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Disinfection of Drinking Water and Trihalomethanes: A Review

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Abstract: *Trihalomethanes (THMs) as the main disinfection by-products (DBPs) during the last four decades have concerned the public and scientific opinion for the possible carcinogenic effect on human health. The purpose of this paper is to investigate the disinfection of drinking water, types of DBPs and the formation of THMs. The formation of THMs during the chlorination process represents a serious health problem, as they significantly increase the possibility of the risk of several types of cancers. In this article we are discuss the health risk imposed by THMs, considered toxic and possible carcinogenic as well as mutagenic to the human body. Thus, their elimination and regular monitoring is imperative. In this article we present the removal technologies for the THMs and their precursors. This article also provides the basic information related to the analytical methods for the determination of the THMs.*

Keywords: *DBPs, Determination of THMs, Disinfectants, Health, THMs, Drinking Water.*

1. INTRODUCTION

The consumption of drinking water that meets the highest quality standards is a priority for all humans. Besides the physiological significance for life, water plays a major role in human pathology in the form of water borne diseases. These can be a result of the inadequate choice of water treatment which may not follow the main hygienic principles, sanitation techniques, and particularly disinfection. The disinfection process can be accomplished in various ways, but the most convenient and most utilized method is disinfection with chlorine. Proper disinfection either removes or neutralizes the causes of epidemics. Therefore, in order to avoid water borne epidemics, monitoring of drinking water is of the utmost importance. Actions must be taken to ensure the quality and to adequately perform the disinfection processes.

Safe drinking water, is the water that meets the generally defined criteria, such as the visible presence of deterrent materials, turbidity, pathogens, colour, taste, odour, presence of metals associated with risk to the public health, organic substances etc. Most of the organic compounds in drinking water are harmful to the health. The most dangerous ones are the disinfection by-products (DBPs), whose main subgroup are the trihalomethanes (THMs). THMs as synthetic organic compounds, which are possible carcinogenic and as such they put are a serious concern for the scientific society and the population in general. THMs are listed as the primary pollutants by the US EPA (United States Environmental Protection Agency), as result of their tumorigenic effects and the harmful effects on the nervesystem, as tested on animals [1].

THMs were discovered in 1974 by Rook J. in the Netherlands and Bellar *et al.* in the USA. THMs form as a result of replacing three hydrogen atoms in methane with halogen elements. During the chlorination process various THMs are formed, while only four of them are the main ones: chloroform ($CHCl_3$) - CF, bromodichloromethane ($CHBrCl_2$) - BDCM, dibromochoromethane ($CHBr_2Cl$) – DBCM and bromoform ($CHBr_3$) - BF. All four together are referred to as total trihalomethanes (TTHMs). In drinking water, chloroform is always with the highest concentration, and often represented by more than 90% of the total concentration of THMs [2].

After THMs were discovered, highly disturbing concentrations of THMs were reported in surface waters, while there were lower concentrations detected in well waters. It was found that all samples taken at the points of chlorination contained THMs, and their concentration increased with time.

Although the THMs concentration in drinking water is relatively low, the fact that a suspected carcinogen can be easily distributed through the public water supply system justifies the research on the formation and control of the THMs.

Natural water contains large number of natural organic substances which are in fulvic and humic form, produced by the decomposition process of the organic matter known as precursor of the THMs. These precursors are not considered to be harmful. They become harmful when reacting with chlorine. When chlorine is applied in normal levels in order to disinfect, it reacts with the natural organic matter (NOM) which is present in the untreated waters and it thus forms THMs. THMs are formed as a result of chlorination of the natural organic precursors, with the following reaction [3]:

$$HOCl + \text{Organic precursor} \longrightarrow THM + \text{Further degradation} \quad (1)$$

After the release of the water from the treatment plant the concentration level of THMs varies, it can increase or decrease. This is as result of continuous reactions in the formation of THMs or processes within the distribution system. The concentration of THMs during the distribution process depends on several factors including: contact times, water flow paths, conditions under which the system is maintained and practices of maintaining a residual disinfectant. The high values of parameters such as: organic matter, temperature, pH, chlorine dosage, bromides and the contact times, all support the increase in the concentration of THMs.

