

## On the THM Formation during *Inline Electrolysis* – First Systematic Laboratory-Scale Studies

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Formation of THM species was studied using parallel plate cells and water systems typical for drinking water composition. Current density was varied between  $50 \text{ A m}^{-2}$  and  $200 \text{ A m}^{-2}$  at room temperature on mixed oxide electrode material as used under practical conditions. Partially, at higher specific charge flow passed, THM concentration exceeded the limiting value of  $50 \mu\text{g dm}^{-3}$ . However, taking into account dilution effects, necessary in practice for adjusting chlorine concentration, no danger for health seems to exist. AOX concentration was higher than THM concentration by factor 4. A serious problem may result from bromide ion presence even at  $\text{mg dm}^{-3}$  level, enlarging bromine-based THM concentration (especially for bromoform) up to critical values. Also, bromate formation is possible.

### 1. Introduction

Sustainable and reliable water supply belongs to the major challenges of the 21. Century (WHO, 2014, UN, 2009). Strategic research and development programmes and many specific activities including water supply and reuse exist worldwide. Water sanitation is one of the most important issues while handling water streams. Primarily, when water is considered as food and in contact with environment, sanitation is of great concern. Physical, chemical and combined disinfection methods can be found in water treatment. Physical methods are known for having lower or even no potential of by-product formation while chemical methods produce inorganic and organic by-products. Many of them are limited by special rules and regulations. Chlorine is one of the most powerful disinfectant. In addition, only application of so called free active chlorine species (dissolved  $\text{Cl}_2$ , HOCl, OCl<sup>-</sup>) is characterized by the long-term reservoir effect giving a disinfection ability over a certain time at hour-scale. Unfortunately, reactivity of chlorine species with organic matter inside water may lead to remarkable amounts of chlorinated compounds, which can be harmful for health. Hundreds of species have been identified (Krasner et al., 2001, Richardson et al., 2007). According to World Health Organisation (WHO) recommendations (WHO, 2011) national countries regulate maximum concentration of hazardous halogenated hydrocarbons in drinking water. Table 1 exemplarily shows parameters according to the German Drinking Water Ordinance (TrinkwV). Microgram-per-Litre scale is typical in this concentration limitation. Chloroform (trichloromethane) and bromoform (tribromomethane) are well-known representatives of the Trihalomethane (THM) group. Other typical THMs, which are found in chemical chlorination, are bromodichloromethane and dibromochloromethane.

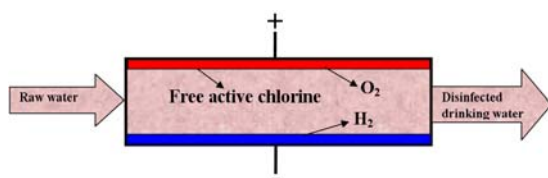


Figure 1: Principle of so-called *Inline Electrolysis*

Besides dosage of chlorine gas, sodium or calcium hypochlorite solutions originating from industrial production, electrochemical generation in the place of use is an additional method of feeding free active chlorine species. If the chloride content of water flowing through an electrochemical cell is the source of chlorine generation, technology is called *Inline Electrolysis* (Figure 1). Technological modifications and

other brand names exist. The method is worldwide applied but is not allowed by law for drinking water treatment in Germany. Whereas studies of inorganic by-products were in the focus within last years no large effort was spent to studying formation of organic by-products. To close this gap results from a research project including water authorities, industry and research groups in Germany are presented here focusing on the study of one electrode material. The aim of the work was to examine in systematic parameter studies THM formation potential in drinking water treated by direct electrolysis at laboratory scale. In this way, more process details were obtained for further sophisticated discussion and decision finding on safe applicability of *Inline Electrolysis*.

## 2. State of knowledge

Since chlorination is widespread, disinfection by-product research is mainly connected with conventional chemical chlorine addition methods. The background of research is the unknown or suspected risk of halogenated hydrocarbons for human health. Based on exposure experiments with living material toxicologists try to develop risk assessment models and suggestions for limiting concentration values (Paustenbach, 2002). Under practical conditions, it is not possible to analyze hundreds of potential hazardous substances. The way out is to classify groups of chemical compounds and to define summary parameters. Latter are known from environmental protection research, for instance as Total Organic Carbon (TOC), Adsorbable Organic Halogens (AOX), Purgable Organic Halogens (POX), and others. In regulations for disinfection THM is a very important parameter (Table 1).

