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COMPARISON OF METHODS FOR DETERMINATION OF TRIHALOMETHANES IN DRINKING WATER

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Abstract

Comparison of 2 methods (head space analysis and liquid-liquid extraction methods) were carried out in this work for determination of trihalomethanes (THMs) in drinking water supplies in Bangkok. Both methods are applicable for determination of the haloform concentrations ranging 0.1 to 200 µg/1. Sampling apparatus and procedure for both head space analysis and liquid-liquid extraction methods are very simple and easy, but possible disadvantages for liquid-liquid extraction are its somewhat low sensitivity and time consumption because the co-extracted non-volatile compounds require several minutes to be eluted from the column with late analysis. A priminary survey for THMs in drinking water supplies in Central Bangkok Metropolitan was conducted using head space analysis. The survey demonstrated that trihalomethanes, chloroform, bromodichloromethane, and dibromochloromethane were found in drinking water supplies obtained from the surface water, but none of these chemicals was detected in the chlorinated water from groundwater. The range of total concentrations of trihalomethanes detected was 25 to 75 ug/1 and the mean value was 44.9 µg/1.

Introduction

Trihalomethanes in drinking water supplies are produced by the action of the chlorine added for disinfection or oxidation, with the naturally occurring precursors (e.g. humic substances) commonly found in source water. In 1974, Rook¹ concluded from his studies of haloform concentrations in water throughout a treatment plant that the haloforms were not present in significant quantities in the raw water, but formed as a result of the chlorination process. Later that year, Beller and Lichtenberg² published

data supporting this conclusion. Further confirmation was published in subsequent United States Environmental Protection Agency Reports³⁻⁵

Analytical methods for determination of trace amounts of these halogenated hydrocarbons in water generally require a preconcentration step. The target species can be either enriched by purging the aqueous phase with a stream of gas followed by trapping⁶⁻¹¹ or by solvent extraction methods¹²⁻¹⁴. Various head space analysis^{1,15-18} and direct aqueous injection methods¹⁹⁻²¹ have also been recommended. However the gas chromatographic methods used in the above studies are very sensitive and, because electron capture or electrolytic conductivity detectors are used, they are highly specific for halogen-containing compounds. However, ideal methods for drinking water analysis are those which can handle a large numbers or samples in a relatively short period of time. Unfortunately, most of the techniques which require preconcentration do not meet these requirements, except for head space analysis and direct aqueous injection methods.

However, while the head space analysis measures only the free haloforms present in the drinking water, the direct aqueous injection method quantitates the total potential halo-forms that can form after chlorination.

In this paper, the head space analysis and the liquid-liquid extraction method are chosen for determination of a trace amounts of trihalomethanes in drinking water supplies, and the results compared with each other.

Materials and Methods

Head Space Analysis

Ten millimeters of water samples are collected in 13 ml of serum vials and the vials are sealed immediately with Teflon-lined septum and aluminium cap using a vial closer. These vials are stood upside down prior to analyze by gas chromatography. One hundred to five hundred ul of the head space vapor in the vials are removed with a gas tight syringe and then injected on gas chromatograph equipped with a suitable separation column and an electron capture detector.

Liquid-Liquid Extraction Method

Ten-ml of water samples are collected in 15 ml glass vessel with cap. They are then capped with a Teflon-coated rubber septum and sealed by crimping the aluminum septum retainer over the lip of the bottle. The samples can then be conveniently transfered to the laboratory for analysis.

In the laboratory, 2 ml of the extraction solvent (pentane in this work) is added directly to the sampling bottle. This is done using a 5-ml syringe with a needle. The needle of syringe is peirced through the septum, and the (2 ml) solvent is injected into the bottles. The partitioning is then brought to equilibrium by shaking the bottles for 3 min vigorously and allow it to stand. Then, an aliquot (1-5 µl) of the organic layer is removed with a microsyringe for chromatographic analysis.

Preparation of Standard solutions

Stock solution containing a mixture of chloroform (1 mg/ml), bromodichloromethane (1 mg/ml), dibromochloromethane (4 mg/ml) and bromoform (20 mg/ml) in methanol was obtained from Kanto Chemical Co. Ltd., (Japan) for head space analysis. This stock was diluted 10 to 100 times with methanol in the cleaned and cooled room. These standard were sealed with Teflon-lined septum aluminum cap and keeped in the refrigerator before use for the preparation of standard solutions.