In recent years in the USA and Europe, there is an increase of research related to THMs, while in the developing countries and East Asia they are neglected, as the majority of the water authorities are satisfied with the World Health Organization (WHO) recommendations of 1984. In plants the following tests are performed: turbidity, jar test, dyes and certain metals. These tests are performed only in the main treatment plants, while in the small ones they only perform the jar test. The monitoring is conducted by the government agencies. The THMs concentration found in drinking water in Europe vary widely (starting from negligible amounts all the way to hundreds of μg/L). This is due to the differences in the sampling process, sample points etc. In 1997, the difficulty of precise assessment and trends of exposure of the population was detailed [4].

The main cities in the R. of Macedonia use chlorine as disinfectant for the drinking water, following worldwide guidelines and practices. Until two years ago, there was no information available that pertained to the concentration level of THMs in drinking water, thus making our research the first one of this kind. The purpose of this article is to provide valuable information for drinking water disinfectants, DPBs and THMs.

2. DISINFECTION AND DPBS

The disinfection of drinking water can be defined as a process that removes or makes pathogenic microorganisms inactive. The protection of the water source is the first challenge. Chemical disinfection, on the other hand, where chlorine or other oxidants are utilized is the ultimate barrier. Ground water usually requires less pre-treatment, whereas surface water includes processes such as coagulation, clarity assurance, and filtration.

Chemical disinfection, primarily using chlorine, ozone, chlorine dioxide or other oxidants has been practiced for many years and has played a major role in the process of elimination of water borne diseases worldwide. However, in this process, all chemical disinfectants produce organic and inorganic by-products that have negative impacts on health. More than 250 DBPs have been identified, but the behavioural profiles of only about 20 DBPs are adequately known. The DBPs are potentially dangerous, but still the risk associated with the general health is considerably smaller compared to the inadequate disinfection. The DBPs are chlorinated acetic acids, chlorinated ketones, and as well as halogenated acetontriniles.

3. DISINFECTION AND THMS

Water treatment is an emerging technology. The final step in the purification of drinking water is disinfection, a procedure that protects the drinking water during the process of distribution, protection from the foreign contaminants and possible growth of bacteria [5]. Hence chlorine is easy to use, especially in its most common form of hypochlorite, it is the primary disinfectant for drinking water. Disinfectants, besides their ability to neutralize pathogens, are used as oxidants in drinking water treatment for the following purposes:

- tasteand odor removal;
- oxidation of iron and manganese;
- maintaining a residue to prevent biological re-growth in the distribution system;
- improve coagulation and filtration efficiency;
- prevent the growth of algae in the sedimentation basin and filters.

According to regulations, water is disinfected prior to being used. This process is called the primary disinfection. Upon further analysis of the water treatment technology in its initial stages, it became obvious that secondary treatment is also necessary. The secondary treatment is for the sole purpose of keeping the water microbiologically safe during the distribution process, and ensuring the presence of residual disinfectant in the water network itself. However, during the disinfection of drinking water, the disinfectant results in THMs upon reaction with organic matter.

4. TYPES OF DISINFECTANTS

Disinfectants are being applied to drinking water in order to protect the population from pathogenic microorganisms [6]. Most common disinfectants are: chlorine, chloramines, chlorine dioxide, ozone and ultraviolet radiation. In most recent times a combination of disinfectants as well as membrane technologies are in use.

4.1. Chlorine

Chlorine and its compounds are the most commonly used disinfectants in the water treatment process. The popularity of chlorine is not only due to the low cost, but also because of its higher oxidation potential which allows minimal residual chlorine level through the distribution system and protect it from microbial re-contamination [7]. The application of chlorine in the drinking water treatment resulted in significant reduction of water borne diseases worldwide, such as typhoid. After War World II disinfection with chlorine became a standard treatment worldwide [8]. When chlorine reacts with water it forms hypochloric acid (equation 2), which then undergoes acid-base reaction to form hypochlorit ion (equation 3). The decomposition of chlorine in HOCl and OCl^- depend on the pH. HOCl is a stronger disinfectant than OCl^-, therefore a lower pH is preferred for disinfection with chlorine. Chlorine (HOCl or OCl^-) attacks the bacterial cells and the virus protein layer by killing them.