Table 1: Limiting concentrations for selected components in German drinking water

Substance	Maximum concentration, $\mu\text{g dm}^{-3}$
Polycyclic aromatic hydrocarbons	0.10
Epichlorhydrine	0.10
Tetrachlorethene + Trichlorethene	10
1,2-Dichlorethane	3
Trihalomethanes	50
Pesticides and similar by-products	0.10-0.50
Polychlorinated biphenyls	0.5
<b>Bromate</b>	10

It is not in the scope of this paper to give a complete overview over all aspect of THM research. Only issues as follows are briefly noted.

### - Health risk potential

Risk assessment research was conducted for many decades of years. Carcinogenic action and treat to pregnant women, adverse outcome on asthma, respiratory and reproductive function are associated with THMs. Dermatitis from swimming pool use and mutagenic effects are under suspicion when bromine-based THMs occur.

### - Formation and distribution

There are studies worldwide to measure THM distribution in water systems. Except chemical and electrochemical drinking and swimming pool water chlorination, formation of THMs was found during sanitation of process water and effluents. In some countries food products are allowed to be washed with chlorine solutions. Another origin is based on bromination of swimming pool waters what is permitted in a series of countries. Also, chloramination may be a source of THM formation. Predictive models try to describe occurrence. Chemical research is focused on kinetics clarification and analysis.

### - Removal of THMs

Different strategies for reducing THM formation and for lowering THM concentration may be concluded. At first, minimization of halogen compounds is recommended (by better control, well-balanced use, replacement of chlorinating technologies by other methods). Secondly, organic matter and microorganisms as precursors can be previously removed by mechanical means (filtration), and, third, treatment of systems containing THMs is possible (end-of-pipe technology). Adsorption is here the method of choice,

microfiltration another option. Lowering pH reduces THM formation but accelerates Haloacetic Acid (HAA) formation. Chemical/electrochemical THM destruction could be an alternative at small-scale application but it is difficult to control the process. Furthermore, chlorate, perchlorate, and bromate formation is possible.

### 3. Experimental

#### 3.1 Cells

Batch experiments as described here preferably (recirculation rate of  $3.3 \text{ dm}^3 \text{ min}^{-1}$ , volume  $6 \text{ dm}^3$  inside a stirred container, varying concentrations and current density) were thermostatically carried out at temperature between  $20^\circ\text{C}$  and  $30^\circ\text{C}$  using a model cell with parallel plate electrodes ( $0.5 \text{ dm}^2$ , distance 4 mm) based on different mixed oxide electrode material of three cell-manufacturing companies. In this paper, results with respect to 2 electrode materials are presented. Electrode polarity was periodically (15 min) changed. Electrode composition was not open to be published. The electrode material was washed in ultrasonic-supported sodium carbonate solution for 10 minutes, rinsed with deionised water (*Ionpure*) and pre-conditioned at  $20^\circ\text{C}$ ,  $200 \text{ A m}^{-2}$  in tap water for 2 hours in the beginning. Current density was varied between 50 and  $200 \text{ A m}^{-2}$ .

#### 3.2 Chemicals

Model and tap waters were used for electrolysis simulating practical conditions. Chemicals from *Alpha Aesar*, *Merck*, *Fisher Scientific* and *Ultrapure* were of purity higher than 99.5 %. Chloride concentration did not exceed  $250 \text{ mg dm}^{-3}$  ( $7.04 \text{ mmol dm}^{-3}$ ). Regional tap water had in average following composition:  $[\text{F}^-]=0.19 \text{ mg dm}^{-3}$ ,  $[\text{Cl}^-]=36 \text{ mg/l}$ ,  $[\text{Br}^-]=0.04 \text{ mg dm}^{-3}$ ,  $[\text{NO}_3^-]=15 \text{ mg dm}^{-3}$ ,  $[\text{SO}_4^{2-}]=242 \text{ mg dm}^{-3}$ ,  $[\text{Na}^+]=10 \text{ mg dm}^{-3}$ ,  $[\text{Mg}^{2+}]=23 \text{ mg dm}^{-3}$ ,  $[\text{Ca}^{2+}]=148 \text{ mg dm}^{-3}$ ,  $\text{TOC}=2 \text{ mg dm}^{-3}$ .

#### 3.3 Analysis

Free active chlorine, here written as  $\text{Cl}_2$ , was analysed using DPD DIN EN ISO 7393-2 method. AOX analysis was carried out according to German DIN EN ISO 9562 method. AOX analyser *TOX10 (Mitsubishi)* with *Sample Preparator ABIMED Microcoulometer* was used. Samples were measured twice while time-depending 2 probes were taken. One of them was stopped after 0.5 h with  $0.1\text{N Na}_2\text{S}_2\text{O}_3$ , the other after 24 h ( $\text{AOX}_{0.5}$  and  $\text{AOX}_{24}$ ). The method was sensitive between 2 and  $20 \mu\text{g}[\text{Cl}^-] \text{ dm}^{-3}$ .

