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# On-line monitoring of ozonation through estimation of $Ct$ value, bromate and AOC formation with UV/Vis spectrometry

P. S. Ross,<sup>\*ab</sup> A. W. C. van der Helm,<sup>c</sup> J. van den Broeke<sup>d</sup> and L. C. Rietveld<sup>a</sup>

The application of ozone in water treatment serves many purposes, such as disinfection and degradation of organic micro-pollutants. To optimise the applied ozone dosage by on-line control, real-time information on the actual  $Ct$  value, the bromate and assimilable organic carbon concentration (AOC) is necessary. With UV/Vis spectroscopy, algorithms have been developed for the on-line determination of the  $Ct$ -value and the formation of bromate and AOC during ozonation. It was shown that these algorithms allow for the calculation of the optimal ozone dosage and provide a reliable indication of the amount of bromate and AOC formed during ozonation.

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## Introduction

The use of ozonation in water treatment serves a number of purposes, such as degradation of organic micropollutants, oxidation of taste, odour and colour producing compounds and the oxidation of organic matter. The primary use of ozonation in drinking water treatment plants, however, remains disinfection.<sup>1</sup> Ozone has proven to be able to inactivate pathogenic microorganisms that have a high resistance to chlorination and chloramination such as protozoa. However, at the same time, undesired disinfection by-products are formed, in particular bromate, which is potentially carcinogenic to humans. Unlike other organic by-products formed during ozonation, bromate is not biodegradable in the biological filters typically used after ozonation.<sup>1</sup>

Van der Helm *et al.*<sup>2</sup> showed that direct control of ozonation based on water quality objectives (*e.g.* pathogen inactivation) resulted in a large reduction of uncertainty and variation of the process performance, also resulting in less by-product formation and in an improved drinking water quality. A commonly used method to determine the disinfection capacity of ozonation is by calculating the exposure of pathogens to ozone, which is expressed as the  $Ct$  value.<sup>3</sup> The  $Ct$  value is the product of the residual concentration of the disinfectant ( $C$ ) and contact time ( $t$ ). Depending on the type of pathogen (*e.g.*, *Giardia*) to be inactivated, the necessary log removal and the water temperature, different  $Ct$  values are required.<sup>4</sup> In order to be able to calculate

the  $Ct$  value, the ozone concentration in water should be determined together with the hydraulic residence time. Several on-line sensors are available for the determination of ozone in water, for example amperometric ozone electrodes. In addition, the determination by means of UV/Vis spectrometry was also proven to be effective.<sup>5</sup> In a full-scale plant, however, the number of sampling points where the ozone concentration in water can actually be determined is usually limited, making it impractical to calculate  $Ct$  based on the dissolved ozone concentration. Therefore, several researchers have tried to identify indicator parameters to determine the disinfection capacity, such as determination of the bromate concentration, which was proven to be linearly related to the  $Ct$  value.<sup>6–8</sup> Although the linear relationship between the  $Ct$  value and bromate concentration has been shown to give a good indication of the  $Ct$  value, online measurement of bromate is currently not available. An on-line measurement of  $Ct$  value to determine the disinfection capacity would make it possible to come to a direct control of the ozone dosage, minimizing the disinfection by-product formation.

Ozone is an unstable oxidant in water. In general when ozone is added to natural water, it decomposes in two phases: the initial phase and the second phase.<sup>9</sup> The ozone decomposition in the initial phase is fast (duration in the seconds range, values of 20–60 seconds have been reported) and is mainly due to compounds that react very rapidly with ozone such as natural organic matter (NOM).<sup>10,11</sup> During the second phase of ozone decomposition (minutes range), ozone decreases with first order kinetics and disinfection of more resistant microorganisms such as *Cryptosporidium*, *Giardia* and *Bacillus spores* takes place.<sup>9,12</sup> The amount of NOM in the water interferes with the amount of ozone left for disinfection.

NOM in surface water bodies originates from run off, vegetative debris and humic substances. Furthermore, NOM can originate from *in situ* sources such as algae, in which case both

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extracellular and intracellular algal organic matter can contribute.<sup>13</sup> When NOM reacts with ozone, the high molecular weight compounds are broken down into smaller fractions, resulting in an increase in carbon available for uptake by bacteria. This can negatively influence the biological stability of the water, an important criterion in distribution systems where no residual disinfectant is used.<sup>14</sup> It is therefore a delicate balance between achieving sufficient disinfection while trying to minimize the by-product formation.

