ANALYSIS OF TRIHALOMETHANE FORMATION POTENTIAL IN RIVER WATER USING DISPERSIVE LIQUID-LIQUID MICROEXTRACTION TECHNIQUE

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They never failed to offer me unconditional love and moral support, giving all my need during the hardest time and teaching me that even the largest task can be accomplished.

I dedicated this thesis to my beloved family:

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My brother, Rayme Herlana
and the youngest, Mohd. Ramdan

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ABSTRACT

Trihalomethanes (THMs) in treated water are formed when natural organic matter (NOM) reacts with chlorine, which is used as a disinfectant agent. Although the chlorination of drinking water provides many advantages, THMs remain a human health concern. High levels of the THMs in water leads to the possible carcinogenic effects which effect human health seriously. A new extraction technique named dispersive liquid-liquid microextraction (DLLME) was developed and applied for the determination of the formation of THMs in treated water. Different experimental conditions, for instance type and volume of disperser solvent, type and volume of extraction solvent, addition of salt and extraction time were investigated to obtain the optimum extraction conditions. In this method, the appropriate mixture of an extraction solvent (20.00 µL carbon disulfide) and disperser solvent (0.25 mL methanol) was injected in 5.00 mL aqueous sample containing the analytes to form a cloudy solution. The analytes were separated and enriched in a settled phase by centrifugation for 2 min at 4,000 rpm. Settled phase formed was determined by gas chromatography with electron-capture detection (GC-ECD). The repeatability and reproducibility of DLLME-GC-ECD were found to range between 1.1% to 11.4% and 3.4% to 10.9% respectively. Good correlation coefficient, R^2 more than 0.9977 were obtained for all THMs compound. The LODs for all THMs compound ranged from 0.011 µg/L to 0.239 µg/L, whereas the enrichment factor (EF) obtained were found in the range of 95 to 283. DLLME-GC-ECD was found to be rapid and simple method which offered better sensitivity and high efficiency compared to conventional method, liquid-liquid extraction (LLE). The method was applied for analysis of total THM formation potential (TTHMFP) in river water. From the monitoring conducted during rainfall season at Batu Pahat, Johor Malaysia, it can be concluded that TTHMFP in Malaysian river waters especially at Johor area are still under the limits of 80 µg/L.

ABSTRAK

Trihalometana (THMs) dalam air terawat terbentuk apabila jirim organik semulajadi (NOM) bertindak balas dengan klorin, yang digunakan sebagai agen disinfektan. Walaupun pengklorinan dalam air minum membawa banyak kebaikan, ia memberi kesan kepada kesihatan manusia. Kandungan THMs yang tinggi di dalam air berkemungkinan memberi kesan karsinogenik yang mempengaruhi kesihatan manusia. Satu teknik pengekstrakan baru, pengekstrakan mikro cecair penyesar (DLLME) dikembangkan dan digunakan untuk penentuan pembentukan THMs dalam air terawat. Keadaan eksperimen seperti jenis dan kandungan larutan pengekstrak, jenis dan kandungan larutan penyesar, penambahan garam dan masa pengekstrakan dikaji untuk mendapatkan keadaan pengekstrakan yang optimum. Dalam kaedah ini, campuran larutan pengestrak (20.00 µL karbon disulfida) dan larutan penyesar (0.25 mL metanol) disuntik ke dalam 5.00 mL sampel air yang mengandungi analit untuk membentuk larutan keruh. Analit dipisahkan melalui emparan selama 2 minit pada 4,000 rpm. Enapan separa pepejal yang terbentuk dikaji dengan kromatografi gas dengan pengesanan penangkapan-elektron (GC-ECD). Kebolehulangan dan perolehan semula DLLME-GC-ECD didapati antara 1.1% hingga 11.4% dan 3.4% sehingga 10.9%. Julat kelinearan yang baik diperolehi dengan pekali korelasi, R^2 melebihi 0.9977 bagi semua sebatian THM. Had pengesanan (LOD) untuk semua sebatian THM berkisar antara 0.011 µg/L dan 0.239 µg/L dan faktor pengkayaan (EF) diperolehi dalam julat 95 – 283. DLLME-GC-ECD merupakan teknik yang pantas dan ringkas,yang menawarkan kepekaan dan kecekapan yang tinggi berbanding kaedah konvensional, pengekstrakan cecair-cecair (LLE). Kaedah ini telah diaplikasikan untuk menganalisis kandungan keupayaan pembentukan jumlah THM (TTHMFP) dalam air sungai. Daripada pemantauan yang dilakukan sepanjang musim hujan, di Batu Pahat, Johor Malaysia, didapati TTHMFP di perairan sungai Malaysia terutamanya di kawasan Johor masih di tahap yang dibenarkan iaitu tidak melebihi 80 µg/L.

