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

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

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27 **Abstract**

28 Trihalomethanes (THMs) are regulated disinfection byproducts (DBPs), analyzed in drinking
29 water due to their toxicological health effects. However, few data exist regarding the content of
30 emerging THMs in drinking water which are present at very low concentrations. This study aimed
31 to monitor hazardous and emerging THMs from drinking water supply in a residential area via
32 solid phase microextraction using gas chromatography. Response surface methodology was
33 employed to evaluate the role of salt concentration, temperature, desorption and extraction times
34 on THMs formation as a result of raw water prechlorination. Maximum THM detection was
35 achieved at 3.25g Na₂SO₄ salt via 30 min extraction time at 80°C along with 8 min of desorption
36 time. The quantification results revealed the presence of total THMs in all drinking water
37 samples, while most of the sites (88%) exceeded the permissible limit set by USEPA. Among I-
38 THM, chloriodomethane was found to be dominant as detected in 79% of samples.

39 **Keywords:** Disinfection by-products; Distribution network; Response surface methodology;
40 Solid-phase microextraction; Water analysis.

41

42 **1. Introduction**

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

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

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

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

70 and expensive as well. According to Santos *et al.* (2011), extraction temperature was the most
71 important factor in THMs extraction from soft drinks.

72 Therefore, it has been challenging to develop and optimize various variables and different
73 conditions to estimate maximum THMs extraction from water. Recently, various statistical
74 experimental designs have been used for this purpose in water distribution networks (Rosero *et al.*
75 *al.* 2012). Response surface methodology (RSM) is a useful technique for designing experiments,
76 building models, analyzing and optimizing effects of several independent variables. It also
77 analyses the relationship between independent variables and resulted responses (Rasheed *et al.*
78 2016). RSM combined to central composite design (CCD) is an efficient tool to study the
79 simultaneous effect of various variables, which influence the responses, with limited number of
80 experiments by eliminating non-significant interactions of variables (Guimarães *et al.* 2008).
81 Gonzelez *et al.* (2011) optimized the extraction conditions for THMs from water samples using
82 response surface methodology's study using a composite 2⁵ factorial design. It was found that the
83 extraction temperature and desorption times are the most influential conditions in the process.

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

86 Following are the study objectives:

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

93 **2. Methods and Material**

94 **2.1. Chemicals and Solvents**

95 Standard analytes (Iodoform, Chloriodomethane, Chloroform, Dibromochloromethane,
96 Bromodichloromethane and Bromoform) and solvents were purchased from Sigma Aldrich
97 (USA) and Merck (Germany) with 99% purity respectively. Whereas, SPME (75 µm Car-PDMS)

98 fiber was obtained from Supelco (USA).

99 **2.2. Chlorination process of treated water at treatment plant**

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

105 The samples collected from the drinking water source and consumer's end within the university
106 (Table 1) were analyzed for physicochemical (free chlorine, UV₂₅₄, pH, TDS, DO, Turbidity, EC,
107 alkalinity, hardness etc) contamination which showed that all the parameters were within the
108 USEPA and WHO limits. It was observed generally, that free chlorine concentration at source
109 ranged between 0.5 - 1.5 mg/L, whereas at consumer's tap ranged between 0.23 to 0.46 mg/L,
110 which lies within the optimum range prescribed by WHO.

111 **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 (Tubewell)	L3W
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

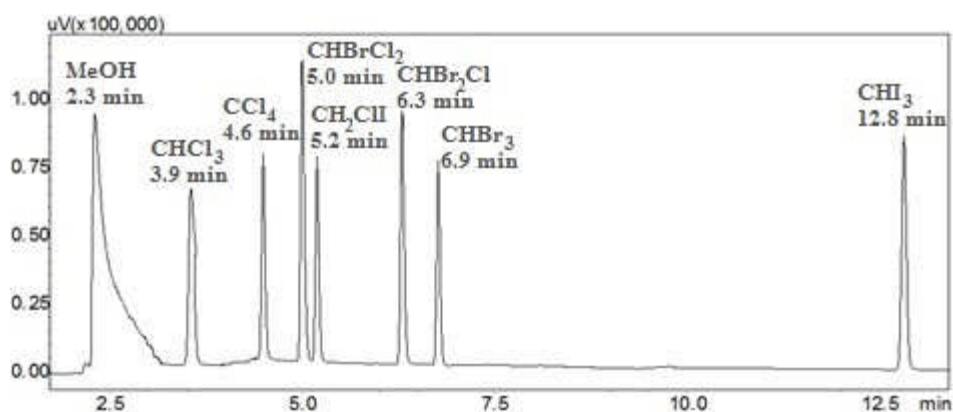
112

113 **2.3. Sampling and storage**

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

118 **2.4. Standard solutions**

119 A THM stock solution of 1000 µg/L was prepared in methanol as per EPA Method 551.1 (USEPA
120 1995). Working standard solutions were prepared to obtain linear calibration curves and detection
121 limits. For spiking THMs standard solution, carbon tetra chloride (CCl₄) solution was prepared
122 in methanol (1000 µg/L) to get a reproducible chromatogram (Fig. 1).