Stock solution containing a mixture of chloroform (1.0 mg/ml), bromodichloromethane (0.1 mg/ml), dibromochloromethane (0.4 mg/ml), and bromoform (2 mg/ml) in methanol was prepared and diluted 100 times with methanol for liquid-liquid extraction method. This standard was then allowed to keep in the refrigerator before use.

Gas Chromatographic Analysis

A Shimazu GC-7A gas chromatograph equipped with 63 Ni electron capture detector used in this study. The column, which is connected to the chromatograph, is 3 mm i.d. x 3 m glass packed with 20% SF-96 + 20% Silicon DC-550 (3 + 2) on Chromosorb W AW-DMCS (80-100 mlsh). The operating conditions are as follows: injection part and detector temperature, 230°C; column temperature, 110°C; and carrier gas, N_2 70 ml/min.

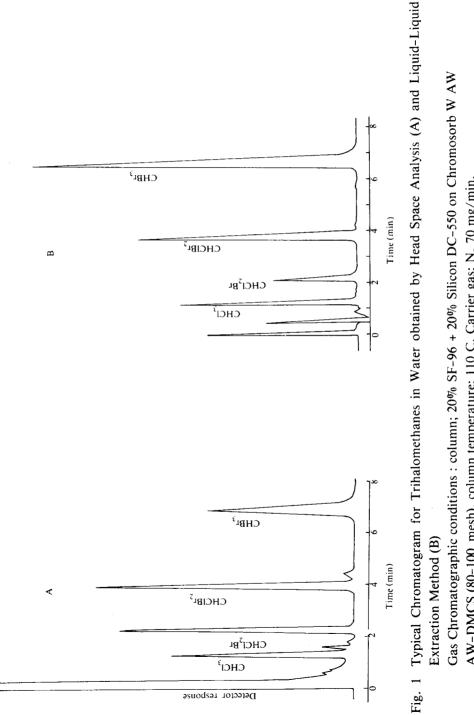
Quantitative measurements for water samples were made using the calibration curves of trihalomethane standard. Since the sensitivity of ECD-gas chromatography is dependent upon the operating time to time and day to day, the calibration curves for trihalomethane standard should be made at the beginning and the end of operating every day.

Results and Discussion

Comparison of head space analysis and liquid-liquid extraction.

Typical ECD gas chromatograms of trihalomethane mixture standard are shown in Fig. 1. The chromatograms in Fig. 1 show a good separation for each trihalomethane on the chromatographic material, employed in this work. Very sharp and symmetrical peaks for all compounds were also observed on these columns.

Calibration curves for each trihalomethane obtained by head space analysis and liquid-liquid extraction method are shown in Fig. 2. With the actual detection chromatographic columns and detector employed in the literature, the applicable range for liquid-liquid extraction method ¹²⁻¹⁴ is approximately 0.5 to 200 µg/1, and for head space analysis ¹⁵⁻¹⁸, approximately 0.1 to 200 µg/1. In our studies, as Figs. 3 and 4 show, the sensitivity for only bromoform obtained by liquid-liquid extraction method was higher than those obtained by head space analysis. However, the sensitivities for chloroform and bromodichloromethane obtained by head space analysis were approximately 2-3 times higher than those obtained by liquid-liquid extraction method (Fig. 3 and 4).



Sample B: ChCl₃ (10 μg/l), CHCl₂Br (1 μg/l), CHClBr₂ (4 μg/l), CHBr₃ (20 μg/l). injected solvent: 1 μl Sample A: $ChCl_3$ (2 $\mu g/l$), $ChCl_2Br$ (1 $\mu g/l$), $CHClBr_2$ (4 $\mu g/l$), $CHBr_3$ (20 $\mu g/l$). injected gas: 200 $\mu g/l$ AW-DMCS (80-100 mesh), column temperature; 110 C, Carrier gas; N₂ 70 mg/min.