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LIST OF SYMBOLS

µg/L	–	Microgram per liter
mg/L	–	Milligram per liter
µL	–	Microliter
mL	–	Milliliter
^{o}C	–	Degree Celcius
m	–	Meter
mm	–	Millimeter
µm	–	Micrometer
R^2	–	Correlation coefficients
ppm	–	Parts per million
ppb	–	Parts per billion
min	–	Minute
w/v	–	Weight per volume
^{o}C/min	–	Degree celcius per minute
mL/min	–	Milliliter per minute
I.S	–	Internal standard

LIST OF ABBREVIATIONS

NOM	–	Natural Organic Matter
THM	–	Trihalomethane
THMs	–	Trihalomethanes
TTHMs	–	Total trihalomethanes
TTHMFP	–	Total trihalomethane formation potential
HAAs	–	Haloacetic acids
DBP	–	Disinfection by-product
$CHCl_3$	–	Chloroform
$CHBrCl_2$	–	Bromodichloromethane
$CHBr_2Cl$	–	Dibromochloromethane
$CHBr_3$	–	Bromoform
DLLME	–	Dispersive Liquid-liquid Microextraction
LLE	–	Liquid-liquid Extraction
HS-SPME	–	Headspace – Solid Phase Microextraction
GC-ECD	–	Gas Chromatography – Electron Capture Detection
GC-MS	–	Gas Chromatography – Mass Spectrometry
SDME	–	Single Drop Microextraction
P&T	–	Purge and Trap
DAI	–	Direct Aqueous Injection
TOC	–	Total Organic Carbon
VOC	–	Volatile Organic Compound
HA	–	Humic Acid
FA	–	Fulvic Acid
USEPA	–	United States Environmental Protection Agency
CAR/PDMS	–	Carboxen/polydimethylsiloxane

PDMS/DVB	–	Polydimethylsiloxane/divinylbenzene
DO	–	Dissolve Oxygen
WTP	–	Water Treatment Plant
CS_2	–	Carbon disulfide
NaCl	–	Sodium chloride
TC	–	Total carbon
IC	–	Inorganic carbon
DLLME-GC-ECD	–	DLLME followed by GC-ECD
DLLME-GC-MS	–	DLLME followed by GC-MS
LLE-GC-ECD	–	LLE followed by GC-ECD
LOD	–	Limit of Detection
LOQ	–	Limit of Quantitation
EF	–	Enrichment factor
ER	–	Extraction recovery
WHO	–	World Health Organization

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Water throughout the world contains natural organic matter (NOM), a result of interaction of hydrological cycle. This NOM is generally formed when plants and animal decompose and are broken into organic matter. Higher amounts of NOM in water affect the quality of water when it deals with drinking water purpose (Christy and Egeberg, 2000). The existence of NOM in the water becomes a big issue when dealing with chlorination process in a water treatment plant.

Chlorine is a commonly used disinfectant in the water treatment process in order to ensure the microbiological safety of the water supplied to consumer. The use of chlorine has been considered to be a cost-effective approach as disinfectant agent (Park *et al.,* 2005 and Zhang and Minear, 2006). However, during disinfection, chlorine may react with NOM in the raw water, resulting in the formation of various disinfection by-products (DBP) such as trihalomethane (THM) and haloacetic acids (HAA) (Miller and Uden, 1983). Trihalomethanes (THMs) can also be detected even in water that has not been subjected to chlorination processes, such as ground water, mineral water, snow, rain water, sea and river water. However, the concentrations of these compounds in unchlorinated water tend to be much lower than those usually found in tap water (Pavon *et al.,* 2008).

Trihalomethanes are classified as possible human carcinogens (Category 2B) by the International Agency for Research on Cancer (IARC). Furthermore, it has been shown that skin absorption and lung inhalation is potentially significant routes of exposure to some disinfection by-product (DBP) in water (Gordon *et al.,* 1998, Fatuzzi *et al.,* 2001 and Xu and Weisel, 2005). Total trihalomethanes (TTHMs) is not a single chemical, but a class of compounds that includes chloroform ($CHCl_3$), bromoform ($CHBr_3$), bromodichloromethane ($CHCl_2Br$) and dibromochloromethane ($CHClBr_2$) (APHA, 1999). In 1979, the USEPA initiated a regulatory standard of 100 µg/L THMs under the "Safe Drinking Water Act" and was later on reduced to 80 µg/L (Kozani *et al.*, 2007).