$$Cl_2 + H_2O \Leftrightarrow HOCl + H^+ + Cl^- \quad (2)$$

$$HOCl \Leftrightarrow OCl^- + H^+ \quad (3)$$

4.2. Chloramines

Chloramines are alternative water disinfectants and they do not cause problems with the taste or water odor, which is common when water is treated with chlorine as a disinfectant. Chloramines main disadvantage is that it requires a very large amount of $c \cdot T$ in order to ensure effective disinfection. Chloramines are more stable in the distribution system than freely available chlorine; therefore they are often used to limit bacterial growth. Their popularity grew as they do not produce high concentrations of DBPs as is the case with chlorine. Chloramination includes the addition of chlorine and ammonia in the water source. In contact with ammonia, chlorine reacts and the results are monochloramine (NH_2Cl), dichloramine ($NHCl_2$) or trichloramine (NCl_3). The following equations (4, 5 and 6) show their formation:

$$NH_4^+ + HOCl \Leftrightarrow NH_2Cl + H_2O + H^+ \quad (4)$$

$$NH_2Cl + HOCl \Leftrightarrow NHCl_2 + H_2O \quad (5)$$

$$NHCl_2 + HOCl \Leftrightarrow NCl_3 + H_2O \quad (6)$$

Monochloramine is the best chemical for the disinfection of water as it does not give the unpleasant taste and odour during the formation of dichloramine or trichloramine. The ratio used for the formation of chloramine is from 3:1 to 5:1, as it limits the formation of dichloramine and trichloramine. In addition, these ratios limit the nitrification and the growth of biofilm, which can occur as a result of using high levels of ammonia [9]. Chloramines in comparison to the free chlorine are not strong disinfectants. However, they are able to produce stable residual disinfectant. Therefore, chloramine is a good secondary disinfectant able to control bacterial growth in the distribution system. Disinfection with chloramine produces lower levels of THMs in comparison with chlorination, but at the same time it produces other by-products including cyanogen chloride.

4.3. Chlorine Dioxide

In water, chlorine dioxide (ClO_2) with iron and manganese can be reduced to chlorite, while at pH > 10 it rapidly hydrolyses and it produces chlorites and chlorates:

$$2\ ClO_2 + 2\ OH^- \Leftrightarrow ClO_2^- + ClO_3^- + H_2O \quad (7)$$

Chlorites are relatively stable in the presence of NOM, but they can oxidize to chlorates from the free chlorine, should it be added as a secondary disinfectant.

$$ClO_2^- + OCl^- \Leftrightarrow ClO_3^- + Cl^- \quad (8)$$

Chlorites and chlorates as inorganic by-products can cause haemolytic anaemia in low level exposures, while in high concentrations can cause an increase of methemoglobinemy [10]. ClO_2 is effective in the process of inactivating the hydro pathogens, but does not act as natural organic material to form THMs. However, some halogenated by-products are created when ClO_2 is used as a disinfectant. Another disadvantage during the use of ClO_2 is the fact that it is a very volatile chemical, unstable and it dissolves very quickly in chlorites and chlorates. The main disadvantages of using ClO_2 compared to chlorine are: high operating costs, health risk due to the residual oxidisers and the result of harmful by-products.

4.4. Ozone

Ozone is a very strong disinfectant when used for primary disinfection of the water treatment plants and sewage as well. Since it does not have a stable chemical residue, it is not used as a secondary disinfectant [11]. Therefore nowadays, ozone is used as disinfectant because it does not form at all, or forms very small amounts of THMs or haloacetic acids (HAA). When ozone reacts with water, it forms free radicals, $HO_2^\bullet$ and $HO^\bullet$ (equation 9-12). They are thought to be active chemicals in the disinfection of pathogens. Free radicals break down the cell wall of bacteria and at the same time neutralize viruses.