THMs as chloroform, bromoform, bromodichloromethane and dibromochloromethane were analysed using a gas chromatograph *Auto System XL* with *ECD Detector* and *Headspace Sampler HS40 (Perkin Elmer)*. For calibration, the *THM Cal Mix* standard (*Supelko*) was used. Deionized water (*USF/Seraland* and *Seralpur*) for dilution was previously boiled to reduce remaining TOC content. Measurement was repeated twice. Parallel samples were stopped after 0.5 h ( $\text{THM}_{0.5}$ ) and 24 h ( $\text{THM}_{24}$ ) by adding  $0.1\text{N Na}_2\text{S}_2\text{O}_3$ . Range of analysis was between 0.1 and  $15 \mu\text{g}[\text{THM}] \text{ dm}^{-3}$ . For comparison, chlorine solutions containing calcium hypochlorite ( $0.6 \text{ mg}[\text{Cl}_2] \text{ dm}^{-3}$ ) were added to systems with same composition.

## 4 Results and discussion

### 4.1 Parameter studies

Higher electrolysis and reaction time on the one hand, and cell current on the other hand normally increase chlorine production if the chloride concentration is higher than approximately  $20 \text{ mg dm}^{-3}$ . This expectation could be approved in all corresponding experiments. However, situation is more complicate. Kinetic studies have shown that maxima in THM formation may occur by enlarging chlorine and/or organic matter level of the treated water (Adin et al., 1991).

Figure 2 presents concentration curves for the four typical THM representatives, which were analysed in samples reacting 0.5 and 24 h correspondingly after sample collection. Measured THM formation is tolerable according limitations by law. Values in Table 2 show that the limiting concentration of  $50 \text{ dm}^{-3}$  were not yet reached at free active chlorine concentration as indicated. Under practical conditions, chlorine concentration in points of addition must be normally controlled at  $1.2 \text{ mg dm}^{-3}$  as maximum in not extremely contaminated waters. For remaining free active chlorine concentration at least  $0.1 \text{ mg dm}^{-3}$  is demanded for supply from waterworks. Therefore, concentration ratios  $\text{THM}_5 : 1.2 \text{ mg}[\text{Cl}_2] \text{ dm}^{-3}$  and  $\text{THM}_{24} : 0.1 \text{ mg}[\text{Cl}_2] \text{ dm}^{-3}$  may serve as additional parameters limiting the allowed range of concentrations. Taking into account the allowed maximum THM concentration of  $0.050 \text{ mg dm}^{-3}$  one obtains the interval 0-0.042 and 0-0.5 for the ratios discussed before. Table 2 includes the  $\text{THM}_5 : \text{Cl}_2$  ratio for another experimental series using not tap water but untreated water sampled in *MIDEWA Waterworks Köthen* with lowered initial THM and AOX values, prior to electrolysis. In addition, in Table 2 AOX concentration is given. Surprisingly, AOX concentration is significantly higher compared to THM concentration. AOX concentration is not a

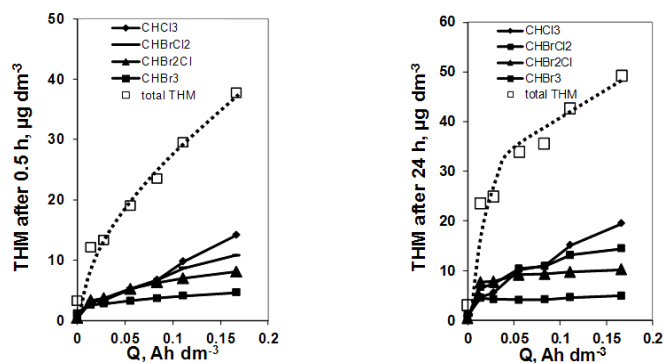


Figure 2: THM formation 0.5 (left) and 24 h (right) after experiments in the discontinuous cell at  $200 \text{ A m}^{-2}$  and at flow rate of  $0.2 \text{ m}^3 \text{ h}^{-1}$  using tap water and electrode material A,  $30^\circ\text{C}$ .

parameter in rules for drinking water but the relatively high concentration measured is probably an indication that AOX should be additionally controlled in drinking water regulation.

