Water disinfection agents and disinfection by-products

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Abstract. The aim of this work is to describe factors of water quality change in the distribution network and legislative requirements in Slovakia for disinfectants and disinfection byproducts (DBPs). In the experimental part, the time dependence of the application of the chlorine dioxide and sodium hypochlorite on the formation of some by-products of disinfection for drinking water from WTP Hriňová is studied. We monitored trihalomethanes, free chlorine, chlorine dioxide and chlorites.

1. Introduction
Disinfection of drinking water, and also ensure of safety water quality is a major challenge 21 century. This challenge is not only about drinking water, but also about utility, industrial, cooling water and water in swimming pools. The aim is always such a disinfection that is acceptable in terms of environmental impact, the formation of disinfection by-products, but at the same time sufficiently effective and affordable.

Raw water, whether surface or underground, used to treatment of drinking water, contains microbiological and biological pollutants. Therefore, it is absolutely necessary to carry out its disinfection. Disinfection uses a wide range of disinfection techniques, each of which has its advantages and disadvantages.

Emphasis should be put on the best quality of the input water which is in equivalence in terms of physio-chemical properties of the water and has the lowest potential to enable the microorganisms to get overpopulated during the water transport in the distribution system. Therefore the selection of water source represents the first step in meeting this requirement.

Disinfection is conditional upon the doses of disinfection agent (oxidizing agent) not only but also by a well performed and efficient water treatment. To remove the soluble organic substances (so called a natural organic matter), the turbidity respectively means to avoid the bacteria to get increased in number in the distribution system during water transport and formation of the disinfection by-products (DBPs). Natural organic pollution is considered as the main precursor of the formation of disinfection by-products. Possible points of oxidizing (disinfection) agent input in the water supply system are schematically presented in the figure 1.

Most frequently used disinfection agents (oxidant) for ensuring the sanitary safety and used in water treatment are:
- Chlorine gas (Cl₂), or sodium hypochlorite (NaClO);
- Chloramines (NH₂Cl, RNHCl);
- Chlorine dioxide (ClO₂);
- UV radiation;
- Ozone O₃;

Chlorine gas (Cl₂), or sodium hypochlorite (NaClO);
and various combinations of them. Combination of oxidants and their impact on formation of the disinfection by-products is a matter of many research projects [1]. In general, when the UV, ClO₂ or O₃ is applied in pre-oxidation as a oxidizing agent, a need for additional disinfection by a chlorine or chloramines resp. appears to ensure the disinfection in the distribution system. Some systems that use the chloramines to reach the disinfection require sufficient amount of free chlorine during the treatment to form chloramines in the distribution system after the NH₄⁺ is added into the system.

![Drinking water treatment scheme with a possible point of addition of oxidizing agent.](image)

Majority of public water supply systems use chlorine compounds for drinking water disinfection. Addition of chlorine can react directly or after the hydrolysis by chlorine acid (HOCl) with organic matter that is common to be presented in the system (precursors such as humine acids, fulvo acids, microorganisms and algae, COOH, phenols, nitrogen organic compounds, etc.) to form halogenated inorganic and organic compounds (disinfection by-products) such as trihalomethans (THMs), halogenated acidic acid (HAA), halogenated acetonitriles (HAN, and etc.), and other substances that has not yet been identified. DBPs of various oxidizing agents are mentioned in the table 1 [2].

| Disinfectant | Disinfectant by-products |
|--------------|-------------------------|
| Chlorine (e.g. gas, sodium hypochlorite, tablets, OSEC) | Trihalomethanes, Haloacetic Acid, Halogenated Acetonitriles, Chloramines, Chlorinated Acetic Acid, Chloral Hydrate, Chloropicrin, Chlorophenols, dichloropropanone, trichloropropanone, bromate, trichloroacetaldehyde, halofurans, bromohydrons |
| Chlorine dioxide | Chlorite, Chlorate and Chloride |
| Chloramines | Dichloramines, Trichloramines, Cyanogen Chloride, Chloral Hydrate, Bromate, Formaldehyde, Aldehydes, Hydrogen Peroxides, Bromoform, |
| Ozone | |

Increase in the concentration of disinfection by-products depends on drinking water quality (ground, surface water resp.), way of the treatment, kind and dose of used oxidant, time of contact of the oxidant with water, concentration of residual oxidant (chlorine), retention time in the distribution system (length of the system), water temperature, pH (formation of THM is more common at the higher pH values), bromides content, concentration nature of organic substances often expressed as total organic carbon (TOC), resp. as UV₂₅₄ : TOC ratio [3].