$$O_3 + H_2O \Leftrightarrow HO_3^+ + {}^\bullet OH^- \quad (9)$$

$$HO_3^+ + {}^\bullet OH^- \Leftrightarrow 2HO_2^\bullet \quad (10)$$

$$O_3 + HO_2^\bullet \Leftrightarrow HO^\bullet + 2O_2 \quad (11)$$

$$HO^\bullet + HO_2^\bullet \Leftrightarrow H_2O + O_2 \quad (12)$$

Ozone can form brominated THMs via oxidation of bromides in order to form hypobromous acid, which brominates precursors. A range of other DBPs can be formed, including bromates, aldehydes and carboxylic acids. Ozone is more effective in the neutralization of microorganisms compared to chlorine. Another advantage of its use in the water treatment is the control of taste and odour, oxidation of humic substances and particle destabilization. Bromates and formic aldehyde can be formed upon disinfection with ozone, when water has high concentration of bromides. Halopropanones and chlorinated hydrates are some by-products formed as a result of disinfection with ozone.

4.5. Ultraviolet Radiation

Ultraviolet radiation is sometimes used as a method of water disinfection. Upon the entry of UV radiation in the cell wall of the microorganism, the UV light damages the DNA or the RNA, while preventing the reproduction of the organism. At low dosages, UV light disinfection is effective for the neutralization of pathogens, thus a low concentration of by-products are formed. However, high percentages of minerals and high turbidity can lower the effect of UV disinfection. In addition, this type of disinfection does not produce residual disinfectant; therefore it can only be utilized as primary disinfectant. When water is disinfected with UV light as primary disinfectant, the usage of chlorine gas as secondary disinfectant is mandatory.

5. STRATEGY FOR CONTROLLING THMS

The studies suggested the methods for controlling and removing the THMs, such as the macroreticular resin ion exchange method after coagulation and the combination of ozone and chlorine for removal of precursor. Activated carbon or air bubbles are also effective methods for removing THMs. Based on the US National Intern Primary Drinking Water, some of the technologies for controlling the THMs are chloramines, chlorine dioxide, moving the chlorination points and application of powdered activated carbon. The basic strategies adopted to reduce the THMs concentration are:

a) changing of process conditions (removal of precursor compounds);

b) usage of various chemical disinfectants; or

c) usage of non-chemical disinfectant (UV radiation or the membrane process).

The formation of THMs can be reduced by removing the precursors, increasing coagulation, and reducing the dosage of chlorine used to the level that it does not impede the disinfection process. Alteration of disinfectants can be made only if it complies with the THMs limit. It also depends on the raw water quality and the treatment process for removal of precursors. An effective method would be to switch from chlorine to chloramine, in order to ensure the presence of a residual disinfectant in the supply system, thus reducing the subsequent formation of THMs within the network.

The practice of using chlorine in several points in some countries, including dosing in untreated water can lead to much higher levels of THMs. Some countries, for example Germany, have a strictly regulated usage and dosage for disinfection chemicals. There are also differences in the terms of usage of the disinfectants. For example, since chlorine dioxide does not contribute to the formation of THMs it is widely used in France, Germany and Italy, but less in the UK and other countries. Since there are differences in regulations, it is obvious that the presence of THMs in drinking water is a matter of high concern for human health in Europe.

In some northern European countries the process of final disinfection using oxidants is no longer utilized. For example, in the Netherlands, chlorine or other oxidants are used in the treatment of only 20% of the total volume of drinkable water. This approach is based either on aquifers, which in turn act as filter for the process of removing the microorganisms or infiltration through sand, thus utilizing it as an effective natural geological filter. In the general treatment there is more intensive use of the barriers against the microorganisms. The success of this strategy is highly dependant on clean distribution systems, with short delays in distribution.

In Malaysia for example, certain conditions dictate the necessity of studying THMs, as the water sources are turbid rivers, with high temperatures and where chlorine is the only disinfectant. The location of the intake points in vicinity of various industries and the unselective discharge of waste has significantly deteriorated the quality of some of the main rivers in the country. All the abovementioned factors indicate the high potential for the formation of THMs.