To be able to quantify the amount of NOM present in water, originally, the total organic carbon (TOC) concentration was measured.<sup>15</sup> When the sample is filtered through a 0.45  $\mu\text{m}$  filter, solids are removed and the dissolved organic carbon (DOC) concentration can be determined. The traditional TOC/DOC analysis consists in oxidation of the organic matter, either by high temperature combustion or oxidation with a chemical oxidiser.<sup>16</sup> Although automated versions of these methods have been developed for use under process conditions, these analysers are complicated instruments which require intensive maintenance. Because they lack the robustness required for application in process control<sup>17</sup> surrogate methods that are simple, rapid and allow monitoring of the operation and performance of a treatment plant in real-time have been studied.<sup>18,19</sup> Many of these surrogate methods are based on the characteristic of NOM to absorb light across a broad range of wavelengths. The absorption spectra, however, are featureless, the absence of distinct peaks being due to the broad and overlapping absorption bands of a multitude of organic compounds that constitute NOM.<sup>20</sup> This is reflected by the numerous correlations found between the NOM in water and the UV absorbance at different wavelengths, varying between 250 and 350 nm.<sup>18,19,21,22</sup> Of the many wavelengths that were identified as an on-line characterization of the organic content of the water, especially UV<sub>254</sub> has been widely adopted. However, collection and interpretation of absorbance data at only UV<sub>254</sub> fails to take advantage of the substantial information that might be embedded in other wavelengths of the UV/Vis spectral data.<sup>23</sup>

Besides the direct use of UV/Vis spectra, the decrease of UV absorbance during a treatment step (differential UV spectroscopy,  $\Delta\text{UV}$ ) was also applied to make sure the relations found, were independent of initial raw water quality parameters such as DOC concentration, pH and NOM properties.<sup>24,25</sup>

The oxidation of NOM promotes the presence of assimilable organic carbon concentration in water.<sup>26</sup> AOC is often used as an indicator parameter with respect to regrowth in (non-chlorinated) distribution systems.<sup>27</sup> Water without residual chlorine is considered biologically stable if the AOC concentration is below 10  $\mu\text{g}$  acetate-C  $\text{L}^{-1}$ , whereas water with residual chlorine is defined biologically stable for AOC concentrations below 50  $\mu\text{g}$  acetate-C  $\text{L}^{-1}$ .<sup>27,28</sup>

Determination of the AOC concentration by the laboratory is a labour intensive procedure, and requires, depending on the method applied, at least 2 days up to 30 days.<sup>27,29,30</sup> A surrogate parameter would be needed if AOC is to be used for on-line assessment and control of biological stability during ozonation. Van der Kooij *et al.*<sup>26</sup> found a linear relationship between the increase in AOC and the decrease in UV<sub>254</sub> absorbance of water

after ozonation. Van den Broeke *et al.*<sup>5</sup> described a correlation between the change in AOC concentration and the change in UV/Vis spectrum during ozonation, pellet softening and biological granular activated carbon (BAC) filtration. This algorithm was developed based on a highly inhomogeneous dataset, which described AOC formation during ozonation, AOC biodegradation during pellet softening as well as biodegradation and adsorption during BGAC filtration. The algorithm showed a good correlation for the AOC formation during ozonation, however this only contained a limited amount of data points determined for only low water temperatures.

In this paper the development of algorithms for the on-line determination of the  $Ct$  value and the bromate and AOC formation using differential UV/Vis spectrometry is described. The dataset used to develop the algorithm contained a wide variety in applied ozone concentrations and seasonal changes. Real-time information on the actual  $Ct$  value helps to optimise the applied ozone dosage, ensuring sufficient disinfection, against minimal ozone dosages, limiting the formation of disinfection by-products. Real-time information about the amount of AOC that is formed during ozonation helps in optimising subsequent treatment steps that are affected by the AOC concentration, such as BAC filtration. The maximum bromate concentration is regulated by law since it is a possible carcinogen. Therefore, bromate formation might limit the allowable ozone dosage, since almost no bromate is removed in subsequent treatment steps.

