THE ASSESSMENT OF TRIHALOMETHANE LEVELS IN DRINKING WATER

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ABSTRACT

The growth of industry in Malaysia has caused several conflicts with the water resources management. Poor planning resulted in the siting of polluting industries and housing areas in critical watersheds that also provide potable drinking water to the general public. The chlorination of water with high organic waste, natural or anthropogenic, is detrimental to the health of the public as the trihalomethanes (THMs) produced are known to be carcinogenic.

1. INTRODUCTION

Drinking water or potable water can be defined as the water delivered to the consumer that can be "safely" used for drinking, cooking and washing.[1] In the past, "safe" means that the finished water has generally been found to meet the established criteria. These criteria has been largely concerned with *(1)* obvious nuisance materials *(2)* turbidity *(3)* phatogens *(4)* color *(5)* taste and odor and *(6)* certain metals associated with public health hazard. The last comprise mostly of inorganic metals.

Interest in the study of residual organics in drinking water started in 1974 with the discovery haloforms or trihalomethanes by Rook J.J.[2] during routine quality control of water treatment at Berenplaat plant, Holland. Gas Chromatographic headspace analysis was used to detect low polar volatiles. However the interpretation of the results has been confused by the appearances of additional peaks in the chromatograms of the chlorinated water. The identification

of the peaks by retention times alone was insufficient until finally confirmed by mass-spectrometer at CIVO-TNO-Institute, Zeist (Holland). The following compounds were found: Carbon Tetrachloride (CCl_4), Chloroform ($CHCl_3$), Dichlorobromomethane ($CHCl_2Br$). Dibromochloromethane ($CHClBr_2$) and Bromoform ($CHBr_3$) plus smaller traces of CH_2Cl_2, CH_2Br_2 and $C_2H_2Cl_2$.

Following the discovery of haloforms by Rook, a report on the occurences in the United States was published in Disember 1974 by Bellar et al.[3]. Gas chromatographic analyses were conducted on several finished waters and several samples were analyzed from a water treatment plant. Highest concentration of 37-150 microgram per liter of these compounds were found in finished waters taken from surface waters. Lower concentrations were detected from finished waters taken from wells. At the treatment plant, all samples taken after chlorination points were found to contain these compounds. Their concentrations were found to increase when the water was stored to settle for a few days.

After the findings by Bellar et. al., it was decided to conduct another survey with specific sites throughout the United States designated as test areas. This survey was called National Organics Reconnaisance Survey (NORS)[4] for halogenated organics. On December 18th 1974, Russell E. Train (administrator of EPA) ordered an immediate nationwide survey to determine the concentration and potential effects of certain organic chemicals in finished waters and named 80 cities to be included in the survey. It was concluded from the survey; four main species of trihalomethanes were widespread in the chlorinated drinking waters in the United States and result from chlorination.

Rook[5,] in June 1975 presented a complete explanation the various factor influencing the formation of trihalomethanes, leaving little doubt that these compounds are formed through the action of cholorine on natural organic precursors (humic and fulvic acids).

The seriousness of the concern about trihalomethanes in drinking water is illustrated by the situation that developed in the city of New Orleans, Louisiana where the tap water contained more chlorinated hydrocarbons than untreated Mississippi River. In addition, the researchers found chlorinated hydrocarbons, including carbon tetrachloride, in blood plasma collected from human volunteers in the city. They also found that the cancer mortality rate was 15 percent higher among white males who drank water from treated the Mississippi River than among those who obtained their water from wells.