123

124

Fig1.TIFF Chromatogram of THMs mixture using SPME fiber

125 **2.5. Instrumental conditions**

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

130 **2.6. HS-SPME**

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

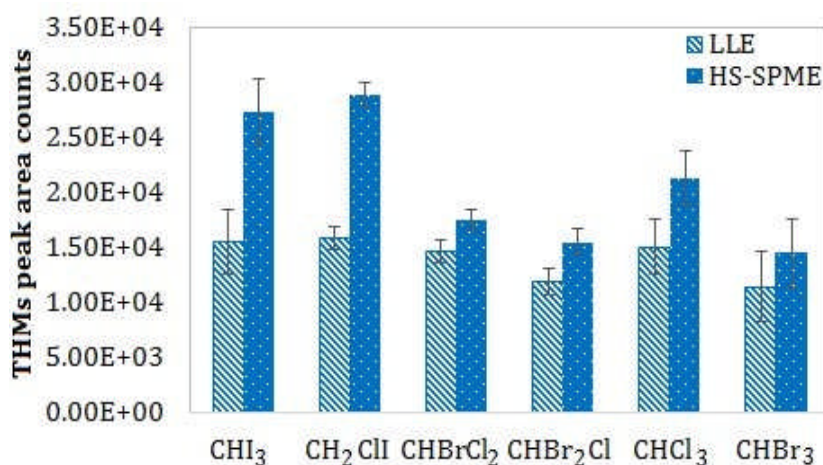
135 **2.7. Liquid-liquid extraction (LLE)**

136 THMs standard (10 μ L) was added to 35 mL distilled water followed by Na_2SO_4 salt and MtBE
 137 as extraction solvent. The vial was sonicated for 5 min. 500 μ L of the organic layer formed was
 138 transferred into a GC vial containing 10 μ L of CCl_4 (internal standard). The extract was then
 139 injected in a GC column for analysis (Allard *et al.* 2012).

140 3. Results and Discussion

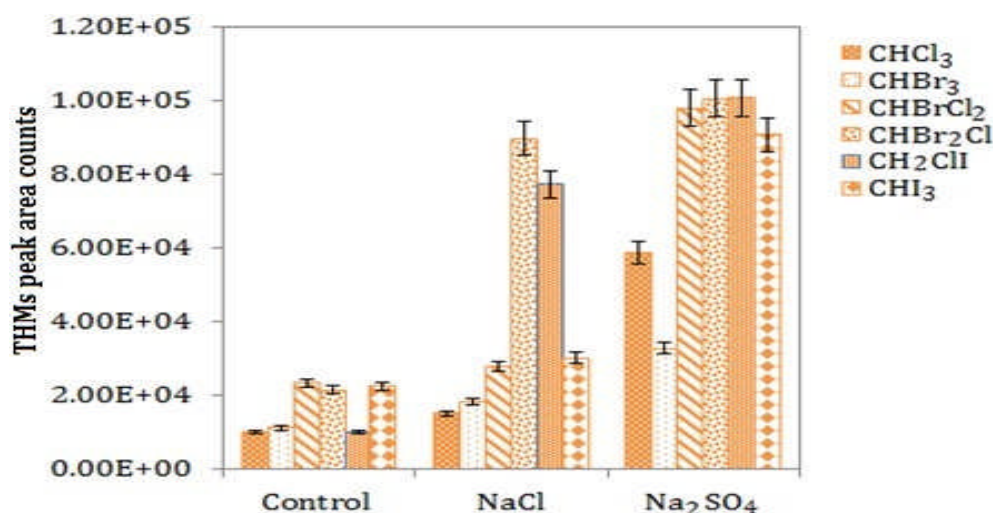
141 3.1. Comparison of HS-SPME and LLE techniques

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



145
146

2(a)



147
148

2(b)

149 **Fig2.TIFF** Comparison studies for THMs extraction (a) Comparison of HS-SPME and LLE
 150 techniques (b) Comparison of various salts using HS-SPME

151 (Note: HS-SPME = Headspace-solid phase micro extraction; LLE = Liquid-liquid extraction)

152 The recovery efficiencies were also calculated for these methods to evaluate the method
 153 performance for THMs. According to USEPA percent recoveries must fall in the range of 70 to
 154 120 for THMs. The HS-SPME gave acceptable recovery values for all THMs (Table 2). As a
 155 result, HS-SPME is proposed to be a reproducible, faster and accurate technique for THMs
 156 analysis as compared to LLE. Cancho *et al.* (1999) determined the recovery values close to 100%
 157 by spiking the water samples at a concentration of 10, 1.5 and 0.5 mg/L with I-THMs.