## Materials and methods

### Origin of samples

Water samples were collected from an ozonation pilot plant at the production location Weesperkarspel of Waternet, the water cycle company of Amsterdam and surrounding areas. Weesperkarspel raw water originates from seepage water from the Bethune polder, a peat-rich area that gives the water a high NOM concentration. This water is pre-treated by coagulation and sedimentation, followed by approximately 100 days retention in a reservoir. Subsequently, the water is filtered over rapid sand filters and transported to the Weesperkarspel treatment plant, which is composed of ozonation, pellet softening, BAC filtration and slow sand filtration.

The pilot plant is a physical model of the full-scale plant located at Weesperkarspel. The flow through the pilot plant ranged from 4 to 15  $\text{m}^3 \text{h}^{-1}$ . The ozone bubble columns were operated in counter-current mode and ozone was dosed in 2 subsequent bubble columns (diameter 0.388 m); the concentration was equally divided over both columns. The height of the columns was 4.2 and 3.6 m, respectively. After the bubble columns the water flowed through 4 contact chambers (diameter 1 m, and height 2.6 m) to ensure enough retention time was achieved and ensuring no residual ozone is present at the outlet of the contact chambers. The hydraulic retention times varied between 25 and 111 minutes (depending on the applied flow). The DOC concentration varied between 5.7 and 6.5  $\text{mg-C L}^{-1}$  and the applied ozone dosages between 1.5 and 4.0  $\text{mg O}_3 \text{L}^{-1}$ . The applied ozone dosages per amount DOC varied from 0.23 to

0.68 (mg<sub>O<sub>3</sub></sub> L<sup>-1</sup>)/(mg-C L<sup>-1</sup>), depending on the conducted experiment. The off-gas was very low compared to the applied ozone dose (about 0.4%, except for the high ozone dosages of 4 mg L<sup>-1</sup> an off-gas concentration of around 5.5% was measured). In the paper the results are related to Ct value and not to ozone dose, therefore the transferred dosage is less important in this case and the applied dosage is given. Four series of experiments (total of 30 different settings) were performed over a 4 year period, covering the seasonal variability in raw water NOM composition and temperature (between 2 and 22 °C). The water quality parameters of the water, the ozone dosages and the temperature are presented in Table 1.

The ozone dosage is determined by the ozone in gas flow, ozone in gas concentration and the water flow, according eqn (1):

$$O_{3,\text{dosage}} = \frac{c_{g_{O_3}} Q_{g_{O_3}}}{Q_w} \quad (1)$$

where  $O_{3,\text{dosage}}$  is the ozone dosage (mg<sub>O<sub>3</sub></sub> L<sup>-1</sup>),  $c_{g_{O_3}}$  is the ozone in gas concentration (g<sub>O<sub>3</sub></sub> Nm<sup>-3</sup>),  $Q_{g_{O_3}}$  is the ozone in gas flow (Nm<sup>3</sup> h<sup>-1</sup>) and  $Q_w$  is the water flow (m<sup>3</sup> h<sup>-1</sup>). Nm<sup>3</sup> is used as a measure for the gas volume under standard conditions (gas pressure of 101 325 Pa and a gas temperature of 273.15 K).

## Analysis

Grab samples were collected from sampling points at the influent and effluent of the ozonation reactor. The grab samples were analysed by a laboratory for AOC (duplicate measurement) by applying the simultaneous incubation of strains P17 and NOX,<sup>31</sup> with a reporting limit of 1 µg-C L<sup>-1</sup> and allowed standard deviation (SD) of 50%. DOC was measured according to the standard methods procedure, with a reporting limit of 0.1 mg-C L<sup>-1</sup>, using a Shimadzu TOC5000a. UV<sub>254</sub>, expressed as the absorbance per meter of cell length, and bromate was determined using standard procedures described in standard methods.<sup>32</sup> Ozone concentration in water was determined using the indigo method described by Bader and Hoigne.<sup>33</sup> On-line UV/Vis absorption measurements were performed using two spectrometers of the type spectro:lyser™, from s:can Messtechnik GmbH, which were equipped with a 35 mm measuring cell. These instruments measure absorbance of ultraviolet and visible light from 200 to 750 nm, with a resolution of 2.5 nm, resulting in a total of 221 wavelengths measured between 200 and 750 nm.<sup>34</sup> One spectrometer was located at the influent of the ozonation reactor and one spectrometer was located at the effluent of the contact chambers, with residence times long enough to ensure no residual ozone was left at this point. The