The growing awareness of possible toxicological hazards and carcinogenic risks associated with long term consumption of drinking water containing trihalomethanes and other organics has resulted in active research in this area for the past decade in the United States and certain part of Europe. Enactments of new federal laws in the United States to limit and control of the levels in trihalomethane are summarized below.[6]

YEAR	AGENCY	ACTIVITY
1974	U.S Congress Safe Drinking Water Act PL 93 - 523	(1) Conduct research to identify and measure contaminants in drinking water.
		(2) Determine the nature, extent, sources of and means of control by chemicals suspected of being carcinogenic.
		(3) Improve methods of preventing subsurface water contamination.
		(4) Establish MCLs for contaminants having an adverse effect on human health.
1975	U.S EPA National Organics Reconnaissance Survey (NORS)	(1) Determine distribution of 4 trihalomethanes.
		(2) Determine effect of raw water source and treatment practices on trihalomethane removal.
		(3) Characterize organic content of finished water in 10 cities.
		(4) Determine correlations between group parameters.
1976	U.S EPA Advanced Notice of Proposed Rule Making (ANPRM)	(1) MCLs for specific organic chemicals.
		(2) Designated treatment technologies.
	U.S National Cancer Institute	(1) Disclosed that chloroform had been found to be carcinogenic to mice and rates.
	U.S Food and Drug Administration	(1) Ban chloroform from cosmetics.
1977	U.S EPA National Organics Monitoring Survey (NOMS)	(1) Monitor 21 specific organic compounds in 113 community water supplies.
		(2) Monitor group parameters.
1978	U.S EPA IPDWR Control of Chemicals Drinking Water : Proposed Rule	(1) Total Trihalomethane (TTHM) MCL at 0.10[a] mg/L
		(2) GAC Filtration to decrease synthetic organic chemicals (Proposed)
1979	U.S EPA : Control of THM in Drinking Water (Final Rule)	(1) TTHM set at MCL of 0.10[a] mg/L
		(2) GAC Filtration (no decision)
		(3) Specific monitoring for organic chemicals (may be required)
1980	U.S EPA : Quality Criteria for Water, Recommended limits for public water supply	Organic chemicals - ambient water criteria for protection of human health.
1983	NIPDWR Trihalomethanes : Final Rule	(1) TTHMs - MCL of 0.10[b] mg/l
		(2) Best treatment technologies for TTHM control identified.

[a] For all community greater than 75,000 people
[b] For all community greater than 10,000 people

A lot of research have been conducted and published on the methods of determining trihalomethane and various factors influencing its formation. Rook[5] himself, along with Trussel et. al[7] and Varma et. al[8] suggested that bromide, pH, chlorine dose, temperature and time influence trihalomethane formation. Hoehn et. al.[9] also suggested that algae was another source of trihalomethane precursor.

At the same time, treatment options had been proposed to control the formation and to remove trihalomethane when formed after chlorination. Rook[10] proposed several methods such as macroretricular anion exchange resin following coagulation, combination of ozone and chlorine for removing precursors from pilot-plant studies. He found that activated carbon or air tripping as effective method of trihalomethane removal. Hoehn[11] made a review on the relate effectiveness of various disinfection methods and suggested that ultraviolet radiation may be a viable competitor as disinfectant. All the alternatives for chlorine was hampered by cost competitor as disinfectant. All the alternative for chlorine was hampered by cost and does not possessed free residual in the distribution system to replace chlorine totally. In February 1983 National Interim Primary Drinking Water (NIPDWR) Trihalomethane : Final Rule, several treatment technologies for trihalomethane control identified to be chloramine, chlorine dioxide, improve clarification, moving chlorine application points and powdered activated carbon (PAC) application.

Several conditions in Malaysia make the study of trihalomethane necessary since Malaysian water sources are taken from coloured river waters, high temperature and chlorine had been used as a sole disinfectant. In most cases conventional treatment processes are employed. The siting of various industries above raw water intake points and the indiscriminate disposal of several types of waste has significantly deteriorated the quality of some of the major rivers in the country such as Sungai Skudai, Linggi, Johor etc.[12] Suspended solids were found the range of 50 - 500 ppm. All these factors indicate high potential or trihalomethane formation and need to be confirmed.

If monitoring carries out proves that trihalomethane are present in Malaysian finished waters and in the treatment plant, then new guidelines should be incorporated into the present ones. The findings should be made known to relevant authorities so that treatment methods can be improved to provide low organic water supply. The cost of improvement techniques will of course result in higher capital expenditure. The AWWARF Trihalomethane Survey[13], carried out in the United States concluded that to comply with 0.10 mg/L Trihalomethane Regulation has resulted in estimated capital expenditure of $31 - $102 millions and yearly operation and maintenance cost of $8 - $29 millions per year.