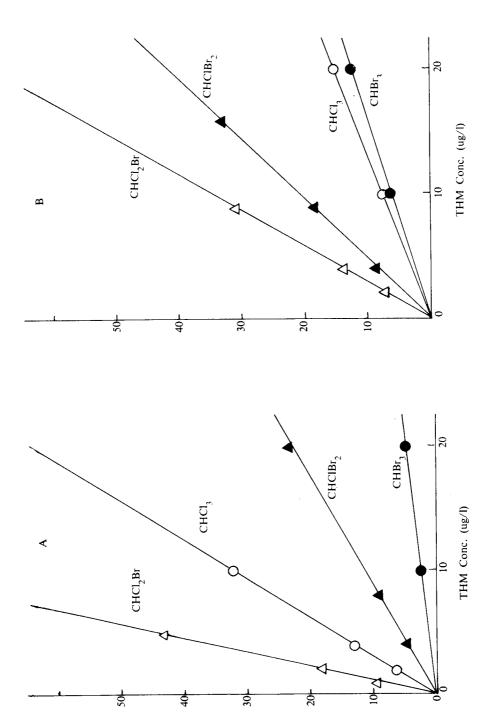


Fig. 2 Calibration Curves for Trihalomethanes obtained Head Space Analysis (A) and Liquid-Liquid Extraction Method (B) Gas Chromatographic Conditions: Same as Fig. 1

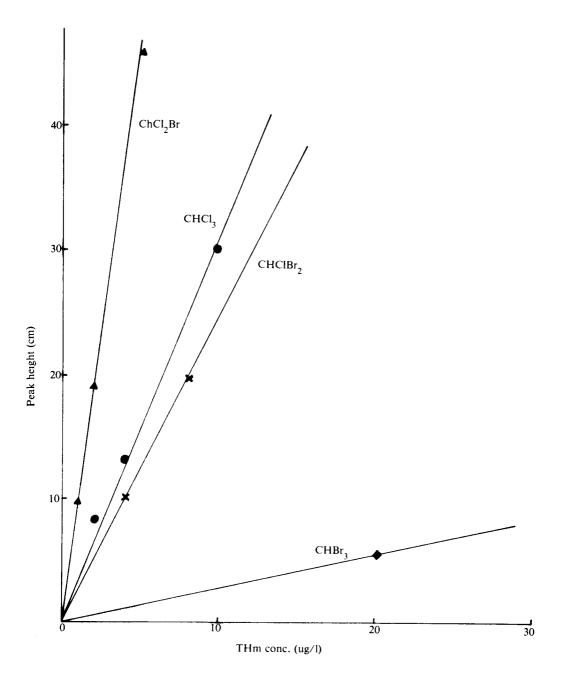


Fig. 3 Calibration Curves for Trihalomethanes obtained by HSA Gas Chromatographic conditions: the same as Fig. 1

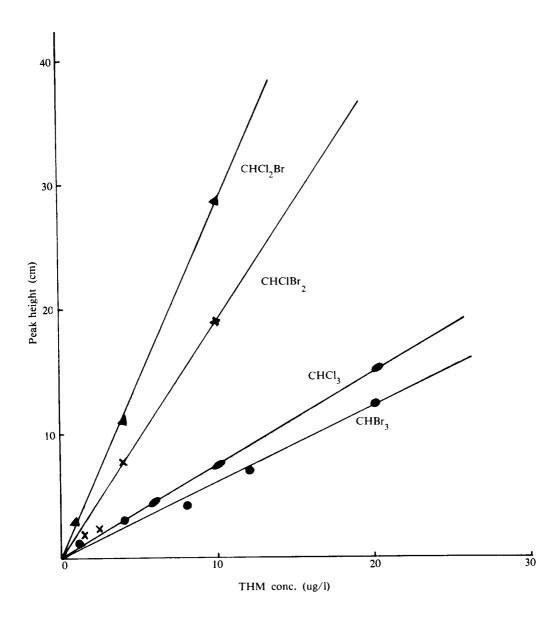


Fig. 4 Calibration curves for Trihalomethanes obtained by LLE Gas Chromatographic conditions: the same as Fig. 1

Sampling apparatus and procedure for liquid-liquid extraction and head space analysis methods are simple and easy but possible disadvantage for liquid-liquid extraction method are interferences i.e., non-volatile compounds and impurities are coextracted into the extracting solvent. So, gas chromatographic analysis time for liquid-liquid extraction method is required more than head space analysis method because non-volatile compounds require several minute to be eluted from the column and interfere with late analysis ²².

Relative retention times and detection limits for trihalomethanes obtained by head space analysis and liquid-liquid extraction methods are summarized in Table1.