**Table 1** Water quality parameters influent, applied ozone dosages, temperature and formed AOC, bromate concentration and Ct value (n.d. = not determined)

Experiment	Ozone dosages mg <sub>O<sub>3</sub></sub> L <sup>-1</sup>	DOC mg-C L <sup>-1</sup>	UV <sub>254</sub> Abs/m	Temp °C	Ct value mg <sub>O<sub>3</sub></sub> L <sup>-1</sup> min <sup>-1</sup>	AOC µg-C L <sup>-1</sup>	Bromate µg L <sup>-1</sup>
1	2.4	5.9	14.6	2.3	n.d.	200	n.d.
2	2.4	6.5	14.6	3.2	n.d.	179	n.d.
3	2.4	6	15.0	3.3	n.d.	178	n.d.
4	2.4	5.8	14.8	4.2	n.d.	169	n.d.
5	2.4	5.8	14.8	4.7	n.d.	126	n.d.
6	2.4	6	14.7	6.4	n.d.	35	n.d.
7	4.0	6.4	15.1	7.1	9.58	203	5.59
8	2.4	5.7	14.4	7.8	n.d.	65	n.d.
9	2.5	5.9	15.4	8.1	1.64	91	1.33
10	2.0	6.4	15.3	8.1	0.98	n.d.	0.65
11	2.5	6.3	14.7	8.7	1.9	n.d.	1.15
12	2.0	5.9	14.8	9.1	0.72	n.d.	0.49
13	1.5	6.6	15.0	9.6	0.17	n.d.	0.31
14	2.5	6.5	14.9	9.6	2.31	n.d.	1.35
15	0.0	6.3	14.9	9.9	n.d.	0	n.d.
16	3.0	6.5	15.1	9.9	3.87	45	2.54
17	1.5	6.5	14.6	11.6	0.21	66	0.11
18	3.5	6.0	14.8	11.7	5.51	n.d.	3.88
19	2.5	5.9	14.4	11.7	1.41	n.d.	1.05
20	3.5	6.1	14.7	12.4	5.35	85	4.6
21	3.5	5.9	14.6	13.1	5.51	85	3.92
22	1.5	6.2	13.1	19.1	0.57	56	0.48
23	2.5	6.1	13.4	19.2	2.43	65	2.63
24	4.0	5.9	13.1	19.2	8.29	76	9.53
25	1.5	6.4	13.3	19.8	0.59	55	0.61
26	4.0	6.4	13.0	20.0	8.35	120	9.08
27	2.5	6.4	13.0	20.0	2.45	110	2.38
28	4.0	5.9	14.5	21.0	n.d.	154	n.d.
29	2.5	6.2	14.2	21.7	n.d.	89	n.d.
30	4.0	6.2	14.3	22.2	n.d.	102	n.d.

spectrometers were cleaned periodically once every 3 months as a precaution, however, no fouling was detected during cleaning.

### Ct value determination

When determining the *Ct* value for a full scale installation, normally a conservative approach is taken and typically the  $T_{10}$  is used for defining the contact time. The reason for this approach has to do with the fact that not a lot of sampling points are available to determine the concentration and full scale installation have a tendency to not behave ideally. The  $T_{10}$  value represents the time required for 10% of a tracer to travel through the reactor, so 90% is still left within the reactor.<sup>1,35</sup> In this pilot plant an extensive number of sampling points are located between the outflow of the contact chamber and the dosage points showing a representative concentration gradient. In total 33 sampling points are available in the pilot plant, 5 for each column with a distance between the sampling points varying between 0.5 and 1 m. The residence time between the sampling points was determined based on tracer tests carried out for the different flow settings described above.

The *Ct* value was calculated based on the concentration of dissolved ozone and the contact time, according to eqn (2):<sup>36</sup>

$$Ct = \sum_{i=0}^{n_{sp}} c_{O_3,i}(t_i/60 - t_{i-1}/60) \quad (2)$$

where *Ct* is the ozone exposure ((mg<sub>O<sub>3</sub></sub> L<sup>-1</sup>) × min<sup>-1</sup>),  $n_{sp}$  is the number of sampling points (–),  $c_{O_3}$  is the ozone concentration in water (mg<sub>O<sub>3</sub></sub> L<sup>-1</sup>) and *t* is the time (s).