2. SCOPE OF RESEARCH

Research activities in this area had been tremendous in the United States and Europe. In Malaysia it has been neglected and most of the relevant water authorities are satisfied with water supply as along as it comply with the WHO Guidelines 1984. At the treatment plant, test are conducted on turbidity, jar test, color and certain metals. These tests are however conducted in bigger treatment plants; at smaller plants only the jar test is available. Monitoring is being done by other government agencies such as the Ministry of Health but the parameters of concern were biological in nature.

It was time that more concern be placed on the monitoring of the organics in the treatment plants to assess the treatment efficiences and the quality of finished water. As a start, with the availability of Gas Chromatography-Mass Spectrometer, trihalomethanes be monitored at several treatment plants in the Klang Valley and vicinity and their water supply at consumer ends. The treatment plants selected were Sungai Linggi, Sungai Langat and Sungai Batu.

The objective of the study is to:

(1)   Determine the levels of each species of trihalomethanes in
   a)   Water sources
   b)   Treatment plants
   c)   Finished waters at consumer's tap

(2)   Determine the efficiencies of various treatment processes in the treatment
       plants in removing trihalomethanes by conventional methods.

(3)   Determine surrogate parameters to find the correlation between them and
       the trihalomethanes.
   a)   Total Organic Carbon (TOC)
   b)   Residual Chlorine
   c)   pH
   d)   Turbidity
   e)   Temperature
   f)   Suspended Solids

Survey forms will be sent to all treatment plants to gather informations on treatment processes, chemical dosage including chlorine, chlorination points etc. It is hoped that these informations and the levels of trihalomethanes found in the above utilities can be to predict the trihalomethanes levels in the treatment utilities not under study.

3. SAMPLING METHODOLOGY AND ANALYSES

Measurements and analyses will be accordance to the methods specified by the *Standard Methods*[4] or methods approved by the U.S Environmental Protection Agency (EPA). Any modification will be cited from methods published in the Journal of American Water Works Association.

3.1   Water Sampling and Storage

Samples are to be collected in 1.2-L glass bottles sealed with TFE lined screw cap[14] or glass stoppered[15]. Care must be taken to avoid turbulence when filling and to ensure that no headspace remained after sealed and stoppered. This amount provide enough samples for duplicate trihalomethane analyses.

Collection points will be at the water sources, in the treatment plant after every stage of process and at consumer's tap.

3.2   Trihalomethane Parameters[15]

The parameters of interest are (1) Instantaneous Trihalomethane (Inst. THM) and (2) Terminal Trihalomethane (Term. THM).

When samples taken for Inst. THM, it was necessary to remove any residual chlorine (dechlor) in the sample that would otherwise assist in continuing trihalomethane formation. This is achieved by adding 1 mL of 3% sodium thiosulphate to the bottle before sampling.

When Term.THM is to be analyzed, the sodium thiosulphate will be omitted and sample stored for 7 days at 20°C.

3.3   Sample Extraction

Bellar et. al[16] had proved that extraction of trihalomethane from water sample using purge and trap method to be precise and accurate to a detection limit of 0.5 ug/L. This has been a widely accepted method for trihalomethane analysis. However the technique involved is not convenient for monitoring program involving lage number os samples.[17] The purge and trap method requires specialized equipment of instrumental modification and is relatively time consuming.

Investigations by Trussell et.al[18], Varma et.al[19] and Dressman et.al[17] concluded the liquid-liquid extraction (LLE) method was a more simple, quick, convenient, inexpensive and reliable technique for monitoring of trihalomethanes in drinking water.

Dressman et.al[17] made a comparison of several methods that have been published using LLE namely by Henderson et.al, Mieure and Richard-Junk. Mieure method was found to be better which can provide the best overall precision; and equally good as compaared to the purge and trap method.

For this research study, the Mieure method will de adopted. The extraction solvent sill be methyl-cyclohexan although the *Standard Method* recommended pentane. Work by Varma et.al[19] showed that methylcyclohexane to be less volatile, easy to work with at ordinary temperature and insoluble in water. It was found to prvide the highest compound percentage recovery.