Due to the health risks posed by THMs, various methods have been applied for determination of THMs and any other volatile organic compound (VOC) in water using gas chromatography (GC) followed by electron capture detection (ECD) or mass spectrometry (MS) (Kozani *et al.*,2007 and Pavon *et al.,* 2008). Numerous sample extraction methods have been used to monitor THM species in water namely liquid-liquid extraction (LLE), purge and trap (P&T), direct aqueous injection (DAI) and headspace techniques (Pavon *et al.,* 2008). New miniaturized extraction technique called headspace-solid phase microextraction (SPME) has also been employed for analysis of THMs in drinking water (Cho *et al.*, 2003).

Even though most studies reported that TTHMs were still within the permissible limits, the increased of THMs level was dependent upon the quality of water sources and treatment facilities (Hassan *et al.,* 1996). Various levels of THMs were reported from different countries with chloroform as the major compound that contribute to the higher level of THMs (Hong *et al.,* 2007, Abdullah *et al.*, 2003, Cho *et al.*, 2003, Yu and Cheng, 1999 and Hassan *et al.*, 1996). Fayad and Iqbal (1985) however reported that bromoform is a major compound of THMs found from most of the major cities of the Eastern Province in Saudi Arabia. Concern with the formation of THM in chlorinated water, development and optimization of sensitive, rapid and simple analytical methods is essential for monitoring THM concentration in water supply as well as for a better understanding of their formation and removal in distribution systems.

1.2 Problem Statement

Most municipal water supply system use chlorine as the disinfectant agent as it is extremely efficient and cost effective. Although the chlorination of drinking water provides many advantages, THMs remain a human health concern. The existence of DBPs in water supply may lead to potential human health risks and many of the DBPs have been classified as probable or possible carcinogens. High levels of THMs in water lead to the possible carcinogenic effects which affect human health seriously.

A study carried out to assess THMs level in drinking water system from several areas in Peninsular Malaysia for the years 1999, 2000 and 2001 reported variation of THMs level were found with relatively high level of THMs usually found during rainfalls season (Abdullah *et al.*, 2003). No study has been conducted for TTHM formation potential (TTHMFP) in river water. Therefore, the aim of this study was to detect and quantify the THMFP in river water especially from Johor area.

1.3 Objectives of Study

The objectives of the study are:

i. To develop a rapid and simple method for analysis of TTHMFP in river water by using dispersive liquid-liquid microextraction (DLLME) coupled with gas chromatography-electron capture detection (GC-ECD).

ii. To compare the newly developed method with other conventional methods in terms of their sensitivity, simplicity and rapid determination of THMs.

iii. To apply the developed technique for monitoring of TTHMFP in Malaysian river water.

1.4. Scope of Research

The scope of the research involved the determination of TTHMFP in river water for household use at Johor Darul Ta'zim, Malaysia by using DLLME technique. The optimum conditions of extraction were determined via extraction and disperser solvents used, extraction time and salt addition effect. LLE technique followed by GC-ECD and DLLME followed by GC-MS were also employed to compare the sensitivity of detector used in analyzing THMs. Monitoring of TTHM in untreated water was carried out during wet (rainfalls) season and samples were collected every fortnight. TTHMFP were analyzed using the developed method.

1.5 Significance of Research

The most significant THMs, based on occurrence and toxicity, are chloroform, bromodichloromethane, dibromochloromethane and bromoform (Cho *et al.,* 2003). This research is carried out to provide a useful and feasible method for determination of THMs in water treatment process. The amount of THMFP will therefore be well monitored and a proper action can be taken in the future to reduce the formation of THMs in treated water.

1.6 Summary of Thesis

This study was divided to two major parts: optimization and comparison of DLLME with conventional method and monitoring of TTHMFP in water sources for water treatment plant. Thesis is divided into 6 chapters where chapter 1 summarizes every chapter covered in this work. The objectives and the scope of this study also mentioned in this chapter.

Chapter 2 presents the introduction to NOM, as one of the important factors that affect the formation of THMs in water. Other factors that affecting THMs formation and other analytical techniques that commonly used for analysis of THMs also covered in this chapter. Furthermore, Chapter 2 describes the details for DLLME, the newly developed technique that has been applied in this work. Chapter 3 describes the experimental part for the analysis of THMs compound. This chapter presents chemical, reagents, preparations and all procedures used throughout the study. Sampling locations for real samples analysis are also described in detail.

Chapter 4 explores the optimization of several parameters in DLLME technique. Type and volume of extraction solvent used, type and volume of disperser solvent used, extraction time and effect of salt addition were explored. Comparison study of DLLME technique coupled with GC-ECD, DLLME technique coupled with GC-MS and conventional technique, liquid-liquid extraction (LLE) are also covered in this chapter.