158 **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 ₂ Cl	CHBrCl ₂	CHI ₃	CH ₂ ClI
HS-SPME/GC/ECD						
recovery % (1000 µg/L)	99.3	69.3	98.3	85.9	73.7	83.6
S.D ^a	0.20	0.10	0.16	0.21	0.22	0.24
R.S.D ^b %	20.8	22.1	16.3	24.0	30.5	28.9
LLE/GC/ECD						
% recovery (1000 µg/L)	95.0	69.4	91.1	71.5	69.8	79.9
S.D	0.25	0.11	0.21	0.20	0.17	0.20
R.S.D %	26.3	24.1	23.1	28.0	26.9	25.0

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

160 3.2. Salt selection for HS-SPME technique

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

168 3.3. Testing method performance

169 Accuracy of HS-SPME technique was evaluated by plotting calibration curves. An acceptable
 170 linear range with regression coefficients (R²) higher than 0.93 was obtained for all THMs, which
 171 correlated with the findings of Stack *et al.* (2000) who indicated 0.9920 to 0.9959 R² value at
 172 THMs concentration ranging from 10 to 160 mg/L. The validity of HS-SPME technique was
 173 estimated in terms of limit of quantification (LOQ) and limit of detection (LOD) (Table 3). The

174 LOQs ranged between 4 ng/L for CHI₃ and 68 ng/L for CHCl₃ respectively. Repeatability and
 175 reproducibility values were found less than 11%. The results demonstrated that proposed HS-
 176 SPME technique is appropriate for measuring THMs at µg/L levels in drinking water.

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

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

178 a. LOD = Limit of detection; b. LOQ = Limit of quantification; c. R.S.D = Relative standard deviation

179 3.4. Optimization of HS-SPME technique using response surface methodology (RSM)

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

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

Coded variables	Levels and ranges				
	Lowest (-α)	Low (-1)	Centre (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

186 3.5. Effect of extraction temperature and extraction time

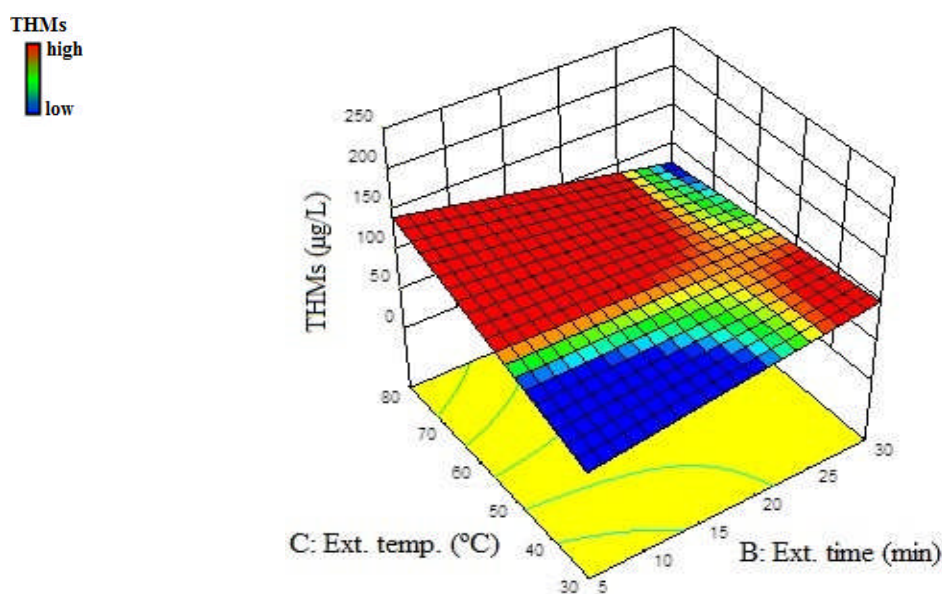
187 Interaction between extraction temperature and extraction time was observed in a 3D response
 188 surface revealing synergetic effect of both variables for THMs (Fig. 3a). This can be attributed to
 189 the fact that increasing the extraction temperature increases the diffusion of the analytes to the
 190 fiber surface. Consequently, the time necessary to reach the equilibrium of partition between the
 191 sample and extractor phase is reduced (Santos *et al.* 2011). In addition, here diffusion coefficients
 192 in both water and headspace are higher thus diffusion of volatile analytes from aqueous phase to
 193 headspace is enhanced. Therefore, with increase in temperature during adsorption period,

194 increased THMs extraction rate was observed. Similar results were also reported by Deok-Hee *et*
195 *al.* (2003).

