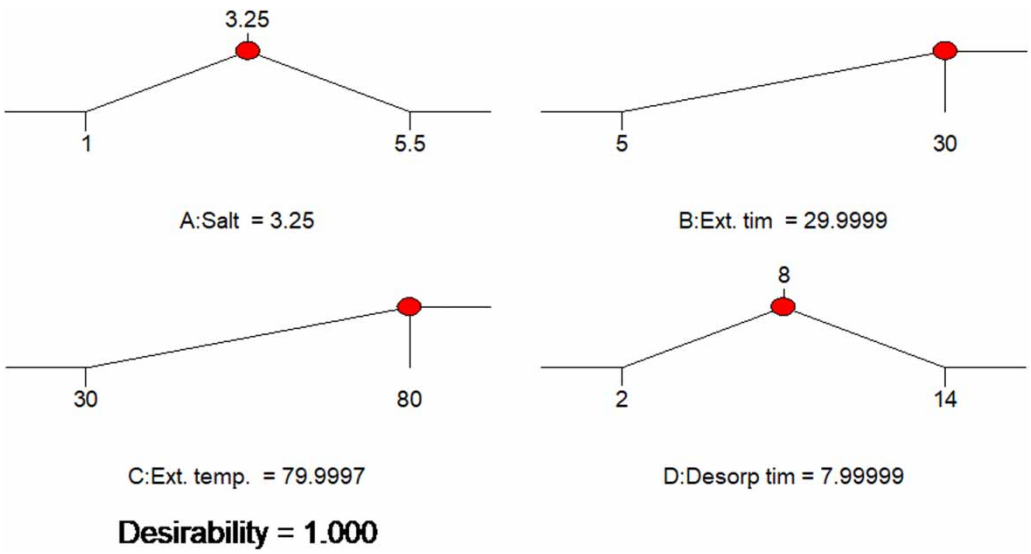

Figure 5 | Ramp function for maximum THMs extraction.

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).