Chapter 5 reports the application of DLLME for monitoring of river water in Batu Pahat area. The qualities of waters are recorded and monitoring was done for 3 months during rainfall season. TTHMFP determined in the waters are also reported in this chapter. Lastly, Chapter 6 presents the overall findings in this study and suggestions for improvement to further studies.

REFERENCES

Abdullah, M.P. and Soh, S.C. (2005). Applicability of Direct Extraction of Solid Phase Micro-Extraction to the Determination of 54 Volatile Organic Compounds in Drinking Water. *Malaysian J. Chem*. 7(1), 019 – 025.

Abdullah, M.P., Yew, C.H., Ramli, M.S. and Ali, R. (2003). Trihalomethanes (THMs) in Malaysian Drinking Water. *Malaysian J. Chem*. 5(1), 056 – 066.

Adin, A., Katzhendler, J., Alkaslassy, D. and Rav, A.C. (1991). Trihalomethanes Formation in Chlorinated Drinking Water: A Kinetic Model. *Wat. Res.* 25, 797 – 805.

Alawi, M.A., Khalill, F. and Sahili, I. (1994). Determination of Trihalomethanes Produced through the Chlorination of Water as a Function of Its Humic Acid Content. *Arch. Environ. Contam. Toxicol.* 26, 381 – 386.

Al-Omari, A., Fayyad, M. and Qader, A.A. (2004). Modeling Trihalomethane Formation for Jabal Amman Water Supply in Jordan. *Environmental Modeling and Assessment.* 9, 245 – 252.

APHA. (1999). *Standard methods for the examination of water and waste water,* 18th ed. Washington, DC: American Public Health Association.

Anthemidis, A.N. and Ioannou, K-I.G. (2009). Recent Developments in Homogeneous and Dispersive Liquid–liquid Extraction for Inorganic Elements Determination. A Review. *Talanta,* 80, 413 – 421.

Artuğ, M. (2004). *Determination of THMFP of the Reservoirs in Turkey: Kinetics Aspect.* Master of Science, Middle East Technical University, Turkey.

Badawy, M.I. (1992). Evaluation of Head Space Technique for the Determination of Trihalomethanes in Water. *Bull. Environ. Contam. Toxicol.* 48, 630 – 634.

Basiouny, M., Elmitwalli, T. and Rabee, M. (2008). *Formulation and Modeling of Trihalomethane in New Benha Water Treatment Plant,* Twelfth International Water Technology Conference, IWTC12, Egypt: Alexandria.

Batu Pahat Land Office. (2011). *Peta Kawasan Daerah Batu Pahat.* Batu Pahat Land office, (Settlement Division), Batu Pahat, Johor Darul Ta'zim, Malaysia.

Belardi, R.P. and Pawliszyn, J.B. (1989). Application of Chemically Modified Fused Silica Fibers in the Extraction of Organics from Water Matrix Samples and their Rapid Transfer to Capillary Columns. *Water Pollut. Res. J. Can.* 24, 179 – 191.

Bolto, B., Dixon, D., Eldridge, R., King, S. and Linge, K. (2002). Removal of Natural Organic Matter by Ion Exchange. *Water Research*. 36, 5057 – 5065.

Bot, A. and Benites, J. (2005). *The Importance of Soil Organic Matter: Key to Drought-Resistant Soil and Sustained Food Production.* FAO Soils Bulletin: 80. Rome, Italy: Food and Agriculture Organization of United Nations (FAO)

CCAL 20A.0. (2006). *Standard Operating Procedure for the Analysis of Dissolved and Total Organic Carbon.* Oregon: Forestry Science Laboratory, Oregon State University, Corvallis.

CDPHE-WQCD (2010). *Regulations 31: The Basic Standards and Methodologies for Surface Water.* Denver, CO: Colorado Department of Public Health and Environment – Water Quality Control Division. 5CCR 1002-31.

Chao, Y. and Jiang, J. (2010). Comparative Performance and Computational Approach of Humic Acid Removal by Clay Adsorption, *J. Environ. Protection.* 1, 24 – 29.

Chawla, R.C., Varma, M.M., Balram, A., Murali, M.M. and Natarajan, P. (1983). *Trihalomethane Removal and Formation Mechanism in Water.* Washington, DC: DC water Resources Research Center, University of the District of Columbia. DC WRRC Report no.48.

Cheng, J., Zhou, Y., Zuo, M., Dai, L. and Guo, X. (2010). Application of Dispersive Liquid–liquid Microextraction and Reversed Phase-high Performance Liquid Chromatography for the Determination of Two Fungicides in Environmental Water Samples. *Int. J. Environ. Anal. Chem.* 90 (11), 845 – 855.

