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STUDY OF EXTRACTION AND DETERMINATION OF CHLORINATED COMPOUNDS IN TREATED DRINKING WATER OF TEHRAN

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ABSTRACT

Chlorine was used for disinfecting drinking water in treatment plants. Disinfection of drinking-water is essential to protect the public from outbreaks of waterborne infectious and parasitic diseases. Chlorine inactivates a wide variety of pathogens and its effects are relatively long lasting. However, a major drawback associated with the use of chlorine as a disinfectant is its potential to react with naturally occurring organic matter (NOM) present in raw water sources to form a number of disinfection by-products (DBPs).

Trihalomethans, haloacetonitriles, haloacetic acids and mx are four important groups of disinfection by-products that are caused by chlorine. There are several methods for extracting and determinating chlorination by-products but EPA standard method is the best. Methyl Tert-Butyl Ether (MTBE) commonly was used for extracting by-products in EPA methods. In this study MTBE used as extracting solvent and rotary evaporator reduced the combined MTBE to a few milliliters that were subsequently injected to GC-MASS for determination chlorinated organic compounds.

There are several chlorinated compounds exist in drinking water of Tehran. AMDIS GC-MS analysis report suggested different compounds of DBPs that they are harmful to human health. The method described enables simultaneous determination of chlorinated compounds with low detection limits and excellent precision.

Keywords: Chlorine, Chlorination by-products, GC-mass, Liquid extraction, MTBE

INTRODUCTION

Chlorine was accepted to disinfect treatment of drinking water in early 1900s. Because of the chlorination, it has dramatically reduced the incidence of waterborne diseases and improved the quality of life. Unfortunately, an unwanted side effect was the formation of harmful by-product upon chlorination. Four important groups of DBPs were studied (trihalomethanes, haloacetonirtiles, haloacetic acids and 3-Chloro-4-(dichloromethyl)-5-hydroxy-2(5*H*)-furanone). The most significant group of disinfection by-products (DBPs) formed during chlorination is the trihaloromethanes (THMs). Compounds of this group chloroform, bromodichloromethane, chlorodibromomethane and bromoform were recognized as potential human or animal carcinogens. The second prevalent group of chlorination by-products (CBPs) is haloacetic acids (HAAs). Some of them (dichloroacetic acid and trichloroacetic acid) are potential animal carcinogens.The predominant chlorine disinfection by-products are the THMs. Nevertheless, they account for only about 10% of the total organic halogen compounds formed by water chlorination (IARC 1991). THMs consist primarily of chloroform, bromodichloromethane, dibromochloromethane and bromoform. When bromide is present in drinking-water, it is oxidized to hypobromous acid by chlorine:

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HOCl + Br- = HOBr + Cl-

HOBr reacts with natural organic compounds to form brominated halomethanes. Similarly, the presence of iodide may lead to the formation of mixed chlorobromoiodo-methanes (Morris 1982; IARC 1991).

Haloacetic acids include monochloracetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA), dibromoacetic acid (DBAA), tribromoacetic acid (TBAA), bromochloroacetic acid (BCAA), bromodichloroacetic acid (BDCAA), and dibromochloroacetic acid (DBCAA). Of this chemical family only MCAA, DCAA, TCAA, MBAA and DBAA are currently regulated as drinking water contaminants. These five regulated HAAs are often referred to as HAA (HEI 2004). The other important group of chlorination by-product is Haloacetonitriles. Haloacetonitriles (HANs) are toxic nitrogenous drinking water disinfection byproducts (N-DBPs). HANs are less frequently studied compared to THMs and HAAs and the occurrence of trihaloace-tonitriles in water is rarely reported. The most abundant HANs after water chlorination are dichloroacetonitrile and its brominated analogs, bromochloroacetonitrile and dibromoacetonitrile (Oliver1980; Reckhow (1984,1990a); Coleman 1984; Trehy1986; Peters 1990).