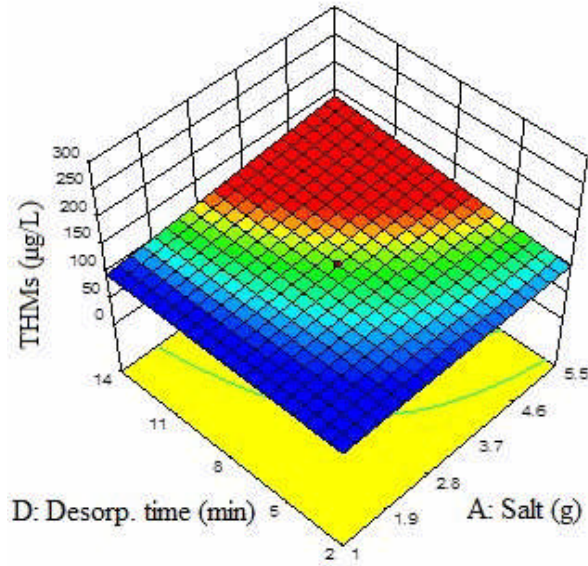
196 While observing the effect of extraction time on THMs extraction in Fig 3a, an increase in THMs
197 extraction (Z-axis) was observed with increased extraction time (B: y-axis: extraction time). The
198 highest extraction was observed at 30 min. Here extraction time was evaluated as an important
199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

203 3.6. Effect of desorption time and salt addition

204 The impact of desorption time (D: x-axis: desorption time) and salt on the THMs extraction was
205 evaluated in Fig. 3b. It is evident that addition of more salt resulted in higher THMs extraction.
206 This could be attributed to the fact that the salt addition increases the ionic strength of matrix and
207 decreases the solubility of analytes so that more analytes are dispersed into the headspace,
208 thereby, contributing to enhanced adsorption on the fiber (Takamatsu & Ohe 2003). Meanwhile,
209 longer extraction time synergistically lead to higher THMs extraction. While desorption times 8
210 min was sufficient to desorb analytes in GC port (Fig. 5). Similar behavior for high molecular
211 weight compounds has been reported earlier (Cancho 1999; San 2007).



3(a)



3(b)

214

215

216 **Fig3.TIFF** 3D response surface showing response of THMs as a function of (a) extraction temperature
 217 and extraction time (b) desorption time and salt

218 **3.7. Response surface modeling (RSM)**

219 Response surface modelling was done to develop relationship between the process variables and
 220 the THMs response. The significance of the model was assessed by applying ANOVA, and finally
 221 the best fitted model equation was obtained as:

222 $THMs \left(\frac{\mu g}{L}\right) = 111.21 + 12.93A + 0.26B + 25.04C + 10.17D + 37.93AB - 6.92AC +$
 223 $9.85AD - 33.82BC + 32.25BD - 1.7CD$ (1)

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

227 $THMs \left(\frac{\mu g}{L}\right) = +111.21 + 12.93A + 25.04C + 10.17D + 37.93AB + 9.85AD - 33.82BC +$
 228 $32.25BD$ (2)

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

233 The coefficient for *AB* was found to be 37.92, higher than the factor *C*, *BC* and *BD*. Thus, the

234

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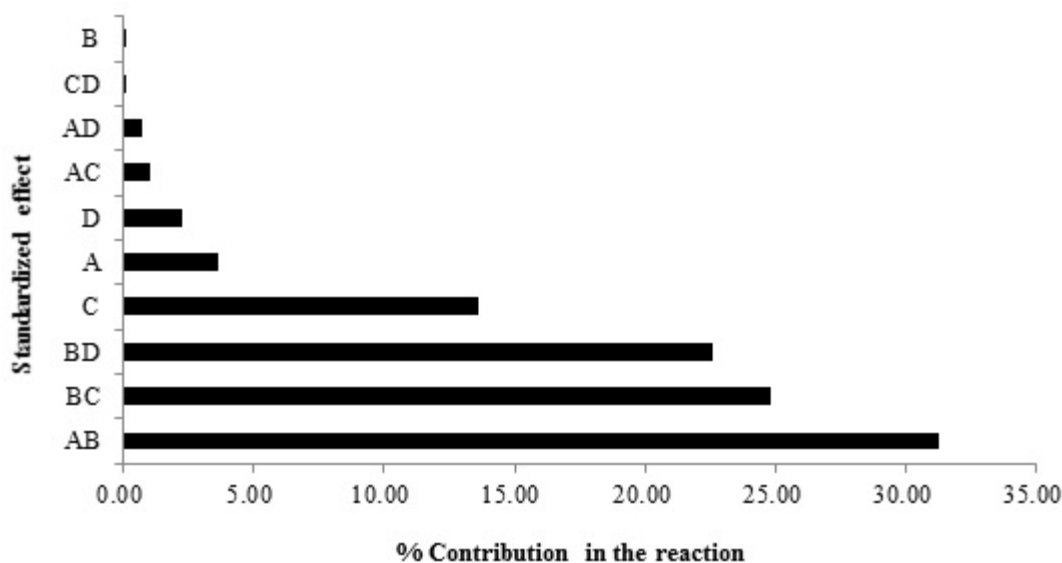
Table 5 Response of contributing factors along p values

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

236 *Significant effect ($p < 0.01$); **Less significant ($p = 0.01 \leq p < 0.05$); †Least significant ($p > 0.1$).