Influence Factors for Head Space Analysis

Head space analysis involves distribution of volatile halogenated compounds between the air and water in the sealed bottle and injection of an aliquot of the air on gas chromatograph equipped with a suitable detector. It is known that the distribution coefficient (D_t air/water) of haloforms is strongly dependent upon the temperature and salt concentration $^{15-18}$.

To ascertain the salting effect on the distribution coefficient, standards were made up in raw drinking waters (collected from the Chao Phraya River on April 2, 1984) and analyzed by head space analysis method. The results are listed in Table 2, and show only slightly higher values for the raw waters which can be explained by salting effect.

Effect of sodiumthiosulfite added into the drinking water (collected from the drinking water supplies in Bangkok Metropolitan area) were also examined by head space analysis method. The results are listed in Table 3, and show no effect during the storage of water samples. This means no occurrence of the reaction of the residual chlorine with the remained organic matter in water, although the published papers ^{17–18} have demonstrated the occurrence of the reactions to increase the haloform concentrations.

Analysis of Drinking Water Samples by Head Space Method

The preliminary survey for THMs in the drinking water supplies collected from the Central Bangkok Metropolitan area on April 1984 are conducted by the use of head space analysis and the results are shown in Table 4.

With this survey, the three THMs (chloroform, bromodichloromethane, and dibromochloromethane) were found in the 35 drinking waters among the 39 samples collected from the different districts of Bangkok, ranging 25 to 75 μ g/1 of total THMs and the average concentration of it was 44.9 μ g/1. This figure is not so high compare to the THMs concentration found in Japan and U.S.A. ranging about 0-60 μ g/1 and 0-350 μ g/1. In addition Japanese and U.S.A. maximum control level of THMs in drinking water are less than 100 μ g/1. Chloroform was found in the highest concentra-

tions and followed by bromodichloromethane and dibromochloromethane, but bromoform was lower than detection limit. Other chlorinated compounds detected by Head Space-ECD-GLC were carbon tetrachloride and dichloroethane; no volatile halogenated hydrocarbons were found for four samples. These drinking waters were collected from Bang Khen, Nong Chok, MinBuri and Lard Krabang districts. In the latter 3 districts, groundwater is used for drinking water sources. It appears to be a correlation between chloroform, bromodichloromethane, and dibromochloromethane concentrations. The ratio between the three chemicals appears to be relatively constant in all water examined, indicating the probability of a common precursor or group of precursors for these halogenated hydrocarbons. Similar correlation between the three chemicals concentrations have been obtained by a earlier survey conducted by EPA¹¹.

To obtain an elementary knowledge of the extent of THMs during water treatment, the concentrations of THMs, total organic carbon, and residual chlorine were measured during the course of treatment at both Bang Khen and Sam Sen (Table 5). The samples were drawn from the rapid mix tank and from the settling tank and filter outlet as well as from the raw and finished water lines. Sampling and analytical procedures were similar to those previously described, with the exception of the determination of residual free chlorine which was done immediately at the plant site using a stabilized neutral orthotoludine field kit.

At both treatment plants the addition of chlorine to the filtered water in the rapid tank results in the formation of appreciable amounts of THMs within only a few minutes. Almost 90% of the TOC found in the raw water is coagulated and removed by flocculation and settling process. Different amount of T-THMs concentrations in each finished water was observed for the treatment systems A-D, although the same raw water was laid into these treatment plants from the Chao Phraya River. The difference in the amounts of THMs in the water may be dependent upon the treatment systems employed and the sampling date.

Conclusion

In this paper, comparison of two methods, head space analysis and liquid-liquid extraction, for determination of trihalomethanes in drinking water was conducted. Head space analysis involves the distribution of volatile halogenated compounds between the air and water in a sealed bottle and injection of an aliquot of the air on gas chromatography. On the other hand, liquid-liquid extraction method involves the extraction with a suitable organic solvent of volatile and non-volatile halogenated compounds from the water and analysis of the organic layer by a gas chromatograph equipped with electron capture detector.

Sampling apparatus and procedure for both head space analysis and liquid-liquid extraction methods are simple and easy, but possible disadvantage for liquid-liquid extraction method are its somewhat low sensitivity comparison with that of head space

RELATIVE RETENTION TIMES AND DETECTION LIMITS OF TRIHALOMETHANES BY GAS CHROMATOGRAPHY TABLE 1.