The European Council Directive of 1998 for drinking water limits the THMs to 100μg/L beginning from 2008. The new regulations for limiting and controlling the THMs are continuously corrected while reducing the level of their content in the drinking water. Some countries have different limits, while others have not yet set the maximum limit that is allowed for THMs. The THMs regulation standards for some countries are given in the table below [12].

Table1. *Drinking water regulation for THMs and $CHCl_3$ in various countries*

Country	THMs (μg/L)	CH_3Cl (μg/L)
Australia	250	-
Canada	350	-
China	-	60
Denmark	10 – 15 (lowest value)	-
France	-	30
Japan	100	60
Korea	100	-
Taiwan	100	-
UK	100	-
USA	80	-
WHO	(the ratio of TTHMs) ≤ 1	200

6. HEALTH EFFECTS OF THMS

As result of the increasing awareness of the potential risk of the toxicity and the carcinogenic risk associated with the long-term consumption of water that contains THMs, research institutions in the USA and some of European countries have shifted their focus on the subject. It is already known that the presence of THMs in drinking water is a major health threat due to its possible carcinogenic potential. Therefore many studies have been conducted in order to remove the THMs precursors or the THMs themselves from drinking water. THMs also negatively impact the environment. Hence, keeping the THMs levels at low concentrations is an imperative.

Even if there are no sources of anthropogenic pollution, there is still a potential threat for the formation of THMs. Some epidemiological studies have reported the ingestion of chlorinated water to have caused various cancers of the oesophagus, the pancreas, urinary tract and the stomach. The studies conducted on THMs have caused a great concern hence chloroform has been established as an animal carcinogen [13], while the acute toxic doses of chloroform can cause depression of the central nervous system, as well as cardiac effects [14].

In 2000, Lin [15] conducted a study in southern Taiwan which identified that the exposure to THMs through ingestion was 47.9 μg/day, while inhalation exposure as a result of showering was 30.7 μg/day. It was determined based on measurements that chloroform constitutes most of the THMs [16]. Numerous epidemiological studies have been conducted to investigate the correlations between chlorination by-products and certain diseases [17] - [18], while the presence of THMs in the drinking water may increases the risk of bladder cancer and may cause defects in the reproductive system. Recently, there are several studies conducted to assess the potential risk of cancer resulting from exposure to THMs in drinking water. Due to lack of available parameters, most studies have focused on the risk associated with chloroform.

Black *et al*, have shown a correlation of risk being higher with the chlorination of untreated water with high percentages of bromides and organic carbon [19]. Lee *et al*, concluded that the risks of cancer and the risk index of THMs in various ways of exposure, is greater when ingested orally compared to inhalation or skin absorption [20]. Similar results were reported by Tokmak *et al* [21].

In a study conducted in order to control bladder cancers, Villanueva *et al* [22], estimated that during long exposures to THMs, either through ingestion, inhalation or skin absorption, the level of individual exposure depends on the modes of exposure. The evaluation of only one method of exposure can lead to errors. It was reported that THMs are absorbed and metabolized, and quickly eliminated by mammals after exposure either orally or by inhalation [23].

Similar studies showed that THMs, was a rodent carcinogen spurred a large number of epidemiology and toxicology studies into chlorinated drinking water. In 1985, this cancer finding was shown to be wrong. The question now is: What do we know about the human health impacts of DBPs in drinking water? According to Steve E. Hrudey and John Fawell [24] bladder cancer has been the most consistent finding from epidemiologic studies in North America and Europe and the possibility that chlorinated drinking water contributes an increased risk of bladder cancer remains a viable hypothesis.

Despite the confusion about chloroform, there is a viable hypothesis that chlorination disinfection by-product (CxDBPs) in drinking water may cause human bladder cancer [25], [26]. This possibility is based on bladder cancer showing the greatest consistency as a cancer outcome that is statistically associated with human exposure to chlorinated drinking water. Because of this possibility, the case for continuing research and sensible precautionary management of CxDBPs in drinking water clearly remains justified, particularly the removal of precursor NOM which should reduce most CxDBPs. However, this precautionary rationale needs to be effectively articulated by regulators and other authorities [24].