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

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



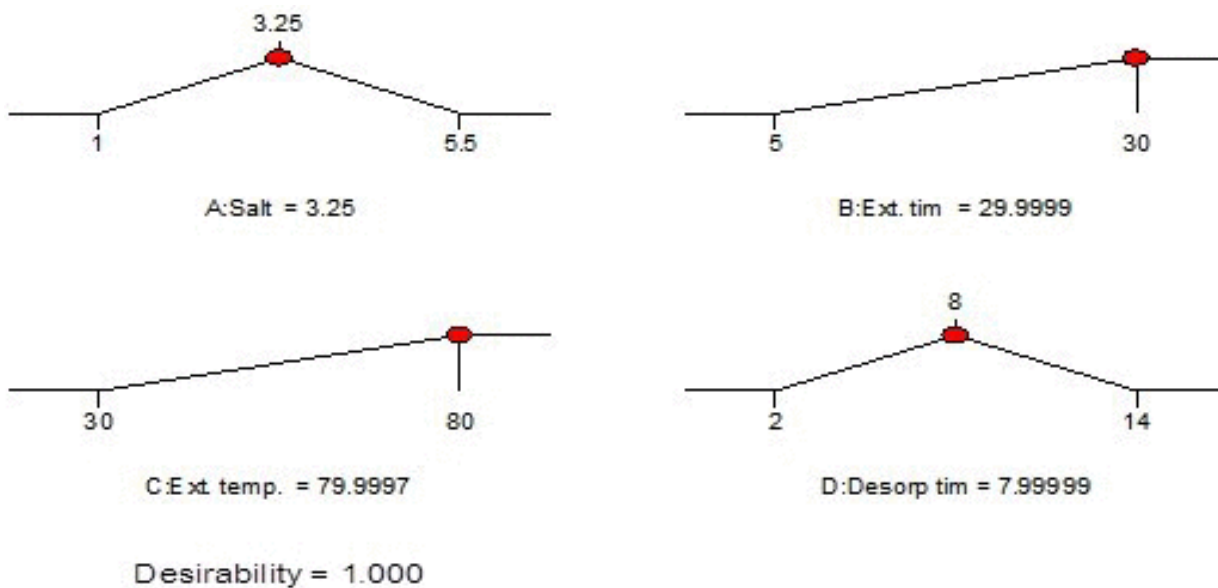
244

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

247 3.8. Optimization modelling for THMs extraction

248 Process optimization is an important step in determining values of factors for which response is
 249 at a maximum (Rasheed *et al.* 2016). Based on the variables selected (Table 4), numerical
 250 optimization was performed by the RSM-CCD to achieve one or more points in factors domain
 251 that would maximize the THMs extraction. The desirability value (D) closer to 1 is considered to
 252 be significant by the RSM software. It was observed that maximum extraction efficiency was

253 obtained when temperature was maintained at 80°C with extraction time of 30 min and 3.25 g
254 salt at 8 min of desorption time at a D value of 1.0 (Fig. 5).