	Head Space Method ^a	Method ^a	Liquid-liquid Extraction Method ^a	ction Method ^a
THMs	Retention Detection time (min) limit ^b (µg/1)	Detection mit ^b (μg/1)	Retention Derection time (min) limit ^b (µg/1)	Detection nit ^b (μg/1)
Chloroform	1.20	0.4	1.15	1.0
Dichlorobromomethane	2.15	0.1	2.05	0.1
Dibromochloromethane	3.80	9.0	3.7	9.0
Bromoform	08.9	4	6.5	2.0

Silicon DC-550 (8 + 2)/Chromosorb W-AW DMCS; column temp. 110 C; injection a: GC condition: 3 mm I.D. x 3 m glass column packed with 20% SF-96 + 20%

and detector temp. 230°C ; carrier gas, N₂ 70 ml/min.

b: detection limit at S/N = 3

TABLE 2. COMPARISON OF SPIKED DISTILLED AND RAW WATER SAMPLES^a

	-					COD	CI-	THMs	THMs concentrations (µg/l)	is (µg/4)
Samp	Sample location	uol		Hd		(mg/l)	(mg/l)	CHCl ₃	CHCl ₂ Br (CHClBr ₂
Distill	Distilled water				_	1	l	6	6	37
Chao	Chao Phraya	River	River 1 (62 km) ^b		6	14.2	12	6	10	38
Ξ	` =	=	2 (36 km)		4	20.7	32	10	10	39
Ξ	=	=	3 (30 km)		4	22.1	120	6	6	36
=	=	=	4 (24 km)	7.36	9	ı	1100	10	11	39
Ξ	Ξ	=	5 (20 km)		0	1	2000	11	10	41
=	· =	=	6 (10 km)		0	l	5500	12	12	43

a) Calculated values for CHCl $_3$ (10 $\mu g/l$), CHCl $_2$ Br (10 $\mu g/l$), and CHClBr $_2$ (40 $\mu g/l$). b) Values in parentheses indicate the distance from the river mouth.

TABLE 3. INFLUENCE OF SODIUM THIOSULFITE ADDED AND STORAGE OF WATER SAMPLES^a

	Sample			Parameter Po	er	Total TH	Total THMs conc.	Ω	Difference
	naic			TOC	Nesidudai IC Cl	जी .	(l/gl/)		001 % L V / (B / V)]
No.	collected analy	analyzed	Ph	(mg/l) (mg/l)	(mg/l)	Sample A	Sample B	A-B	WI X [& //8-&)]
-	3/5/84	7/5/84	7.2	1.30	8.0	49.30	49.10	+0.15	+0.3
2	3/5/84	7/5/84	7.2	1.25	8.0	78.80	79.90	-1.10	-1.4
33	4/5/84	7/5/84	7.1	1.40	0.7	75.30	08.69	+5.50	+7.3
4	4/5/84	7/5/84	7.3	2.0	0.5	72.50	09.69	+2.90	+4.0
5	4/5/84	7/5/84	7.2	1.8	0.4	97.80	93.60	+4.20	+4.3
9	4/5/84	7/5/84	7.3	1.6	0.5	91.50	89.90	+1.60	+1.7
7	8/5/84	9/5/84	7.0	1.20	8.0	51.30	49.20	+2.10	+4.1
∞	8/5/84	9/5/84	7.1	1.50	0.7	47.50	51.20	- 3.70	- 7.8
6	8/5/84	9/5/84	6.9	1.30	0.7	49.20	48.70	+0.50	+1.0
10	8/2/84	9/5/84	7.0	1.70	8.0	51.60	53.70	- 2.1	- 4.0

These samples were collected from drinking water supplies in Bangkok Metropolitan а<u>)</u>

b) Sample A: before addition of sodium thiosulfite solution.

Sample B: after addition of sodium thiosulfite solution at sampling site. ઇ

TABLE 4. TRIHALOMETHANES CONCENTRATIONS IN DRINKING WATER SUPPLIES COLLECTED FROM BANGKOK METROPOLITAN AREA ON APRIL 1984.