Cho, D-H., Kong, S-H. and Oh, S-G. (2003). Analysis of Trihalomethanes in Drinking Water using Headspace-SPME Technique with Gas Chromatography. *Water Research.* 37, 402 – 408.

Christy, A.A. and Egeberg, P.K. (2000). Characterisation of NOM from the Nordic Typing Project Water Samples by Chemometric Analysis of their Near Infrared Spectral Profiles. *Chemometric and Intelligent Lab Systems.* 50(2), 225 – 234.

Clark, R.M. and Sivaganesan, M. (1998). Predicting Chlorine Residuals and Formation of Total Trihalomethanes in Drinking Water. *J. Environ. Engrg.* 124, 1203 – 1210.

Cowman, G.A. and Singer, P.C. (1996). Effect of Bromide Ion on Haloacetic Acid Speciation Resulting from Chlorination and Choramination of Aquatic Humic Substances. *Environ. Sci. Technol.* 30(1), 16 – 24.

Dai, X.Y., Ping, C.L., and Michaelson, G.J. (2006). Charaterizing Soil Organic Matter in Arctic Tundra Soils by Different Analytical Approach. *Org. Geochem.* 33, 407 – 419.

EPA, EPA Method 501.2. (1979). *Analysis of Trihalomethanes in Drinking Water by Liquid-liquid Extraction.* EPA 500-series November 1979. New York: Genium Publishing Corp.

Farajzadeh, M.A., Seyedi, S.E., Shalamzari, M.S. and Bamorowat, M. (2009). Dispersive Liquid–liquid Microextraction using Extraction Solvent Lighter than Water. *J. Sep. Sci.* 32, 3191 – 3200.

Fatuzzi, G., Righi, E., Predieri, G., Ceppelli, G., Gobba, F. and Aggazzotti, G. (2001). Occupational Exposure to Trihalomethanes in Indoor Swimming Pools. *Sci. Total Environ.* 264, 257 – 265.

Fayad, N.M and Iqbal, S. (1985). Analysis of Drinking Water for the Detection of Trihalomethanes. *Bull. Environ. Contam. Toxicol.* 35, 576 – 582.

Fiorentino, G., Spaccini, R. and Piccolo, A. (2006). Separation of Molecular Constituents from a Humic Acid by Solid-phase Extraction Following a Transesterification Reaction. *Talanta.* 68, 1135 – 1142.

Garcia, C., Tiedra, P.G., Ruano, A., Gomez, A. and Garcia-Villanova, R.J. (1992). Evaluation of Liquid-liquid Extraction Technique and Application for the

Determination of Halo-organic Compounds in Chlorinated Water. *J. of Chromatogr.* 605, 251 – 255.

Garcia-Villanova, R.J., Garcia, C., Gomez, J.A., Garcia, M.P. and Ardanuy, R. (1997). Formation, Evolution and Modeling of Trihalomethanes in the Drinking Water of a Town: I. at the Municipal Treatment Utilities. *Wat. Res.* 31 (6), 1299 – 1308.

Gopal, K., Tripathy, S.S., Bersillon, J.L. and Dubey, S.P. (2007). Chlorination Byproducts, their Toxicodynamics and Removal from Drinking Water. *J. Hazard. Mater.* 140, 1 – 6.

Gordon, S.M., Wallace, L.A., Callahan, P.J., Kenny, D.V. and Brinkman, M.C. (1998). Effect of water temperature on Dermal Exposure to Chloroform. *Environ. Health Persp*. 106, 337 – 345.

Goslan, E.H., Fearing, D.A., Banks, J., Wilson, D., Hillis, P., Campbell, A.T. and Parsons, S.A. (2002). Seasonal Variations in the Disinfection By-product Precursor Profile of a Reservoir Water. *J. Water Supply: Research and Technology-AQUA* 51, 457 – 482.

Grob, K. (1984). Further Development of Direct Aqueous Injection with Electron-Capture Detection in Gas Chromatography. *J. Chromatogr.* 299, 1 – 11.

Guay, C., Rodriguez, M. and Serodes, J. (2005). Using Ozonation and Chloramination to Reduce the Formation of Trihalomethanes and Haloacetic Acids in Drinking Water. *Desalination.* 176, 229 – 240.

Hassan, A.A.M, Benfenati, E. and Fanelli, R. (1996). Detection and Quantification of Trihalomethanes in Drinking Water from Alexandria, Egypt. *Bull. Environ. Contam. Toxicol.* 56, 397 – 404.