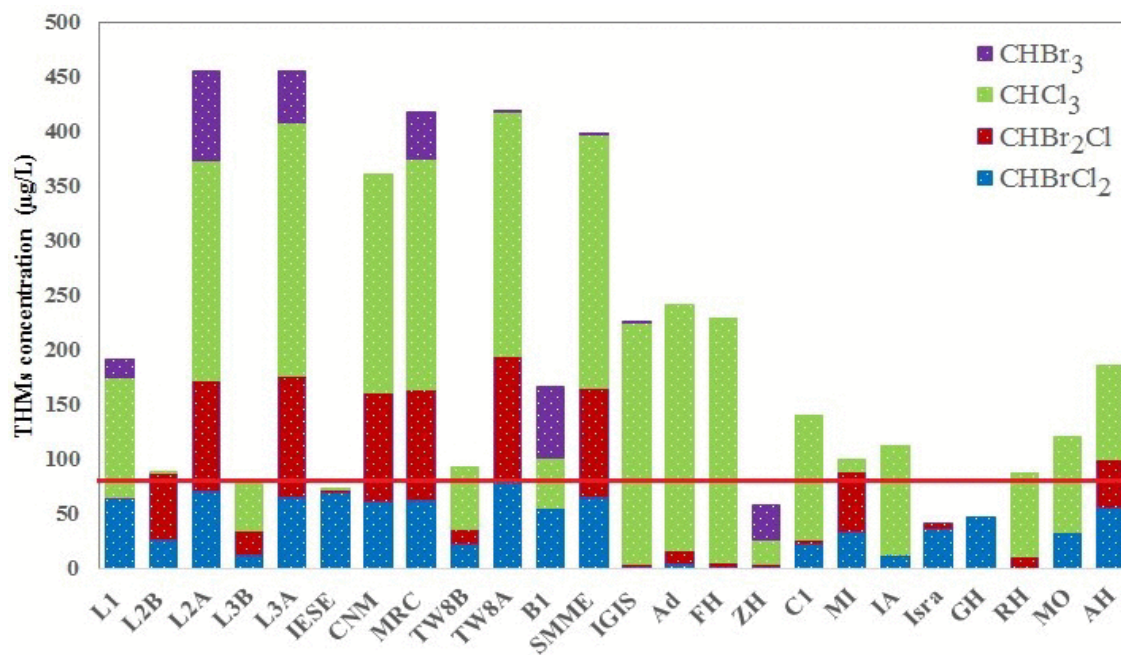
255

256 **Fig5.TIFF** Ramp function for maximum THMs extraction

257 3.9. THMs monitoring from drinking water samples by the optimized HS-SPME technique

258 The HS-SPME technique optimized by the RSM software was then employed for determination
259 of THMs from the water samples of an educational institution in Islamabad, Pakistan. Samples
260 were collected and analyzed as per standard protocol. The concentration of total and iodinated
261 THMs is shown in Fig. 6 (a) and (b) respectively. For TTHMs, among all sites, sites L2A, L3A,
262 CNM, MRC, TW8A and SMME had high concentration of TTHMs as shown in Fig. 6 (a). The
263 respective chromatographic peaks for TTHMs and I-THMs can be observed in Fig. 7a and 7b
264 respectively. Fig. 7 shows clearly identifiable chromatographic peaks from sites L2A and MRC.
265 The large peak signal of chloroform showed high content of chlorine present at these sites to react
266 with organic matter which resulted in high THMs yield at site L2A and MRC. This high
267 concentration of TTHMs could be attributed to the presence of high UV_{254} absorbance, TDS and
268 residual chlorine. Some 88% sites exceeded the standard values while highest concentration was
269 observed to be 455.9 $\mu\text{g/L}$ at site L2A. UV_{254} absorbance is the indicator of NOM in water, which
270 is one of the most significant precursors of THMs development (Chang *et al.* 2001; Singer 1999).
271 At all the sampling sites, chloroform was detected in the highest ratio (Fig. 6a), with maximum
272 concentration of 233.4 $\mu\text{g/L}$ observed at site L3A. While I-THMs were detected in approximately

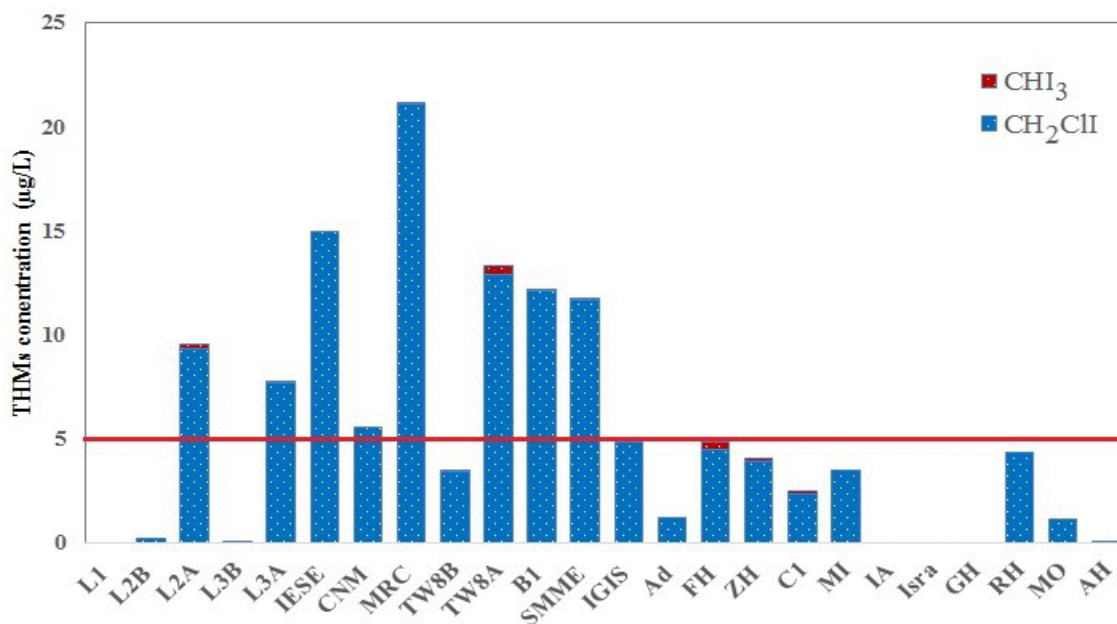
273 85 % of the samples as shown in Fig. 6b. Chloriodomethane was the dominant specie, found in
 274 79% of the tested samples with highest mean value of 101.1 $\mu\text{g/L}$ at MRC, while on remaining 8
 275 sites, it exceeded the threshold values of 0.2 - 5 $\mu\text{g/L}$. However, iodoform was detected in lowest
 276 concentration ranging from 0.012 - 0.433 $\mu\text{g/L}$ in 45% of the samples, whereas in other sites it
 277 was within the threshold values.