Table 2: AOX, THM and  $\text{THM}_{0.5}:\text{Cl}_2$  ratio formed during the experiment at  $200 \text{ A m}^{-2}$  vs. specific charge passed using untreated tap water from regional waterworks ( $[\text{F}]=0.19 \text{ mg dm}^{-3}$ ,  $[\text{Cl}]=40 \text{ mg dm}^{-3}$ ,  $[\text{Br}]=0.04 \text{ mg dm}^{-3}$ ,  $[\text{NO}_3^-]=14 \text{ mg dm}^{-3}$ ,  $[\text{SO}_4^{2-}]=195 \text{ mg dm}^{-3}$ ,  $\text{TOC}=2 \text{ mg dm}^{-3}$ )

time	Q	$\text{Cl}_2$	$\text{AOX}_{0.5}$	$\text{AOX}_{24}$	$\text{THM}_{0.5}$	$\text{THM}_{24}$	$\text{THM}_{0.5}:\text{Cl}_2$
min	$\text{Ah dm}^{-3}$	$\text{mg dm}^{-3}$	$\mu\text{g dm}^{-3}$	$\mu\text{g dm}^{-3}$	$\mu\text{g dm}^{-3}$	$\mu\text{g dm}^{-3}$	
0	0	-	25	30.7	3.2	3.01	-
5	0.014	0.41	36.5	42.4	12.14	23.54	0.029
10	0.028	0.87	41.7	84.4	13.27	24.87	0.015
20	0.056	1.23	46.6	89.4	18.99	33.84	0.015
30	0.083	1.54	61.8	111.2	23.44	35.35	0.015
40	0.111	1.69	74.8	109	29.52	42.53	0.017
60	0.167	1.83	87	168.8	37.66	49.09	0.021

Data shown in Table 3 were obtained by adjusting chloride concentration in regional tap water adding NaCl. Because THM concentration exceeded  $50 \mu\text{g dm}^{-3}$  (Compare also Figure 3 for chloride concentration of  $117 \text{ mg dm}^{-3}$ ), in addition, THM values are shown that would be obtained after diluting the system to  $1.2 \text{ mg}[\text{Cl}_2] \text{ dm}^{-3}$ . They are in agreement with legislation and comparable to those typical for chemical water chlorination (not shown here).

Table 3: Comparison of chlorine and THM formation in the end of discontinuous experiments at  $200 \text{ A m}^{-2}$ ,  $0.2 \text{ m}^3 \text{ h}^{-1}$  using tap water at different chloride concentration, electrode material A,  $30^\circ\text{C}$ .

Chloride	$36 \text{ mg dm}^{-3}$	$117 \text{ mg dm}^{-3}$	$250 \text{ mg dm}^{-3}$
Chlorine, $\text{mg}[\text{Cl}_2] \text{ dm}^{-3}$	1.83	4.12	5.6
$\text{THM}_{24}$ , $\mu\text{g dm}^{-3}$	49.1	69.7	72.4
$\text{THM}_{24}$ after dilution to $1.2 \text{ mg}[\text{Cl}_2] \text{ dm}^{-3}$	32.2	20.3	15.5

Figure 3 reveals that at enlarged chloride concentration (chlorine formation) favourably trichloromethane (chloroform) is formed whereas formation of the other THMs remains unspecific. The effect is known both from chemical chlorination and electrochemical chlorination in earlier studies (Eichelsdorfer and Schöberl, 1989).

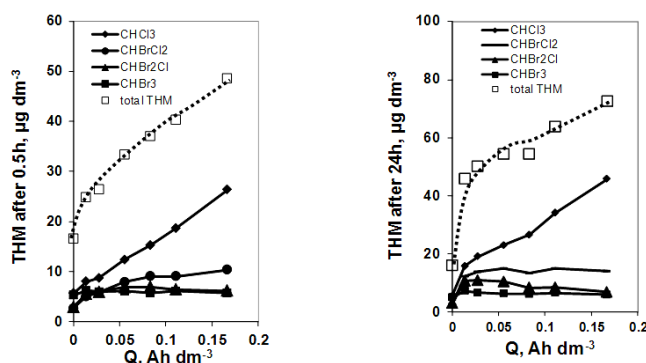


Figure 3: THM formation 0.5 h (left) and 24 h (right) after discontinuous experiments at  $200 \text{ A m}^{-2}$  and at a flow rate of  $0.2 \text{ m}^3 \text{ h}^{-1}$  using tap water at  $117 \text{ mg}[\text{Cl}] \text{ dm}^{-3}$ , and electrode material A,  $30^\circ\text{C}$ .

Table 4 includes corresponding results from experiments using electrode material B that was characterized by higher electrocatalytic properties with respect to chlorine evolution.

Table 4: Comparison of chlorine and THM formation in the end of discontinuous experiments at  $200 \text{ A m}^{-2}$  and  $0.2 \text{ m}^3 \text{ h}^{-1}$  using tap water with different chloride concentration, material B;  $30^\circ\text{C}$ .