Hong, H.C., Liang, Y., Han, B.P., Mazumder, A. and Wong, M.H. (2007). Modeling of Trihalomethane (THM) Formation via Chlorination of the Water from Dongjiang Ricer (source water for Hong Hong's drinking water), *Sci. Total Environ*, 385, 48 – 54.

Iriarte, U., Álvarez-Uriarte, J.I., López-Fonseca, R. and González-Velasco, J.R. (2003). Trihalomethane Formation in Ozonated and Chlorinated Surface Water. *Environ Chem Lett.* 1, 57 – 61.

Josephen, J. (1982). Humic Substances. *Environ. Sci. Tech.* 16, 20A – 24A.

Jabatan Pengairan dan Saliran (2010). *Rainfalls Data; Johor State.* Infobanjir System Project. Department of Irrigation and Drainage Malaysia. Kuala Lumpur: National Flood Monitoring Centre, Ampang.

Jabatan Pertanian (2002). *Penggunaan Tanah Sekarang Daerah Batu Pahat, Johor.* Agricultural Department of Peninsular Malaysia, (Management and Conservation Division of Land Resources), Batu Pahat, Johor Darul Ta'zim, Malaysia.

Jabatan Pertanian. *Peta Tanah Mukim Daerah Batu Pahat, Johor.* Agricultural Department of Peninsular Malaysia, (Management and Conservation Division of Land Resources), Batu Pahat, Johor Darul Ta'zim, Malaysia.

Juan, P.M.S., Carrillo, J.D. and Tena, M.T. (2007). Fibre Selection based on an Overall Analytical Feature Comparison for the Solid-phase Microextraction of Trihalomethanes from Drinking Water. *J. Chromatogr. A.* 1139, 27 – 35.

Kimbrough, D.E. and Suffet, I.H. (2002). Electrochemical Removal of Bromide and Reduction of THM Formation Potential in Drinking Water. *Water Research*. 36, 4902 – 4906.

Kirmeyer, G.J., Foust, G.W., Pierson, G.L., Simmler, J.J. and LeChevallier, M.W. (1993). *Optimizing Chloramine Treatment.* Denver, CO: AWWA Research Foundation and AWWA.

Kozani, R.R., Assadi, Y., Shemirani, F., Hosseini, M.R.M. and Jamali, M.R. (2007) Determination of Trihalomethanes in Drinking Water by Dispersive Liquid-Liquid Microextraction then Gas Chromatography with Electron-Capture Detection. *Chromatographia.* 66, 81 – 86.

Kumar, A., Gaurav, Malik, A.K., Tewary, D.K. and Singh, B. (2008). A Review on Development of Solid Phase Microextraction Fibers by Sol-gel Methods and their Applications. *Anal. Chim. Acta.* 610. 1 – 14.

Lee, M.R. and Fulazzaky, M.A. (2011). *Assessment of Bekok River Water Quality Status and its Suitability for Supporting the Different Uses: A Review.* Proceeding of the International Conference on Advanced Science, Engineering and Information Technology, ISC 2011, Bangi, Malaysia.

Lekkas, T.D. and Nikolaou, A.D. (2004). Development of Predictive Models for the Formation of Trihalomethanes and Haloacetic acids for the Chlorination of Bromide-rich Water. *Water Qual. Res. J. Canada.* 39(2), 149 – 159.

Leong, M-I and Huang, S-D. (2008). Dispersive Liquid–liquid Microextraction Method based on Solidification of Floating Organic Drop combined with Gas Chromatography with Electron-capture or Mass Spectrometry Detection. *J. Chromatogr. A.* 1211, 8 – 12.

Livens, F.R. (1991). Chemical Reactions of Metals in Humic Material. *Environmental Pollution.* 70, 183 – 208.

Luks-Betlej, K. and Bodzek, D. (2002). Occurrence of Trihalomethanes, Particularly Those Containing Bromine, in Polish Drinking Waters. *Polish J. Environ. Studies.* 11(3), 255 – 260.

Miller, J., and Uden, P. (1983). Characterization of Non-volatile Chlorination By-products of Humic Substances. *Environ. Sci. Technol*. 17, 150 –157.

Ministry of Health. (2004). *National Drinking Water Quality Standard Guidelines.* Kuala Lumpur: Engineering Services Division.

Najm, I.N. and Krasner, S.W. (1995). Effects of Bromide and NOM on By-product Formation. *J. Am. Water Works Ass.* 87,106 – 115.

Nikolaou, A., Lekkas, T., Golfinopoulos, S. and Kostopoulou, M. (2002). Application of Different Analytical Methods for Determination of Volatile Chlorination By-products in Drinking Water. *Talanta.* 56(4), 717 – 726.