	Sampling Station	Date		THMs cor	centrations	s (μg/l)	
			CHCl ₃	$CHCl_2Br$	CHClBr ₂		
						_	'HM's
1.	Rajdamnoen Klang Rd.	20/4/84	50	13	3	LD**	66
	(Bangkok)*						
2.	Rajdamnoen Klang Rd.	20/4/84	48	12	2	LD	62
	(Bangkok)						
3.	Siam Center (Pathumwan)	23/4/84	30	5	2	LD	37
4.	Rajprasong (Pathumwan)	23/4/84	32	5	2	LD	39
5.	Chulalongkorn U.	23/4/84	27	4	2	LD	33
	(Pathumwan)						
6.	Rong-muang Rd.	23/4/84	35	7	2	LD	44
	(Pathumwan)						
7.	Nares Rd. (Bangrak)	23/4/84	28	6	2	LĐ	36
8.	Lertsin Hospital (Bangrak)	23/4/84	44	9	3	LD	56
9.	Supaporn Dormitory	18/4/84	31	8	3	LD	42
	(Dusit) ^a						
10.	Mission Hospital (Dusit)	20/4/84	33	9	2	LD	44
11.	Nakorn Chaisri Rd. (Dusit)	23/4/84	26	6	3	LD	35
12.	›› ››· ››	23/4/84	22	5	2	LD	29
13.	" "	23/4/84	20	4	2	LD	25
14.	Sam Sen Railway St. (Dusit)	24/4/84	29	7	3	LD	39
15.	Dusit Zoo (Dusit)	25/4/84	43	10	3	LD	56
16.	Amporn Park (Dusit)	29/4/84	35	10	3	LD	48
17.	Wachira Hospital (Dusit)	24/4/84	35	9	3	LD	47
18.	Dusit District Off. (Dusit)	24/4/84	32	8	4	LD	44
19.	Chitrlada Palace (Dusit)	17/4/84	39	10	2	LD	51
20.	National Environment	17/4/84	52	14	3	LD	69
	Board (Phaya Thai) ^a						
21.	Pra Mongkud Hos.	17/4/84	39	10	2	LD	51
	(Phaya Thai)						
22.	Ministry of Foreign Affairs	17/4/84	30	8	2	LD	40
	(Phaya Thai)						
23.	Dept. of Science Service	17/4/84	32	9	3	LD	44
	(Phaya Thai)						
24.	Cement Thai Building	17/4/84	30	8	2	LD	40
	(Phaya Thai)						

	Sampling Station	Date		THMs Co	ncentration	(µg/l)	
			CHCl ₃	CHCl ₂ Br	CHClBr,	CHBr ₃	Total
			J	2	_	J	THMs
25.	Soi Aree (Phaya Thai)	17/4/84	29	7	2	LD	38
	Soi Ratchakru	17/4/84	22	6	1	LD	29
	(Phaya Thai)						
27.	Army Welfare Dept.	17/4/84	26	6	2	LD	34
	(Phaya Thai)						
28.	A shop near NEB	17/4/84	42	10	1	LD	53
	(Phaya Thai)						
29.	Rama VI Rd. (Phaya Thai)	17/4/84	26	5	1	LĐ	32
30.	Prachanives Rd.	18/4/84	LD	LD	LD	LD	LD
	(BangKhen) ^b						
31.	Phaholyothin Soi 18	24/4/84	58	11	3	LD	72
	(Bang Khen)						
32.	,, ,,	24/4/84	23	8	3	LD	34
33.	Kasetsart U. (Bang Khen)	25/4/84	LD	LD	LD	LD	LD
34.	Pornchai Equipment	25/4/84	44	9	3	LD	56
	(Bang Khen)						
35.	Bang Khen Prison	25/4/84	35	10	3	LD	48
	(Bang Khen)						
36.	Chemical Dep. Royal	25/4/84	46	10	3	LD	59
	Thai Army						
37.	Liabwaree Rd.	28/4/84	LD	LD	LD	LD	LD
	(Nong Chok)	*******					
38.	Romklao-Ramkamhaeng	28/4/84	LD	LD	LD	LD	LD
••	Rd. (Minburi)	2011101					
39.	Sukhumvit Rd. Soi 77	28/4/84	LD	LD	LD	LD	LD
	(Lard Krabang)						

^{*} Name in parentheses indicates the district in Bangkok.

^{**} LD = Lower detection limit

a) A range of water quality parameters of pumping water collected from Sam Sen treatment plant on April was 0.46-4.2 NTU for Turbidity, 6.97-7.45 for pH andl. 6-2.2 mg/l for Total residual chlorine, respectively.

b) A range of water quality parameters of pumping water collected from Bang Khen water treatment plant on April were 0.37-0.42 for Turbidity, 6.15-7.18 for pH, and 1.2 for Total residual chlorine, respectively.