The last important disinfection by- products is mx. MX (3-Chloro-4-(dichloromethyl)-5-hydroxy-2(5*H*)-furanone) is produced as a by-product during disinfection of water containing humic substances using chlorine, chlorine dioxide or chloramines (Backlund 1988; Kanniganti 1992; Xu 1997).

EPA 500 series methods are a number of extraction and analyzing methods for these by-products. 551.1 EPA method is intended as a stand-alone procedure for either the analysis of only the trihalomethanes (THMs) or for all the chlorination disinfection byproducts (DBPs) with the chlorinated organic solvents and gas chromatography. Methyl-t-butyl ether (MTBE) is recommended as the primary extraction solvent in this method. However, due to safety concerns associated with MTBE and the current use of pentane by some laboratories for certain method analytes, pentane is offered as an optional extraction solvent for all analytes except chloral hydrate.

EPA 552.2 is a gas chromatographic (GC) method applicable to the determination of halogenated acetic acids in drinking water and MTBE as extraction solvent.

METHODS

The sample was collected from urban drinking water in laboratory. 1000 ml of sample extracted with 250 ml MTBE. The combined MTBE was reduced to a few milliliters in rotary evaporator. The reduced sample subsequently injected to GC-MASS.

The GC-MASS experiments were performed on a Varian CP-3800. GC column (30m × 0.25 µm film thickness) used for chromatographic separation. The GC parameters were as follows: split less injection mode for 0.75 min and split (20:0) on at 0.75 min, injector temperature at 250 °c, and helium carrier gas at a flow rate of 1 ml min^{-1} in constant flow mode. The GC oven temperature was initially held at 55° c for 1 min, then ramped to 100 °c at 10 ºc min^{-1}. A second ramp of5°c min -1 to 150 ° c was followed by a 3 ramp of 30ºc min^{-1} to 250 °c. The oven temperature was then held at 250 °C for 10 min. The injection volume was 1µL. The MS parameters were as follows: electron impact at 70, mass range of 60–350 amu, filament current of 95µA. CID fragmentation was performed using non-resonant excitation mode. The trap temperature was 150 °C, the transfer line temperature 250 °C, and the manifold temperature 50 °C (Kubwao 2009).

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RESULT AND DISCUSSION

GC analysis result showed several peaks in chromatogram plot (figure 1).