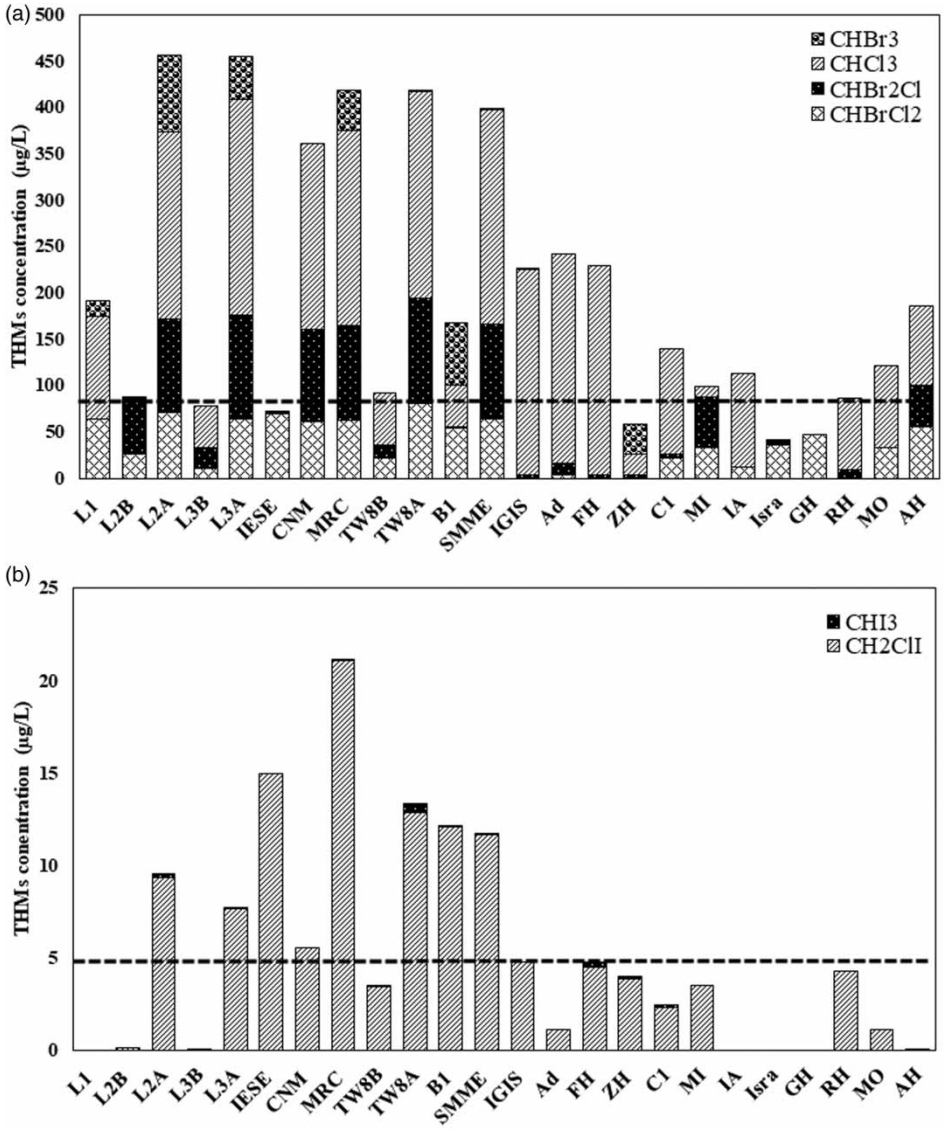

Figure 6 | Mean THMs concentration in drinking water samples using optimized HS-SPME technique: (a) mean TTHMs; (b) mean I-THMs. TTHMS = total THMs; I-THMS = iodinated THMs.

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

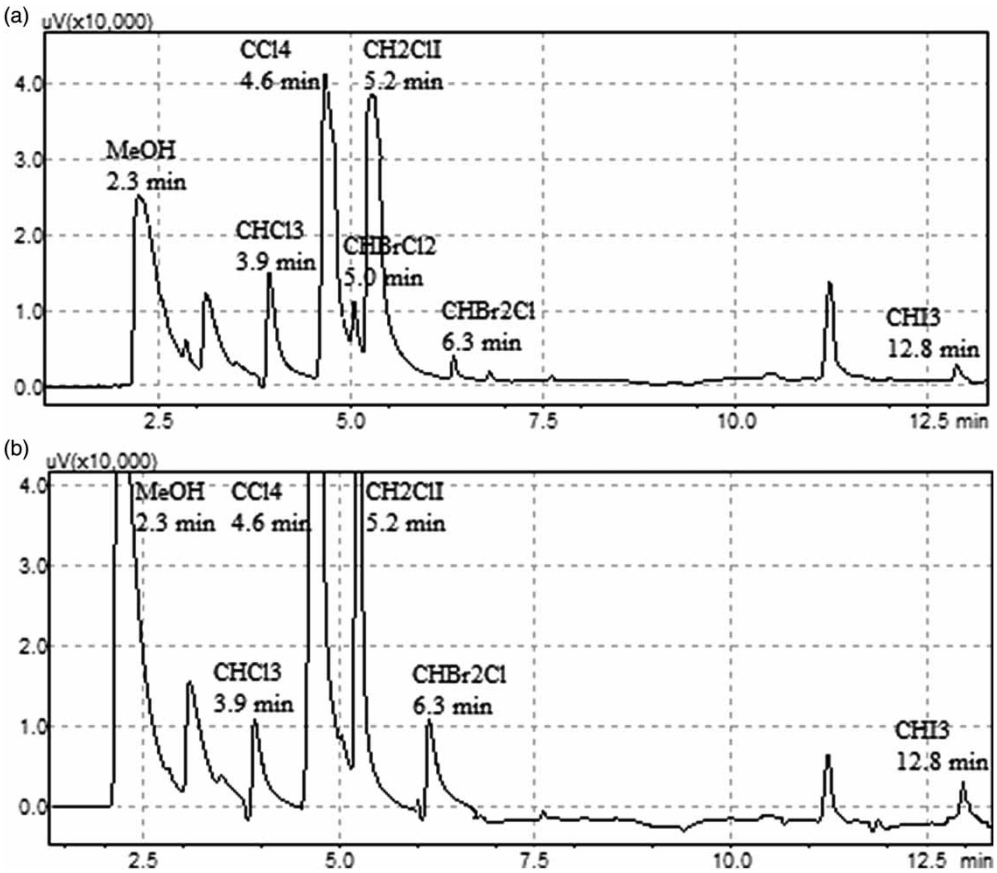

Figure 7 | Chromatograms of drinking water collected from sampling sites (a) L2A, location 2 after chlorination; and (b) MRC, Material Recovery Centre.

and I-THMs. Similar findings were also reported by Bergamaschi *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_2SO_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