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279

6(a)



280

281

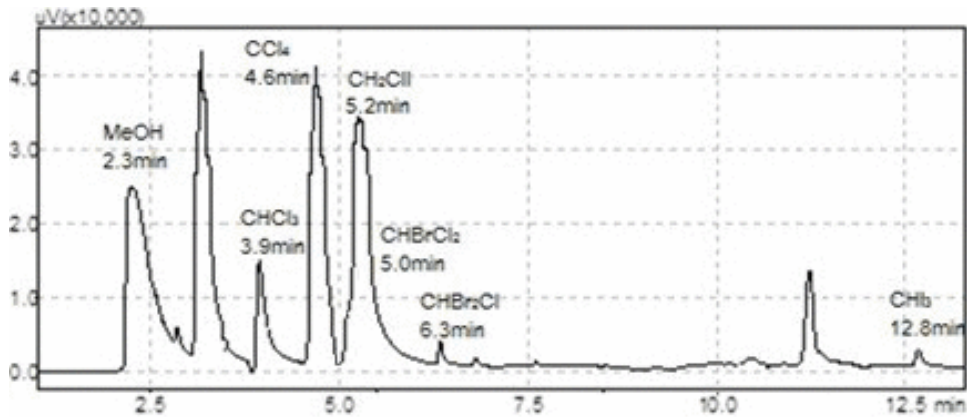
6(b)

282 **Fig6.TIFF** Mean THMs concentration in drinking water samples using optimized HS-SPME technique

283 (a) Mean TTHMs (b) Mean I-THMs

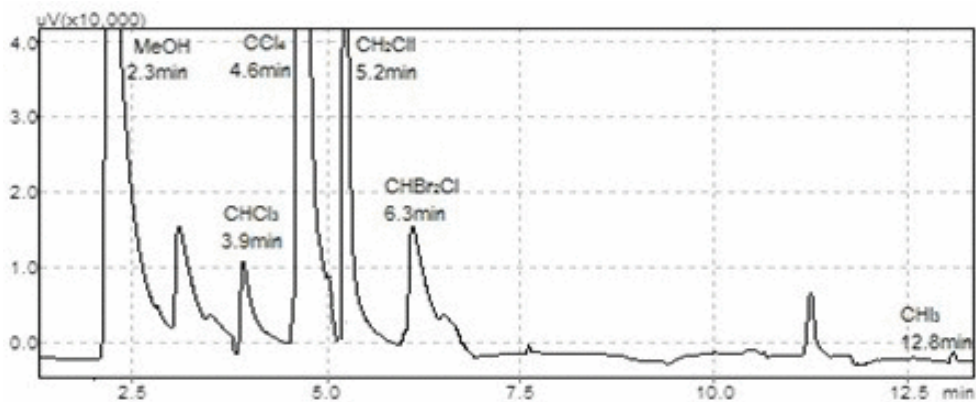
284 (Note: TTHMS = Total THMs; I-THMS = Iodinated THMs)

285 Another reason could be attributed to the close occurrence of sampling sites to the chlorination
286 source as more residual chlorine was available to react with the precursor UV₂₅₄ absorbance,
287 yielding high concentration of TTHMs and I-THMs. Similar findings were also reported by
288 Bergamaschi *et al.* (1999) and Karanfil *et al.* (2002).