A study conducted in California by the State Health Department found that women exposed to high levels of THMs had a 17.5% higher chance of a miscarriage, while women with less exposure to THMs 9.5% [27]. Epidemiological studies have consistently warned of the growing risk of bladder cancer, cancer in the stomach, intestines and rectum, as a result of the usage of chlorinated surface water [28]. Therefore THMs regulation is being given great significance by various countries, for example USA, EU, Canada, Japan etc.

Waters in swimming pools are recycled for a long period of time, as they are polluted by swimmers who are a source of organic compounds and microorganisms. Thus, continuous disinfection of the water in the swimming pools is necessary in order to minimize the risk of possible microbiological contamination as well as to prevent possible outbreaks of infectious disease. The determination of the level of THMs in the swimming pools is an imperative as well as a necessity for protecting public health [29].

6.1. Studies Conducted on Humans

Lin and Hoang developed exposure models while considering three major scenarios associated with the potential exposure to THMs [30]. These scenarios included showering, activities prior to and upon

cooking and the cooking process. Results showed that the average inhalation exposure to THMs were 26.4, 1.56, 3.29 μg/day respectively. Total exposure results were comparable with the results for direct ingestion, thus indicating that inhalation is an important method of exposure to THMs. There are a lot of reports available, which discuss the negative effects, including toxicological effects of the THMs. Some of the side effects of THMs are summarized in Table 2.

Table2. *Toxicological information for THMs [31]*

DBP	Compound	Clasification*	Damaging effects
THMs	$CHCl_3$	B2	Cancer, liver, kidney and reproductive effects
	$CHClBr_2$	C	Nervous system, liver, kidney and reproductive effects
	$CHCl_2Br$	B2	Cancer, liver, kidney and reproductive effects
	$CHBr_3$	B2	Cancer, nervous system, liver and kidney effects

**A: Human carcinogen; B1: possible human carcinogen (with some epidemiological evidence); B2: Possible human carcinogen (with enough laboratory evidence) C: Possible human carcinogen; D: Not classified*

A study conducted in Italy showed lower average weight of the new-borns amongst women that consumed more than 30 years of chlorinated water – the lower weight correlated with the somatic parameters [32]. Kallen *et al* reported on the effects that THMs had on the somatic parameters, body length, the head volume, the low weights at birth as well as premature birth [33]. However another study conducted in Taiwan found no evident link between the low weight at birth and chlorination, but the information provided shows that municipalities that were using chlorine had a much higher rate of premature births [34].

6.2. Studies Conducted in Animals

Amongst all by-products, THMs draw a lot of attention due to chloroform being an animal carcinogen. Studies on animals showed that chloroform has resulted in liver tumors (male rats) and liver tumors in mice (male and female). The International Agency for Research on Cancer has determined that the evidence for the chloroform being carcinogenic is sufficient [35]. The results have suggested that the mode of action in which chloroform acts is as tumour-genesis in the cytotoxicity in liver and kidney, thus cytotoxicity has spread which in turn could be the key component of the carcino-genesis in these tissues [36].

BDCM is as well carcinogenic for mice, therefore upon applying certain dosages is has resulted in tumors in the intestines and kidneys (both male and female), and upon exposure in drinkable water, it results in liver tumors (this time male only) [37]. Studies in mice have showed that BDCM increases the weight of the liver, while causing cell spreading and just as chloroform it causes hypomethilation of the DNA (on female mice), and the damage caused to the liver histologically seems to be different [38].

Same as BDCM, bromoform causes tumors in the intestines, polyps adenomatous and adencocarcinomas amongst mice. BDCM also causes abnormal crypt-foci (male mice) just like other bromine THMs [39]. Whilst in the liver of female mice, BDCM fosters a similar type of toxicity as chloroform, resulting in an increase of the weight of the liver, enhanced cell proliferation and c-myc hypomethylation [38].

7. METHODS FOR DETERMINATION OF THE THMS

The quantitative level of THMs in μg/L (ppb) in the drinking water is a fairly new challenge. There are only few scientific papers that determine the presence of THMs with UV-VIS spectrophotometry, while there are more which utilize gas chromatography (GC). The gas chromatography enables the analysis of the THMs as well as other organic compounds with low boiling temperatures.