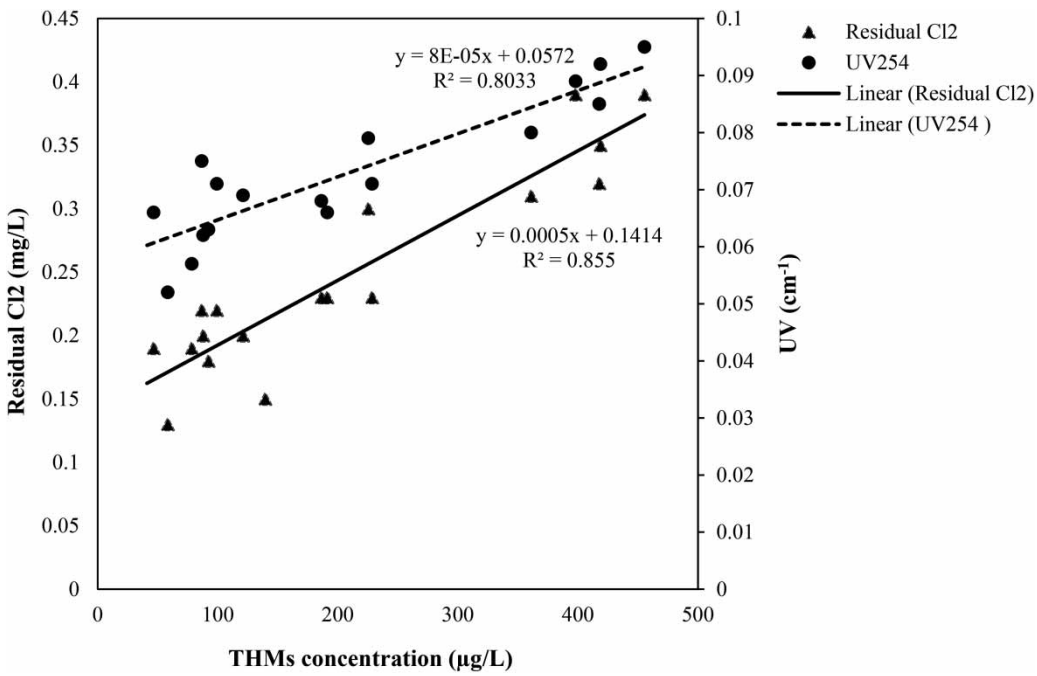

Figure 8 | Linear correlations of THMs with UV_{254} and residual Cl_2.

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

The authors acknowledge the financial support provided by the National University of Sciences and Technology (NUST), Pakistan to pursue the research work and providing the opportunity and facilities to undertake the research. The authors are very grateful to the construction and maintenance (C & M) staff of NUST for their support during the sampling process.

REFERENCES

Aguirre-González, M., Taborda-Ocampo, G., Dussan-Lubert, C., Nerin, C. & Rosero-Moreano, M. 2011 Optimization of the HS-SPME technique by using response surface methodology for evaluating chlorine disinfection by-products by GC in drinking water. *Journal of the Brazilian Chemical Society* **22** (12), 2330–2336.

Allard, S., Charrois, J. W., Joll, C. A. & Heitz, A. 2012 Simultaneous analysis of 10 trihalomethanes at nanogram per liter levels in water using solid-phase microextraction and gas chromatography mass-spectrometry. *Journal of Chromatography A* **1238**, 15–21.

Amjad, H., Hashmi, I., Rehman, M. S. U., Awan, M. A., Ghaffar, S. & Khan, Z. 2013 Cancer and non-cancer risk assessment of THMs in urban drinking water supplies of Pakistan. *Journal of Ecotoxicology and Environmental Safety* **91**, 25–31.

APHA 2012 *Standard Methods for the Examination of Water and Wastewater*, 22nd edn. American Public Health Association, Washington, DC.

Bahri, M. & Driss, M. R. 2010 Development of solid-phase microextraction for the determination of trihalomethanes in drinking water from Bizerte, Tunisia. *Desalination* **250**, 414–417.

Bergamaschi, B. A., Fram, M. S., Kendall, C., Silva, S. R., Aiken, G. R. & Fujii, R. 1999 Carbon isotopic constraints on the contribution of plant material to the natural precursors of trihalomethanes. *Organic Geochemistry* **30**, 835–842.

Cancho, B., Ventura, F. & Galceran, M. T. 1999 Solid-phase microextraction for the determination of iodinated trihalomethanes in drinking water. *Journal of Chromatography A* **841**, 197–206.