### Calibration procedure spectral algorithms

Based on the principles for determining concentration-spectra relationships described by Otto<sup>37</sup> and Langergraber *et al.*<sup>38</sup> developed a multivariate calibration procedure using partial least squares (PLS) regression models evaluating the entire spectra. Langergraber *et al.*<sup>38</sup> used normalized spectra and reference measurements. Instead of using normalized raw spectra, Karlsson *et al.*<sup>39</sup> and Thomas *et al.*<sup>40</sup> suggested using the derivative spectra, either second or first derivative, respectively. The derivative spectrum gives information about the slope of the spectrum and shows the shoulders and inflection points, therefore enhancing the visibility of the fine structure. The derivative gives the relative changes between absorbance values obtained at adjacent wavelengths and it can help in removing the undesired contribution of turbid media.<sup>40</sup> When trying to link the change in concentration during a treatment step, differential spectra can be used as described by van den Broeke *et al.*<sup>5</sup> In this study Stepwise regression in Matlab®<sup>41</sup> was used to determine the wavelengths that have a statistically significant contribution in the regression. This is a systematic method for adding and removing terms from a multi-linear model. The approach is similar to partial least squares (PLS) regression.<sup>41</sup> Subsequently multiple linear regression (MLR) analysis was carried out to determine the combination of model terms that best expresses the response (target parameter, *e.g.*, change in AOC concentration and *Ct* value).<sup>42</sup> Since this study focused on the change in concentration during ozonation, the differential spectra were

used. The changes in UV absorbance were obtained by subtraction of the effluent spectra from the concurrent influent spectra. The spectra were compensated for turbidity by using the ana:pro Version 5.9c software from s::can Messtechnik GmbH. Because of the precision of the instruments, only spectra with a differential value of more than 0.2 Abs/m were considered.<sup>5</sup> For this type of water, the 35 mm probe was out of range between 200 and 230 nm. These wavelengths were not taken into consideration when developing the algorithms. For each algorithm it was evaluated whether differential spectra, normalized differential spectra or the first derivative of the differential spectra gave the best results. Subsequently the algorithm giving the best results is given as the proposed model in the results section.

The change in AOC concentration was calculated from the AOC concentrations obtained from the laboratory analyses. Since the AOC concentration was determined in duplicate, the mean values were used during the development of the algorithm. The combined SD varied between 4 and 25%, indicated by means of the error bars in Fig. 5. The *Ct* values were determined based on eqn (2) using a total of 33 ozone in water concentrations and corresponding residence times. The bromate concentration was determined by laboratory analyses.

## Results and discussion

### Ozone concentration, Ct value and bromate formation

At the ozonation pilot plant a total of 33 sampling points were available for sampling and determination of the dissolved ozone concentration. In Fig. 1, the dissolved ozone concentration across the plant is displayed for 3 settings from Table 1 (a low ozone in water dosage 1.5 mg<sub>O<sub>3</sub></sub> L<sup>-1</sup> (experiment 12), average dosage 2.5 mg<sub>O<sub>3</sub></sub> L<sup>-1</sup> (experiment 9) and the highest dosage of 4.0 mg<sub>O<sub>3</sub></sub> L<sup>-1</sup> (experiment 22) for a DOC concentration of 5.9 mg-C L<sup>-1</sup>).

In Fig. 1, the ozone dosage points can be distinguished by the increase in the dissolved ozone concentration. Since the flow through the contact columns was different for some of the experiments the contact time also differed, therefore the peaks for the 3 runs are displayed at different times. The calculated *Ct* values, together with the bromate and AOC concentrations measured during the experiments are listed in Table 1. In this table the experimental conditions are summarized as well.

Since the formation of bromate is an undesired by-product of ozonation, in Fig. 2 the bromate concentrations measured at the outflow of the contact chambers for the different experiments listed in Table 1 is plotted against the total *Ct* values.