289
290

7(a) L2A



291
292

7(b) MRC

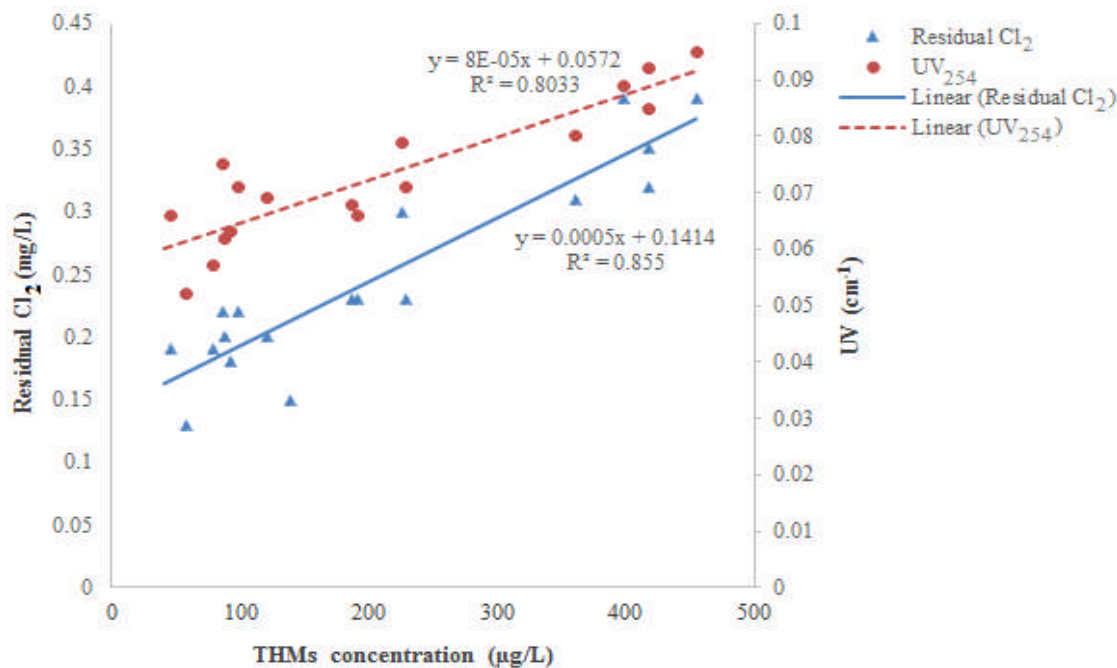
293 **Fig7.TIFF** Chromatograms of drinking water collected from sampling sites (a) L2A (b) MRC

294 (Note: L2A = Location 2 after chlorination; MRC = Material Recovery Centre)

295 3.10. Correlations between THMs and residual chlorine and UV₂₅₄

296 A correlation between THMs concentration, residual Cl₂ and UV₂₅₄ absorbance was assessed by
297 regression analysis, keeping in view the findings of Chang *et al.* (2001) and (Singer 1999) as
298 mentioned above.

299 The results showed a strong positive linear correlation between residual Cl₂ and UV₂₅₄
300 concentration with THMs formation with R² = both 0.80 (Fig. 8). These results are in accordance
301 with literature (Chowdhury *et al.* 2007). Hence it proves that the potential reason for THMs
302 contamination in drinking water was the presence of NOM and residual Cl₂.



303
304 **Fig8.TIFF** Linear correlations of THMs with UV₂₅₄ and residual

305 **4. Conclusions**

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

- 308 (1) The physical and chemical parameters (pH, EC, temperature, UV₂₅₄ absorbance, residual Cl₂,
309 TDS, turbidity, DO etc.) of drinking water samples meet the permissible limits recommended
310 by WHO.
- 311 (2) The HS-SPME and LLE techniques were compared to achieve the maximum THMs response.
312 The results showed significant ($p < 0.1$) increase in peak areas for HS-SPME, which is an
313 excellent alternative extraction technique comparable to LLE.
- 314 (3) HS-SPME technique was optimized using RSM-CCD for THMs determination. Optimum
315 conditions for THMs extraction were 30 min extraction time at 80°C with addition of 3.25g
316 Na₂SO₄ salt and 8 min of desorption time.
- 317 (4) The optimized method was used to determine THMs in an institutional drinking water
318 samples which revealed THMs presence in 90 % of the samples, with 30 % exceeding the
319 U.S.EPA limit, indicating the possibility of adverse public health risks suggested by various
320 researchers such as cancer, adverse reproductive disorders, taste/odor problems, organoleptic
321 issues and consumer complaints. As THMs are more common in the public water systems,

322 therefore they are a threat to any water supply that uses chlorine, thus a large population may
323 be affected by this contamination, ultimately putting pressure on population dynamics.

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

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

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

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

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

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

338 • Granular activated carbon (GAC) adsorption may be used to remove NOM, the major
339 precursor of DBPs.

340 • Multiple other drinking water treatment processes, including pre-ozonation, conventional
341 treatments (coagulation/sedimentation, pre/post-sand filtration), ozone biological activated
342 and carbon advanced treatment, may also be investigated depending upon the available
343 resources and need of the particular area.

344 • New approaches may be developed to effectively control THMs formation, in chlorinated
345 drinking water by targeting intermediate aromatic halogenated DBPs.

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