TABLE 5. PARAMETER MEASUREMENTS AND MEAN VALUE IN TREATMENT SYSTEMS A-D.

Measurements		Mean para	meter value	
	Α	В	С	D
	Raw Water			
pН	7.40	7.40	7.40	7.40
TOC (mg/l)	4.58	4.58	4.58	5.20
T-THMs (μg/l) 4.58	LD	LD	LD	LI
	Clarifier Efflu	uent		
pН	7.00	7.00	7.00	6.9
TOC (mg/l)				
T-THMs (µg/l)	LD	LD	LD	LI
Residual-Cl (mg/l)	0	0	0	0
	Filter Effluen	t		
pH	7.00	7.00	7.00	6.9
TOC (mg/l)	1.82	1.42	1.09	2.0
T-THMs (µg/l)	LD	LD	LD	LI
Residual-Cl (mg/l)	0	0	0	0
	Plant Effluen	t		
pH	7.00	7.20	7.05	6.9
TOC (mg/l)	1.60	1.60	1.30	1.2
T-THMs (μg/l)	50.00	38.00	29.00	66.0
Residual-Cl (mg/l)	1.37	1.28	1.58	1.9

A: taken from Sam Sen Water Treatment Plant System I on March 27, 84.

B: taken from Sam Sen Water Treatment Plant System II on April 12, 84.

C: taken from Sam Sen Water Treatment Plant System III on April 12, 84.

D: taken from Bang Khen Water Treatment Plant on April 4, 84.

analysis and interferences; i.e., nonvolatile compounds and impurities are coextracted into the extracting solvent. Therefore gas chromatographic analysis time for liquid-liquid extraction method is more than that for head space analysis method, because nonvolatile compounds require several minutes to be elutes from the column.

A preliminary survey for THMs in drinking water supplies in Central Bangkok Metropolitan was conducted by the use of head space analysis method. The survey demonstrated that trihalomethanes; chloroform, bromodichloromethane, and dibromochloromethane, were found in the drinking water supplies obtained from the surface water, but none of these chemicals was detected in the chlorinated drinking water from the groundwater. The range of total THMs detected was 25 to 75 μ g/1 and mean value was 44.9 μ g/1.

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บทคัดย่อ

การศึกษาวิธีวิเคราะห์หาปริมาณไทรฮาโลมีเธน ได้เปรียบเทียบจากวิธีการวิเคราะห์ 2 วิธี คือ วิธี head space และวิธี liquid-liquid extraction โดยใช้น้ำตัวอย่างจากน้ำบริโภคในเขตกรุงเทพมหานคร วิธีการวิเคราะห์ทั้ง 2 วิธีนี้สามารถใช้วิเคราะห์หาปริมาณความเข้มข้นของ haloform ได้ในช่วงระหว่าง 0.1 ถึง 200 ไมโครกรัมต่อลิตร วิธีการเก็บตัวอย่างน้ำเพื่อใช้ในการวิเคราะห์โดยวิธี head space และ liquid-liquid extraction เป็นวิธีที่ง่ายและสะดวก แต่การวิเคราะห์โดยวิธี liquid-liquid extraction มีข้อเสียบางประการในแง่ของ ความไว ที่ต่ำกว่า และการใช้เวลา วิเคราะห์ที่นานกว่า ทั้งนี้เนื่องจากสารประกอบประเภทไม่ระเหย ใช้เวลา 2 - 3 นาที ในการชำระล้างจากคอลัมน์

การสำรวจเบื้องต้นเพื่อวิเคราะห์หาปริมาณไทรฮาโลมีเธนในน้ำบริโภคในเขตกรุงเทพมหานคร ได้ดำเนิน การโดยเลือกใช้วิธี head space จากผลการสำรวจไทรฮาโลมีเธน ในรูปของคลอโรฟอร์ม โบรโมไดคลอโรมีเธน และ ไดโบรโมคลอโรมีเธน ในน้ำบริโภคซึ่งได้จากน้ำผิวดินสำหรับในน้ำบาดาลที่ผสมคลอรีน ไม่พบสารดังกล่าว ปริมาณ ความเข้มข้นของไทรฮาโลมีเธนมีวิเคราะห์ได้ พบว่าอยู่ในช่วง 25 ถึง 75 ไมโครกรัมต่อลิตร และค่าเฉลี่ย 49.9 ไมโครกรัม ต่อลิตร