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THMS FORMATION BY CHLORINATION OF THE WATER – PARAMETERS AND REACTIONS

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Introduction

In the water treatment process, in order to ensure the microbiological safety of the drinking water, chlorine is a commonly used disinfectant. During disinfection, chlorine may react with natural organic matter in the raw water, resulting in various disinfection by-products (DBP) formation, such as trihalomethanes and haloacetic acids, with potential human health risks. DBP formation varies with quality of water source: concentrations and properties of natural organic matter, chlorine dose, contact time water – chlorine, temperature, pH.

Precursor is general term used to describe the organic content of raw water that react to form THMs. It is believed that precursors are mainly humic and fulvic acids which are the degradation products of plant material, but low molecular weight methyl ketones, metadihydroxy aromatic compounds, algae and their extracellular products have also been cited as precursors.

Chlorine reacts with both fulvic and humic acids. It also reacts with bromide ion and ammonia. In the presence of ammonia, hypochlorous acid HOCl will react to form chloramines. The chloramines can further react in the presence of HOCl to form end products, either nitrogen gas or nitrate ion. When bromide ion is present, hypobromous acid HOBr is formed. This reacts in a manner similar to chlorine, forming brominated amines. It is believed that THMs are formed when organic carbon compounds react with either HOCl or HOBr via the generalized haloform reaction. Bromide ion reacts rapidly and irreversibly with HOCl to form HOBr, which can form brominated THMs in a similar way to HOCl.

THMs formation can be represented with the following haloform reactions:

$2R – CO –CH_3 + 3Cl_2 + light \rightarrow 2R – COCCl_3 + 3H_2$ and a subsequent hydrolysis:

$2R – COCCl_3 + 2H_2O + light \rightarrow 2RCO – OH + 2CHCl_3$

Materials and methods

All experiments were carried out using a GC/MS Agilent – MPS Gerstel with automated device SPME. The sample is collected and dispensed via a PDMS fibber in injector, detection by microECD

SPME integrates sampling, extraction, concentration and sample introduction into a single solvent-free step. Analytes in the sample are directly extracted and concentrated to the extraction fibre. The method saves preparation time and disposal costs and can improve detection limits.

The temperature programmes used for the oven and for the SPME system are specified.

Results and conclusions

Chlorine consumption and THMs formation were very rapid during the first hours of the reaction followed by a more gradual decay and formation after 7 hours. The rapid and slow decay rates are likely due to different competing reactants, such as the oxidation of inorganic compounds (rapid) and substitution reactions with NOM (relatively slow).

The kinetics of the formation of THMs can be different, depending on the chlorine dose, water pH, water temperature and organic matter content.

Temperature: Lower total trihalomethane levels occur during the winter months. These depressed levels are attributed to lower precursor level (lower algal production) and lower temperatures.

pH effect: It is well established that yields of THMs are affected by changes in pH. This may be due in part to the catalytic effect it has on the degradation reactions of the hypohalites.

Residence time: The THMs concentrations formed after chlorination, increase with the residence time (contact time water/chlorine)

Chlorine dose effect: Chlorine reacts in many phases: immediate chlorine demand exerted by reaction with inorganic matter, then additional chlorine begins to react with available organic material. In the second step was a nearly linear relationship between chlorine dose and the concentration of THMs produced.

Total organic carbon effect: The THM formation is strongly dependent on the amount of naturally present humic substances, generally referred to as total organic carbon (TOC): it increases with increasing TOC in presence of free chlorine residuals.

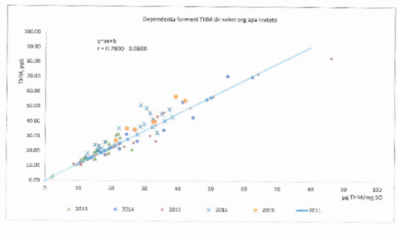

Figure 1. Influence TOC on THMs formation

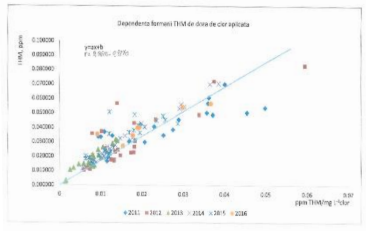

Figure 2. Influence chlorine dose on THMs formation

The effect of several parameters on the formation of THMs from chlorination of water was investigated. The results indicated that increasing the residence time, temperature, pH, free chlorine and TOC increases the THMs formation. The brominated–THM species formation increase with the presence of bromide ions in the chlorinated drinking water, mainly bromoform.