It can be observed that the bromate formed during ozonation is linearly related with *Ct*. Besides the bromate formation in summer (temperature between 19 and 22 °C) is higher than in winter (at lower temperatures between 3 and 13 °C), which is in accordance with previous studies.<sup>43,44</sup> The observed differences in bromate concentration stems from the changing water matrix and seasonal effects (*e.g.*, temperature), since the bromide concentration in the raw water did not fluctuate. Based on the *Ct* values required for the inactivation of *Giardia* for different temperatures published by the USEPA,<sup>4</sup> roughly half of the *Ct* value is required in summer to achieve same log-removals as in winter. Although the bromate formation in

summer is higher than in winter (slope is almost 2 times as steep), the negative effect on bromate formation is counteracted since only half of the  $Ct$  value is required in summer to achieve similar log-removals.

### Algorithm for on-line estimation of $Ct$ value achieved during ozonation

A total of 19  $Ct$  values and differential absorbance spectra were available to develop an algorithm for the on-line estimation of  $Ct$  value during ozonation. The strongest relationship was found with the first derivative of the differential spectrum and  $Ct$  values. The change in slope at a wavelength of 265 nm ( $\Delta UV_{265}$ ) was found to be the only wavelength demonstrating a statistically significant relation with the  $Ct$  values ( $R^2 = 0.88$ ) (eqn (3) and Fig. 3):

$$Ct_{est} = -2.42 - 193.1\Delta UV'_{265} \quad (3)$$

with  $\Delta UV'$  representing the first derivative of the differential spectrum. No additional wavelengths were required to correct for the influence of other substances present in the water.

The dataset displayed in Fig. 3 contains 5  $Ct$  values determined in summer and 11  $Ct$  values determined in winter. As can be seen the  $Ct$  results cover a wide range of values, both in summer and winter, highlighting the strength of the dataset used for the development of the algorithm. Ozone preferentially oxidizes electron rich moieties such as aromatic carbon-carbon double bonds and aromatic alcohols.<sup>45</sup>

Westerhoff *et al.*<sup>10</sup> indicated that a good correlation was found between reactivity of ozone and the  $UV_{254}$  and  $UV_{280}$  nm. Double bonds and aromatic alcohols can be typically measured between 254 and 280 nm.<sup>19,22</sup> The found differential wavelength indicates that a change in slope occurs at  $UV_{265}$  nm which lies within the range of wavelengths that are known to have a strong correlation with aromatic bonds being susceptible to ozone and therefore is likely to react.

Although a good correlation is found, the algorithm sometimes overestimates the  $Ct$  value. If immediate control would be applied based on these overestimated values, the ozone dosage would be lowered, resulting in a lower  $Ct$  value and thus lower disinfection capacity than is actually required. This could affect the log-removal and thus the disinfection capacity of the system. Therefore, it is important to realize that based on this algorithm it is possible to get a good impression of the  $Ct$  value achieved during ozonation, but that for operational purposes it is important to check the predicted  $Ct$  value on a regular basis. Verification can be done by measuring the bromate formation and relating this to the  $Ct$  value using the linear relation observed, and by taking large volume samples which should be tested on the presence of indicator organisms.

### Algorithm for on-line estimation of bromate formation during ozonation

A total of 19 bromate concentrations and differential absorbance spectra were available to develop an algorithm for the on-line estimation of bromate formation during ozonation. The

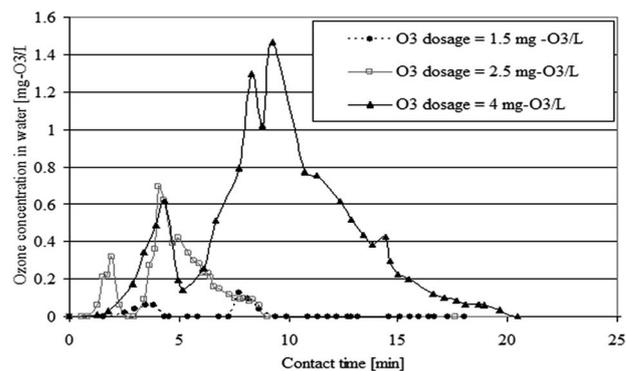


Fig. 1 Dissolved ozone concentration measured at 33 sampling points for three different dosages.

strongest correlation was found between the normalized differential spectra (differential spectrum divided by the influent spectra) and the bromate concentrations. In total 2 wavelengths turned out to show a significant relationship with bromate concentration ( $R^2 = 0.92$ ) (eqn (4) and Fig. 4):

$$BrO_{3,est} = 13.21 + 273.96\Delta UV_{250,norm} - 236.15\Delta UV_{270,norm} \quad (4)$$