Nikolaou, A.D, Kostopoulou, M.N. and Lekkas, T.D. (1999). Organic By-product of Drinking Water Chlorination. *Global Nest: Int. J.* 1(3), 143 – 156.

Ojeda, C.B. and Rojas, F.S. (2009). Separation and Preconcentration by Dispersive Liquid-liquid Microextraction Procedure: A Review. *Chromatographia*. 69(11-12), 1149 – 1159.

Owen, D.M., Chowdury, Z.K. and Krasner, S.W. (1992). *Predicting THM Formation in Bromide-rich Water.* Proceedings Water Quality Technology Conference, Toronto, Ontario, Canada: AWWA, 1779.

Park, N., Kwon, B., Sun, M., Ahn, H., Kim, C., Kwoak, C., Lee, D., Chae, S., Hyung, H. and Cho, J. (2005). Application of Various Membranes to Remove NOM

Typically Occurring in Korea with Respect to DBP, AOC and Transport Parameters. *Desalination.* 178, 161 – 169.

Pavon, J.L.P., Martin, S.H., Pinto, C.G. and Cordero, B.M. (2008). Determination of Trihalomethanes in Water Samples: A Review. *Anal. Chim. Acta.* 627, 6 – 23.

Pawliszyn, J. (1997). *Solid Phase Microextraction: Theory and Practice*. New York: Wiley-VCH. 15 – 30.

Piccolo, A., (2002). The Supramolecular Structure of Humic Substances. A Novel Understanding of Humus Chemistry and Implications in Soil Science, Advance in Agronomy. 75, 57 – 134.

Popp, P. and Paschke, A. (1997). Solid Phase Microextraction of Volatile Organic Compounds using Carboxen-Polydimethylsiloxane Fibers. *Chromatographia.* 46 (7/8), 419 – 424.

Pourmoghaddas, H. and Stevens, A.A. (1995). Relationship between Trihalomethanes and Haloacetic Acids with the Total Organic Halogen during Chlorination. *Wat. Res.* 29(9), 2059 – 2062.

Rezaee, M., Yamini, Y. and Faraji, M. (2010). Evolution of Dispersive Liquid-liquid Microextraction Method. *J. Chromatogr. A.* 1217, 2342 – 2357.

Rezaee, M., Assadi, Y., Hosseini, M.R.M, Aghaee, E., Ahmadi, F. and Berijani, S. (2006). Determination of Organic Compounds in Water using Dispersive Liquid-liquid Microextraction. *J. Chromatogr. A.* 1116, 1 – 9.

Richardson, D.S. (2003). Disinfection by-products and others emerging contaminants in drinking water. *Trends Anal. Chem*. 22, 666 – 684.

Riđanović, L., Riđanović, S., Jurica, D. and Spasojević, P. (2010). *Evaluation of Water Temperature and Dissolved Oxygen Regimes in River Neretva.* BALWOIS, Ohrid: Republic of Macedonia.

Rodriguez, M.J., Vinette, Y., Sérodes, J-B. and Bouchard, C. (2003). Trihalomethanes in Drinking Water of Greater Québec Region (Canada): Occurrence, Variations and Modelling. *Environ. Monit. Assess*. 89, 69 – 93.

Schnitzer, M. and Khan, S.U. (1972). *Humic Substance in the Environment.* New York: Marcel Deckel Inc. 243 – 612.

Selvaraju, G. (2004). *Characterization of NOM from Peat Swamp Canal.* Bachelor of Science project report, Universiti Teknologi Malaysia, Malaysia.

Singer, P.C. (1994). Control of Disinfection By-products in Drinking Water. *J. Environ. Eng.-ASCE*. 120(4), 727 – 744.

Stevens, A.A., Moore, L.A. and Miltner, R.J. (1989), Formation and Control of Non-Trihalomethane Disinfection By-products. *J. AWWA.* 81(8), 54 – 60.

Tan, L.W. (2007). *UV-VIS and Fluorescence Spectroscopic analysis of soil humic acid.* Master of Science dissertation, Universiti Teknologi Malaysia, Malaysia.

Thacker, N.P., Kaur, P. and Rudra, A. (2002). Trihalomethane Formation Potential and Concentration Changes during Water Treatment at Mumbai (India). *Environ. Monit. and Assess.* 73, 253–262.

Trehy, M.L., Zhang, L., Qian, X. and Yang, G. (2001). *Determination of Trihalomethanes in Water by Purge-and-Trap Gas Chromatography with Mass Spectrometry and Electron Capture Detector.* In: Symposia Papers presented before the Division of Environmental Chemistry. San Diego, CA: ACS. 41(1).