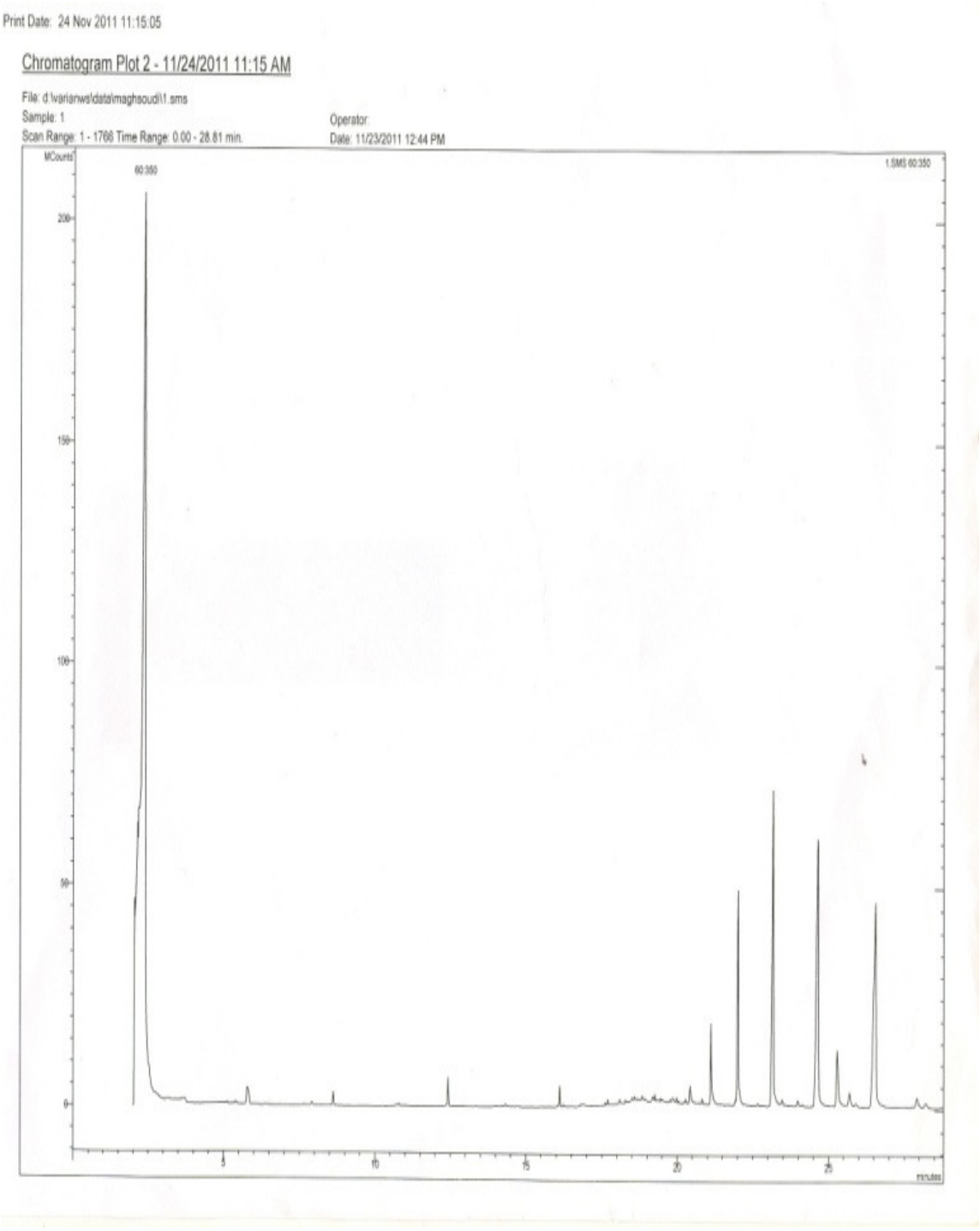

Figure1. Chromatogram plot

AMDIS GC-MS analysis report suggested different compounds. We introduce many related compounds to our study in this report and listed them in table 1.

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Table1. AMDIS GC-MS analysis report **Table1. AMDIS GC-MS analysis report**

Compound	*Time (min)*
2-chloro- propanoic acid	2.0289
4- chloro butantrile	2.1533
Furan	2.1633
Cyanogen chloride, pentanol-5-chloro-acetat, 5-chloro-pentene	2.2784
6-chloro-tetrazolo[1,5-b] pyridazine , 2,3-dichloro-propanol, 2-chloro propanoic	2.2967
1,1-dichloro-ethane, 2-chloro-propanoic acid, 2-chloro-methyl ester-propanoic acid	2.3016
1,1-dichloro-propane, 1,2-dichloro-propane , 2-chloroethyl-methyl-sulfone , 2-chloro-1,2-propanediol, butyl ester- carbono chloridic acid	2.3115
4-chloro-butanenitrile	2.3364
Chloro-ethene, 1,1-dichloro-propane, chloride-cyclobutanecarboxylic acid	2.3614
furan	2.4750
tetra hydro furan	3.9090
dioxide chlorine	9.4463
furan	17.3043
octanesulfonyle chloride	22.0093
2-chloro-decanoate-chloromethyl	23.1319
5-(2-methyl-3-methylene-2-butyl)2(5h)-furanone, 5-chloro2-(2-propenyl) pentanale	23.1384
2,2–isopropylidenebis(tetrahydrofuran)	23.1586
Tetrahydro-2-furanmethanamine, 2-furanmenthanol-tetrahydro-acetate, N-tetra hydrofurfuryl-2-chloro-propanamide	24.6419

The epidemiological investigation of the relation between exposure to chlorinated drinking water and cancer occurrence was considered problematic because any increase in relative risk over that in the people drinking unchlorinated water is likely to be small and therefore difficult to detect in epidemiological studies. In all of the studies evaluated, estimates of exposures were imprecise and surrogates (e.g surface versus groundwater) do not reflect exposure during the relevant time periods for the etiology of the cancers in question. Many

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variables, such as smoking habits, dietary practices, use of alcohol, socio-economic status, and ethnicity are known to affect cancer incidence and were not taken into account in most of the studies (IARC 1991).