3.4.   Qualitative and Quantitative Determination of Trihalomethane

Gas chromatography is the technique of choice for the separation of thermally stable and volatile organics and inorganic compounds.[20] The availability of versatile and specific detectors and tha coupling of gas chromatography to a mass spectrometer further enhance the usefulness of gas chromatography.

Mass spectrometer provides qualitative and quantitative informations about the atomic and molecular composition of organic and inorganic materials. The main advantage over other detectors is that it is able to identify inknowns and confirm the presence of suspected compounds. This fact was used by Rook[2] in identifying new peaks during monitoring of water supply from Barenplat treatment plant.

Gas chromatography mass spectrometer (GC/MS) model HP 5890 Series II will be used for this research project. The equipments are located at Process-Control Laboratory.

3.5   Measurement of Surrogate Parameters

a)   **Total Organic Carbon (TOC)** - this parameter is indirectly related to the trihalomethane precursors. High TOC level will indicate higher potential of trihalomethane precursors. Investigation by Rook[10], indicates only 0.2% of the precursor carbon has reacted to produce trihalomethane.

TOC will be determined by using "Boat Sampling Method" detected by Infra Red Analyser. This instrument is situated in the Environmental Engineering Laboratory.

b)   **Suspended Solids**

Raw water will be analyzed for suspended solids. This measurement is necessary to evaluate the quality of raw water at test treatment plants. Correlation may exist between the suspended solids and the trihalomethane formation potentials.

Method of determination will be according to the method sspecified in the *Standard Methods*.

3.6   Other Measurements

Free Residual Chlorine, pH and Turbidity measurements will make use of Hach Spectrophotometers Model DR/2000. The methodss are simpler, quicker and high precision of results are not required. All the methods are adapted from the *Standard Method* s and approved by the USEPA.

APPENDIX A

LIQUID-LIQUID EXTRACTION (LLE)

THE APPARATUS

a. Extraction vessels
    1. For samples that does not form an emulsion, use 14 mL screw-cap vials with a TFE faces silicone septum.
    2. For sampel that form an emulsion, use 15 mL screw-cap centrifuge tube with a TFE cap liner.
b. Syringes, 10 mL glass hypodermic with luerlok top.
c. Syringe valve, two-way with luer ends.
d. Pipet, 2 mL transfer.
e. Volumetric Flasks, glass stoppered, 10 and 100 mL.
f. Extraction solvent-methlyl cyclohexane.

THE PROCEDURE

1. Remove plungers from 10 mL syringe and attach a closed syringe valve.
2. Open sample bottle, carefully pour sampel into syringe barrel until it overflows. Replace plungers and compress sampel.
3. Open syringe valve and vent any residual air while adjusting sampel volume to 10 mL.
    Close valve.
4. Pipet 2 mL extraction solvent into the vessel.
5. Inject the contents of syringe into the vessel. Seal with TFE-faces septum.
6. Shake vigorously for 1 minute and let stand for 1 minute until phases seperate.
    If phases do not seperate, centrifuge to facilitate seperation.
7. Transfer the upper phase to GC vial by piecing the septum using a clean syringe for GC/MS analysis.

APPENDIX B

GAS CHROMATOGRAPHIC COLUMN

COLUMN DESCRIPTION

Column   :   HP-1 (Cross-Linked Methyl Silicone)
                   25 m x 0.32 mm x 0.52 um film
                   (HP Part No. 19091Z - 112)

Carrier   :   u (He) = 49 cm/sec

Oven   :   Temperature program

100^oC (8 min)

10^oC/min

40^oC/min

Compounds detected will be:

1.   Chloroform
2.   1,1,1-trichloroethane
3.   Carbon tetrachloride
4.   Bromodichloromethane
5.   1,1,2-trichloroethane
6.   Dibromochloromethane
7.   Tetrachloroethylene
8.   Bromoform
9.   o-dichlorobenzene
10.   1,2,4-trichlorobenzene

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