Chloride	$36 \text{ mg dm}^{-3}$	$117 \text{ mg dm}^{-3}$	$250 \text{ mg dm}^{-3}$
Chlorine, $\text{mg}[\text{Cl}_2] \text{ dm}^{-3}$	4.6	5.7	9.5
THM <sub>24</sub> , $\mu\text{g dm}^{-3}$	59.9	51.5	61.9
Ratio THM:chlorine	0.013	0.010	0.006
THM <sub>24</sub> after dilution to $1.2 \text{ mg}[\text{Cl}_2] \text{ dm}^{-3}$	15.6	10.8	7.8

The measured THM values, which are comparable to the results in Table 3, are slightly decreased although chlorine formation is higher. Kinetics details are not known, electrochemical processes can be involved and even maximum effects seem possible varying concentration parameters (Adin et al, 1991). Also, when current density is chosen too high DPD method may starts to be disturbed by oxidants formed in addition to active chlorine (Bergmann, 2006). So, deeper discussion is not possible at the moment.

#### 4.2 Influence of bromide ion concentration

Bromide is usually water constituent in regions near oceans. Concentration in lower  $\text{mg dm}^{-3}$  range is possible. When treated with ozone, bromate formation proceeds. In contrast to this, in electrochemical systems bromide ion may easily be oxidized to bromine (active bromine). The latter is reactive with respect to active chlorine (White 1999). Conclusively, lower chlorine-based THMs are expected when drinking water contains chloride and bromide ions at the same time. Resulting from the large variety of obtained results, in Figure 4 THM formation spectrum in bromide containing tap water is shown (electrode material A). To demonstrate the high reactivity, time axis was chosen instead of specific charge passed. In selected experiments NaBr was added to the tap water adjusting bromide concentrations up to  $10 \text{ mg dm}^{-3}$ . As can be seen from Figures 2 and 3 in case of significant absence of bromide, organic matter to THM reaction capacity is not yet reached due to continuing chloroform formation. Figure 4 demonstrates that after relatively short electrolysis time all available organic matter was converted to THMs with the available bromine - excluding the  $10 \text{ mg dm}^{-3}$  curve. Even at the lowest natural Br- concentration level significant high amounts of THMs were formed finally resulting in nearly constant concentration, so that side reactions seem not to play an important role. Bromoform is the most dominant THM component (Figure 4, left diagram). After a few minutes (equivalent to ca.  $0.28 \text{ Ah dm}^{-3}$ , compare Table 2) bromoform concentration was stable for the lower bromide concentrations chosen. Bromoform and chloroform as well, however, may continue reacting over many days in presence of sufficient bromine or chlorine - due to slower kinetics in consecutive reactions.

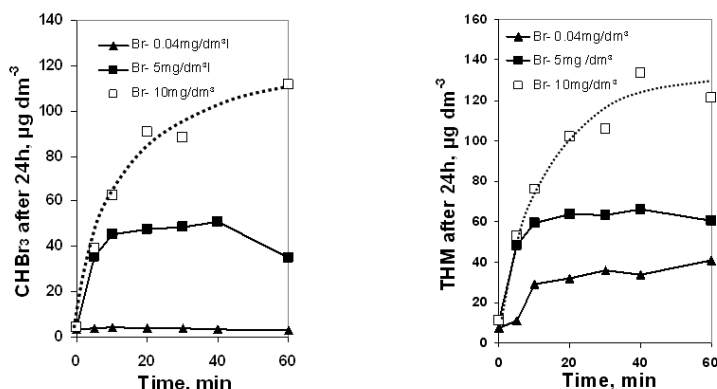


Figure 4: Bromoform formation 0.5 h (left) and THM formation 24 h (right) after experiments in the discontinuous cell at  $200 \text{ A m}^{-2}$  and at flow rate of  $0.2 \text{ m}^3 \text{ h}^{-1}$  using tap water without and with  $\text{Br}^-$  addition, and electrode material A,  $20^\circ\text{C}$ .

## 5. Conclusions

- Regarding total amounts, THM formation during *Inline Electrolysis* is comparable with chemical drinking water chlorination in absence of bromide. Chloroform is the predominant chlorine species.
- In allowed field applications, TOC, chlorine production and THM must be measured and/or controlled.
- AOX formation seems to be a significant problem. Further research has to clarify whether AOX must be included into the list of controlling parameters or not.
- If bromide ions are present, bromine-based THMs are easily formed. Bromide analysis is absolutely necessary if electrolysis is applied.
- Bromoform is the main species amongst all detected bromine-based THM components.

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