It is being generally considered that the high concentrations of chloroform and other THMs appear when the pre-chlorination of raw water is used. Concentrations of THM are especially high when the retention time of pre-chlorinated raw water in the distribution system is long. When there is a sufficient concentration of residual chlorine in the distribution system and the retention time is long enough all the organic precursors are changed to form the THMs.

Impact of retention time of the water in the distribution system on increase in disinfection by-products concentration is presented in the work of Chen et al. [4]. Concentration of disinfection by-products was monitored in the central distribution system in New Jersey over one year and in 4...
localities while the water retention time was drafted as 0, 1, 2 and at least 3 days. Water was disinfected with chloramine to contain free residual chlorine at the concentration 0.5 mg/L. By increasing the retention time in the distribution system the concentration of THMs was increasing but the concentration of halogenated acetonitriles, kethons, chlorpicrine and halogenated acetic acid was decreasing. Changes in the concentrations were more rapid over the summer months in comparison with changes in the winter months.

In the England, an impact of retention time of water in the distribution system was monitored for several years while a THMs concentration increase was found and was up to 40-60% which corresponded to increasing of the distance from the drinking water treatment plant. It was determined within this monitoring that the content of free residual chlorine was decreased from 0.4 mg/l below the detection limit while the retention time was set to be 2-4 days. Authors [5] used a limit temperature of the water 10°C to categorize the water samples into winter category (< 10 °C) and summer category (> 10 °C) and they found that the average of summer concentrations of THMs in the model distribution system is higher than the average of THMs winter concentrations.

Changes in disinfection by-products in the model distribution system were monitored within the work [6] while samples were taken from two distribution systems. Dose of chlorine, temperature and incubation time were adapted to the conditions in drinking water treatment plant. Free residual chlorine was utilized completely in three days of water retention in the system. Concentration of THMs and halogenated acetic acid was increasing while the halogenated acetonitriles were increasing at the beginning and decreasing thereafter.

Laboratory studies aimed to measure the changes in THMs concentration in the samples of water depending on the retention time give a proof that the concentration was increased in the supplying system but the results are not consentient [7,8,9]. Different values are for instance caused by the use of various disinfection agents, used sampling method and the nature of sampled water. For example, the THMs concentration in the sample that was taken every 4 hours from the constantly flowing water tap varies within the range 40% [10].

Strategy of removal of the precursors can be divided into three groups:

- selection of proper source;
- physico-chemical removal of precursors (classic coagulation, accelerated coagulation on granulated activated carbon – GAC, membrane separation);
- oxidation (processes which lead to a change of precursors and that increase the biodegrability).

Pursuant to Government Regulation No. 354/2006 Coll. as amended, the limit values of disinfection agents and disinfection by-products in drinking water in Slovakia shows in table 2; these values complies with the recommendations of the World Health Organization (WHO) and Council Directive 98/83/EC [11].

Table 2. Disinfectants and their by-products (according to the GR No. 354/2006 for drinking water).

| Parameter                  | Symbol | Unit | Limit | Parameter                  | Symbol | Unit | Limit |
|----------------------------|--------|------|-------|----------------------------|--------|------|-------|
| chlorine                   | Cl₂    | mg/L | 0.3   | chlorine dioxide           | ClO₂   | mg/L | 0.2   |
| bromodichloromethane       | BDCM   | mg/L | 0.015 | chlorite                   | ClO₂⁻  | mg/L | 0.2   |
| trihalomethanes            | THMs   | mg/L | 0.15  | trichloromethane           | CHCl₃  | mg/L | 0.04  |
| 2,4-dichlorophenol         | DCF    | mg/L | 0.002 | tribromomethane            | CHBr₃  | mg/L | -     |
| 2,4,6-trichlorophenol      | TCP    | mg/L | 0.2   | ozone                      | O₃     | mg/L | 0.05  |

2. Experimental part

The time dependence of the action of the disinfectant on the formation of disinfection by-products for treated water from WTP Hriňová was study. The chemical composition of drinking water before adding a chlorine disinfectant is shown in table 3.
Table 3. The chemical composition of drinking water from WTP Hriňová (21.5.2017).