Chang, E. E., Chiang, P. C., Ko, Y. W. & Lan, W. H. 2001 Characteristics of organic precursors and their relationship with disinfection by-products. *Chemosphere* **44**, 1231–1236.

Chowdhury, S., Champagne, P. & Husain, T. 2007 Fuzzy risk-based decision-making approach for selection of drinking water disinfectants. *Journal of Water Supply: Research and Technology – AQUA* **56**, 75–93.

Deok-Hee, C., Sung-Ho, K. & Seong-Geun, O. 2003 Analysis of trihalomethanes in drinking water using headspace-SPME technique with gas chromatography. *Water Research* **37**, 402–408.

Dos Santos, M. S., Martendal, E. & Carasek, E. 2011 Determination of THMs in soft drink by solid-phase microextraction and gas chromatography. *Food Chemistry* **127** (1), 290–295.

Guimarães, A. D., Carvalho, J. J., GonÇalves, C. & Alpendurada, M. D. F. 2008 Simultaneous analysis of 23 priority volatile compounds in water by solid-phase microextraction–gas

chromatography–mass spectrometry and estimation of the method's uncertainty. *International Journal of Environmental Analytical Chemistry* **88**, 151–164.

Karanfil, T., Schlautman, M. A. & Erdogan, I. 2002 Survey of DOC and UV measurement practices with implications for SUVA determination. *Journal of American Water Works Association* **94** (12), 68–80.

Pawliszyn, J. 1997 *Solid Phase Microextraction: Theory and Practice*. John Wiley & Sons, London, UK.

Plewa, M. J., Wagner, E. D., Jazwierska, P., Richardson, S. D., Chen, P. H. & McKague, A. B. 2004 Halonitromethane drinking water disinfection byproducts: chemical characterization and mammalian cell cytotoxicity and genotoxicity. *Environmental Science and Technology* **38**, 62–68.

Rasheed, S., Campos, L. C., Kim, J. K., Zhou, Q. & Hashmi, I. 2016 Optimization of total trihalomethanes (TTHMs) and their precursors removal by granulated activated carbon (GAC) and sand dual media by response surface methodology (RSM). *Water Science and Technology: Water Supply* **16** (3), 783–793.

Richardson, S. D., Plewa, M. J., Wagner, E. D., Schoeny, R. & DeMarini, D. M. 2007 Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfection by-products in drinking water: a review and roadmap for research. *Mutation Research/Reviews in Mutation Research* **636**, 178–242.

Rosero, M. M., Aguirre, M., Pezo, D., Taborda, G., Dussán, C. & Nerin, C. 2012 Solventless microextraction techniques for determination of trihalomethanes by gas chromatography in drinking water. *Water Air Soil Pollution* **223**, 667–678.

San, J. P. M., Carrillo, J. D. & Tena, M. T. 2007 Fiber selection based on an overall analytical feature comparison for the solid-phase microextraction of trihalomethanes from drinking water. *Journal of Chromatography A* **1139**, 27–35.

Singer, P. 1999 Humic substances as precursors for potentially harmful disinfection by-products. *Water Science and Technology* **40** (9), 25–30.

Stack, M. A., Fitzgerald, G., O'Connell, S. & James, K. J. 2000 Measurement of trihalomethanes in potable and recreational waters using solid phase micro extraction with gas chromatography-mass spectrometry. *Chemosphere* **41**, 1821–1826.

Takamatsu, H. & Ohe, H. S. 2003 Measurement of the effect of salt on vapor-liquid equilibria by using headspace gas chromatography. *Journal of Chemical and Engineering Data* **48**, 277–279.

USEPA 1995 *Determination of Chlorination Disinfection by-Products and Chlorinated Solvents in Drinking Water by Liquid-Liquid Extraction and Gas Chromatography with Electron-Capture Detection*. Environmental Monitoring Systems Laboratory Office of Research and Development, Method 551.1, USEPA, Washington, DC, USA.

USEPA 2003 *Office of Water (4606M), EPA 816-D-03-002. National Primary Drinking Water Regulations: The Stage 2 Disinfectants and Disinfection Byproducts Rule Implementation Guidance*. USEPA, Washington, DC, USA.

Zia, M. A., Khalil-ur-Rehman, F. A. & Latif, R. 2005 Microbiological and chemical aspects of drinking water and treatment to enhance its quality. *Journal of Research (Science)* **16**, 11–18.

First received 1 January 2018; accepted in revised form 14 September 2018. Available online 10 October 2018