Trussell, R.R. and Montgomery, J.M. (1991). *Control strategy 1: Alternative Oxidants and Disinfectants.* In: Water Research for the New Decade. Proceedings of Annual AWWA Conference 1991. Philadelphia, PA. 43

Urano, K., Wadaa, H. and Takemasa, T. (1983). Empirical Rate Equation for Trihalomethane Formation with Chlorination of Humic Substance in Water, *Water Research.* 17(12), 1797 – 1802.

USEPA. (1998). *Control of Trihalomethane in Drinking Water.* In; National Primary Drinking Water Regulations. Washington: US EPA.

Uyak, V. and Toroz, I. (2006). Modeling the Formation of Chlorination By-Products during Enhanced Coagulation, *Environ. Monit. and Assess.* 121(1-3), 501 – 515.

Vilhunen, S., Vilve, M., Vepsäläinen, M. and Sillanpää, M. (2010). Removal of Organic Matter from a Variety of Water Matrices by UV Photolysis and UV/H_2O_2 Method. *J. Hazard. Mater.* 179, 776 – 782.

Volk, C., Wood, L., Johnson, B., Robinson, J., Hai, W.Z., and Kaplan, L. (2002). Monitoring Dissolved Organic Carbon in Surface and Drinking Waters. *J. Environ. Monit.*, 4, 43 – 47.

Vora-adisak, N., and Varanusupakul, P. (2006). A Simple supported Liquid Hollow Fiber Membrane Microextraction for Sample Preparation of Trihalomethanes in Water Samples. *J. Chromatogr. A.* 1121, 236 – 241.

Wei, G., Li, Y. and Wang, X. (2008). Application of Dispersive Liquid-liquid Microextraction combined with High-performance Liquid Chromatography for the Determination of Methomyl in Natural Waters. *J. Sep. Sci.* 30, 3262 – 3267.

White, G.C. (1992). *The Handbook of Chlorination and Alternative Disinfectants,* 3rd ed. New York: Van Nostrand Reinhold, NY.

WHO. (1993). *Guidelines for Drinking Water Quality*. Geneva: WHO.

Wolfe, R.L., Ward, N.R. and Olson, B.H. (1984). Inorganic Chloramines as Drinking Water Disinfectants. *J. AWWA.* 76(5), 74 – 88.

Wu, W.W., Benjamin, M.M. and Korshin, G.V. (2001). Effects of Thermal Treatment on Halogenated Disinfection By-products in Drinking Water. *Wat. Res.* 35, 3345 – 3550.

Xu, X. and Weisel, C.P. (2005). Dermal Uptake of Chloroform and Haloketones During Bathing. *J. Expos. Anal. Environ. Epidemiol*. 15, 289 – 296.

Ye, B., Wang, W., Yang, L., Wei, J. and Xueli, E. (2009). Factors Influencing Disinfectant By-products Formation in Drinking Water of Six Cities in China. *J. Hazardous Mat.* 171, 147 – 152.

Yew, C.H. (2003). *Perkembangan Teknik Analisis dan Kajian Pemodelan Aras Kepekatan Trihalometana dalam Sistem Bekalan Air Minum. Doktor Falsafah.* Universiti Kebangsaan Malaysia, Malaysia.

Yu, J.C. and Cheng, L-N. (1999) Speciation and Distribution of Trihalomethanes in the Drinking Water of Hong Kong. *Environ. Int.* 25(5), 605 – 611.

Zang, X-H., Wu, Q-H., Zhang, M-Y., Xi, G-H. and Wang, Z. (2009). Developments of Dispersive Liquid-liquid Microextraction Technique. *Chin. J. Anal Chem.* 37(2), 161 – 168.

Zhang, X. and Minear, R.A. (2006). Removal of Low-molecular Weight DBPs and Inorganic Ions for Characterization of High-molecular Weight DBPs in Drinking Water. *Water Research.* 40, 1043 – 1051.

Zhao, X., Fu, L., Hu, J., Li, J., Wang, H., Huang, C. and Wang, X. (2009). Analysis of PAHs in Water and Fruit Juice Samples by DLLME Combined with LC-Fluorescence Detection. *Chromatographia*, 69(11-12), 1385 – 1389.

Zularisam, A.W., Ismail, A.F. and Salim, R. (2006). Behaviours of Natural Organic Matter in Membrane Filtration for Surface Water Treatment – A Review. *Desalination.* 194, 211 – 231.

Zulkifli, S. (2007). *Leacheability Study of Acid Sulphate Soil in Bekok Catchment.* Master of Engineering. Universiti Teknologi Malaysia, Malaysia.