| Parameter       | Unit | Limit | Hriňová | Parameter       | Unit | Limit | Hriňová |
|-----------------|------|-------|---------|-----------------|------|-------|---------|
| Temperature     | °C   | 8 - 12| 7,8     | COD-Mn          | mg/L | 3.0   | 1,36    |
| pH              |      | 6.5– 8.5 | 7.57   | TOC             | mg/L | 5.0   | 1.2     |
| conductivity    | mS/m | 125   | 12.3    | Humic substances| mg/L | 2.5   | 0.98    |
| alkalinity      | mmol/L | -     | 0.04    | absorbance A^254 |      | 0.08  | 0.042   |
| acidity         | mmol/L | -     | 0.42    | turbidity       | FTU  | 5     | 1       |
| Ca + Mg         | mmol/L | 1.1–5.0 | 0.46    | oxygen          | %    | > 50  | 82.69   |

Sodium hypochlorite and chlorine dioxide as the disinfectant were used. To 500 ml of bottles filled with water from WTP Hriňová was added an exact amount of disinfectant at certain time intervals, i.e., a concentration of 0.3 mg/L so that there is no air in the sample. These samples were analyzed in an accredited laboratory of the Water Research Institute in Bratislava and the following parameters were observed: trihalomethanes and some other chlorinated organic substances, free (residual) chlorine, chlorine dioxide and chlorites.

3. Results and discussion

The results are shown in table 4 and figure 2. The values of the analyzed parameters are very low, mostly below the detection limit of the analytical method. This can be explained by the low value of humic substances and by the fact that laboratory experiments can not replace the actual operation of the group water supply.

Table 4. Experiment results (values in µg/L).

| Compounds                      | Sodium hypochlorite | Chlorine dioxide | Limit |
|--------------------------------|---------------------|------------------|-------|
|                                | 24 hours            | 12 hours         | 24 hours | 12 hours |
| Chloroform                     | < 5.0               | 6.6              | < 5.0   | < 5.0    | < 5.0   | 40    |
| Bromodichloromethane           | < 2.0               | < 2.0            | < 2.0   | < 2.0    | < 2.0   | 15    |
| Dibromochloromethane           | < 13.0              | < 13.0           | < 13.0  | < 13.0   | < 13.0  | -     |
| Bromoform                      | < 12.0              | < 12.0           | < 12.0  | < 12.0   | < 12.0  | -     |
| Trihalomethanes                | < 13.0              | < 13.0           | < 13.0  | < 13.0   | < 13.0  | -     |
| Free chlorine [mg/L]           | < 0.10              | < 0.10           | < 0.10  | < 0.10   | < 0.10  | 0.3   |
| Chlorine dioxide [mg/L]        | -                   | -                | 0.02    | 0.02     | 0.02    | 0.2   |
| Chlorites [mg/L]               | -                   | -                | 0.14    | 0.15     | 0.16    | 0.2   |

Figure 2. Course of the decomposition of ClO₂ and the formation of ClO₂⁻ in water.
4. Conclusion
Most of the disinfection methods produce by-products, which depend mainly on the quality of water, the method of water treatment, the type and amount of oxidant used, the oxidant contact time with water, residence time in the distribution system, but also the temperature and pH of the treated water. Concentration of disinfection by-products are regulated by permitted maximum values in drinking water.

The application of the chlorine dioxide and sodium hypochlorite on the formation of some by-products of disinfection for drinking water from WTP Hriňová was studied. The results confirmed formation of chloroform after 72 hours contact time of sodium hypochlorite with water. When chlorine dioxide (ClO₂) was used, chloride compounds immediately forms in the beginning of water treatment (0.14 to 0.16 mg chloride per 0.3 mg of chlorine dioxide used). ClO₂ was decomposed after 8 hours to form chlorites (0.15 mg/l), concentration of chlorine dioxide are decreased to 0.03 mg/L. An advantage of using chlorine dioxide is that it does not form halogenated by-products (THMs) as it is the case with chlorine or sodium hypochlorite.

The basic prerequisite for introducing arbitrary disinfectant in water treatment is the perfect knowledge of the water quality as well as knowledge of the technological properties - chemical stability in the distribution system. In order to avoid by-products, it is necessary to remove the precursors from the water and also to use a disinfectant to prevent the formation of halogenated by-products (THMs). An important role in choice of disinfectant plays a residual chlorine concentration in the distribution network.

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