MX induced cancer at multiple sites in male and female rats MX has not been tested for carcinogenic activity in rats. In male and female rats, MX induced thyroid gland follicular cell adenoma and carcinoma at all doses tested. Combined incidence of thyroid gland follicular cell adenoma and carcinoma reached 90 percent in the treated animals. Also in both sexes, statistically significant increased incidences relative to controls were observed for liver adenoma and carcinoma (combined) as well as adrenal gland cortical adenoma in the high-dose groups only. In females, MX significantly increased liver cholangioma and cholangiocarcinoma (combined) in multiple dose groups; in males, a dose-related trend for cholangioma was observed. Significantly increased incidences were also observed for benign and malignant mammary gland tumors in females. Marginally significant findings were observed for lymphoma and leukemia (combined) in females and pancreas Langerhans' cell adenoma and carcinoma (combined) in males (Komulainen 1997, 2000). There are two types of health effects that have been suggested by some as associated with THMs: cancer and reproductive/developmental health effects. EPA has concluded that there is evidence to support a potential association between long term exposure to high levels of THMs and bladder cancer as well as suggestions of an association with colon and rectal cancers. However, for the reproductive and developmental health effects, current health effects data are inconclusive and do not show causality (EPA 1998, 2001).

HAA's have low human and animal toxicity. At levels encountered in drinking water they are not expected to produce any acute health effects. However, over long periods of time, exposure to levels of HAAs at or above the maximum contaminant level can cause injury to the brain, nerves, liver, kidneys, eyes and reproductive systems. Animal studies suggest that HAAs increase the risk of cancer, and they are currently classed as possible human carcinogens. Decreased fertility and spontaneous abortion have been linked to HAA exposure in animals (HEI 2004).

The largest source of human exposure to THMs is from the consumption of chlorinated drinking water. Besides consuming water, other water uses in the home may contribute significantly to total chloroform exposure both from breathing in chloroform vaporized into the air and from it passing through the skin during bathing. Swimming in chlorinated pools will also contribute to the total exposure from the same exposure paths. One study observed that a greater percentage of chloroform passed through the skin when bathing water temperatures were increased. Chloroform does not concentrate in plants; therefore, the contribution from food to total chloroform exposure is small.

Evidence of chloroform's acute effects on humans has been obtained primarily during its past use as an inhalation anesthetic. In addition to central nervous system effects, chloroform anesthesia was associated with cardiac arrhythmias and abnormalities of the liver and kidneys. Inhalation exposure experiments with animals revealed that high levels are toxic to the liver and secondarily to the kidneys. Skin contact with undiluted chloroform may cause a burning sensation, redness, and blistering.

Acute effects of exposure to the other THMs are not documented in the literature, but are expected to be similar to chloroform. Chronic oral exposure of humans to chloroform at high doses results in adverse effects on the central nervous system, liver, kidneys, and heart (EPA 1998).

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CONCLUSION

Chlorine is often added to drinking water to kill harmful microorganisms. It also reacts with ammonia, iron and other metals and some organic compounds to improve water quality. There is a limit to the use of chlorine as its negative results may be seen with too much amounts. Also, the formation of chloroform and other suspected carcinogens is possible. Therefore, there is a need to determine the levels of chlorine and its by-products present in the treated water.

There are several chlorinated compounds exist in drinking water of Tehran. They are harmful to human health. Chlorinated drinking water should be seriously determined and measured in treatment plants. Obtaining an analytical result in a short period of time is extremely important for ensuring chemical engineering safety. The method is relatively unsusceptible to matrix effects. AMDIS GC-MS was successfully used to determine chlorinated compounds in drinking water.

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