TTHMs analyses in the laboratory are performed by various methods of chromatography. The most widely used method is EPA 502, purge and trap/electrolytic conductivity detection method. Two other methods, EPA 501 and the 551 New Information Collection Rule Method use the solvent extraction/electron capture detection. Usage of chromatography methods requires expensive equipment, adequate training and enough time required for analysis. Moreover, these methods are relatively expensive and take a lot of time in the laboratory.

A number of analytical techniques have been reported on the analysis performed on the THMs in water, such as direct water injections, liquid-liquid extraction, headspace technique, gas phase micro-

extraction technique and the solid phase micro-extraction technique. The direct injection of the water causes problems with the stability of the columns as well as the critical temperatures for the columns and injectors.

The conventional liquid-liquid extraction is a difficult technique and is very time consuming, and is prone to form emulsions. It requires evaporation of large volumes of solvents and has toxic flammable chemicals. The fact that the headspace method utilizes aliquot, only with a fraction of the total volatile samples, leads to a concern about its sensitivity. The purge and trap technique consumes a lot of time and requires a special tool.

The liquid phase micro-extraction is developed as a method of minimizing the pre-treatment of the sample with the solvent, which utilizes very little toxic organic solvents. However, the disadvantages of this method are decomposition of the organic solvents and the formation of air bubbles, it is time consuming, and it does not reach equilibrium.

Lately, the quick and simple concentration method of liquid-liquid micro-extraction has been developed. This method consists of two steps: a) injection of the extraction mixture and distribution of the solvent in the liquid sample solution and b) centrifuging the turbidity solution. Determination of the analyte can be performed with Gas Chromatography Mass Spectrometry (GC-MS). Methanol is used as a distribution solvent.

Due to the regulatory requirement imposed by EPA and the Council of Europe, the determination of DBPs and THMs has become very significant for the water production companies as well as health protection. Difficulties as well as costs of these analyses impose methods with lower cost, which can be performed in real time.

The UV-Vis spectrophotometry method mainly relies on Fujiwara's base chemical reaction, in which THMs with a certain reagent gets transferred into a pink colored compound that absorbs in accordance with Ber's law, 525 nm wavelength. The new method of spectrophotometry (HACH) enables the determination of TTHMs in the drinking water and it does not require extraction and sample concentration. Another benefit is that the new method does not use any hazardous reagents. The UV-Vis spectrophotometry method is suitable as are the other EPA methods (524.2 Purge and trap gas chromatograph mass spectrometry, Liquid Extraction 551.1 Electron Capture Detection gas Chromatograph liquid extraction and GC 552.2 Electron Capture Detection), as result of cheaper equipment and reagents, as well as the reduction of processing the result and saving time.

Fuji Electric Co., Ltd. has produced the automated analyser for the determination of the TTHMs, for continuous monitoring of water supply systems. This analyser determines the TTHMs based on fluorescence measuring, with a detection limit of 0 – 200 μg/L and for a total analysis time of 4 minutes [40].

8. CONCLUSIONS

The disinfection of drinking water is essential for the prevention of water borne diseases and it has significantly contributed in lowering the mortality rate due to infectious diseases; while at the same time improved public health. Unfortunately, disinfection results in DBPs and THMs that are possible carcinogenic. Their formation during the disinfection process is a serious health problem due to THMs resulting in several possible types of cancer. THMs and HAA are the most represented DBPs of the chlorinated water. With chloramine their amount is significantly reduced. Ozone, ClO_2 and UV result in non-chlorinated by-products. As result of their oxidative properties, ClO_2 or O_3, increase the aldehydes, ketones, carboxylic acids and brominated organic compounds. Bromates, chlorates and chlorites are considered as inorganic DBPs.

The concentration of THMs in drinking water can be reduced by choosing the suitable disinfectant, that will dismiss the THMs from drinking water as well as their organic precursor. Where is possible, the removal of the precursor can be done efficiently and effectively by conventional coagulation technologies. Determination of the THMs is mainly done with the chromatographic techniques, although UV-Vis spectrophotometry and fluorescence can be applied as well.

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