Peldszus *et al.*<sup>46</sup> reported that potassium bromate absorbs light well at low wavelengths, with the highest absorbance at 190 nm gradually decreasing to zero at 270 nm. The wavelengths found were at 250 and 270 nm. The first wavelength lies within the absorbance range to what Peldszus *et al.* reported. The other wavelength lies at the boundary and is likely to correct for other compounds present in the water. The found relationship can help to directly control the bromate formation. The concentration ranges the algorithm was calibrated for varied between 0 and 10  $\mu g BrO_3 L^{-1}$ , temperatures ranged between 3 and 22 °C and  $Ct$  values 0.2 and 10  $mg L^{-1} min^{-1}$ . The average bromide levels were 92  $\mu g L^{-1}$  with a standard deviation of 3  $\mu g L^{-1}$ . These ranges represent a wide spectrum applicable for drinking water applications.

### Algorithm for on-line estimation AOC formation during ozonation

Besides the on-line determination of the disinfection capacity, the formation of AOC is also important, since the AOC

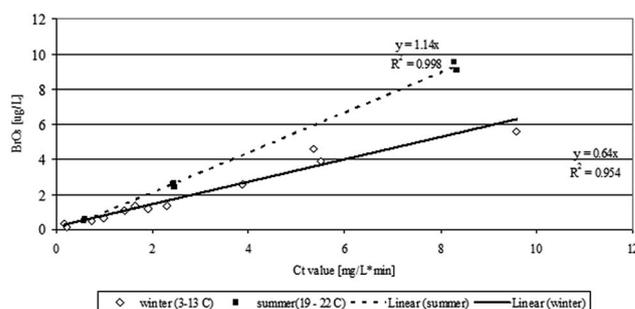


Fig. 2 Bromate concentration versus the  $Ct$  value distinguished between summer and winter.

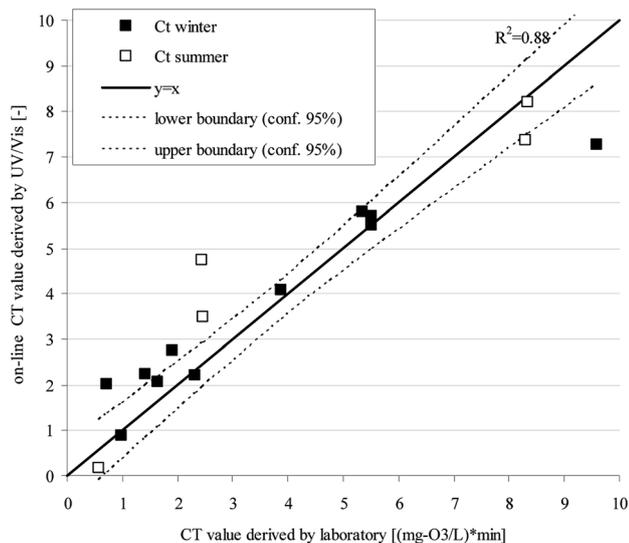


Fig. 3 Correlation between the Ct value during ozonation determined from the dissolved ozone concentration measured by the laboratory (X-axis) and from the change in UV absorbance (Y-axis).

concentration affects the biological stability of the water produced. In literature it was shown that during ozonation a correlation exists between the change in  $UV_{254}$  and the AOC formation.<sup>26</sup> Fig. 5 illustrates the change in  $UV_{254}$  against the amount of AOC formed as observed during this study.

It can be seen that for this research the correlation between the AOC formation and  $\Delta UV_{254}$  is not very strong. Therefore it was investigated whether it was possible to find a stronger correlation based on the use of multiple wavelengths. A total of 19 data points were available to calibrate the algorithm on. The strongest calibration was found by using the derivatives of the differential spectrum. The calibration resulted in an algorithm developed based on a total of 4 wavelengths and a  $R^2 = 0.74$  (Fig. 6 and eqn (5)):

$$\Delta AOC_{est} = 37.5677 + 7467.54\Delta UV'_{320} - 17\,533.3\Delta UV'_{347.5} + 7558.3\Delta UV'_{427.5} + 16\,028.2\Delta UV'_{435} \quad (5)$$

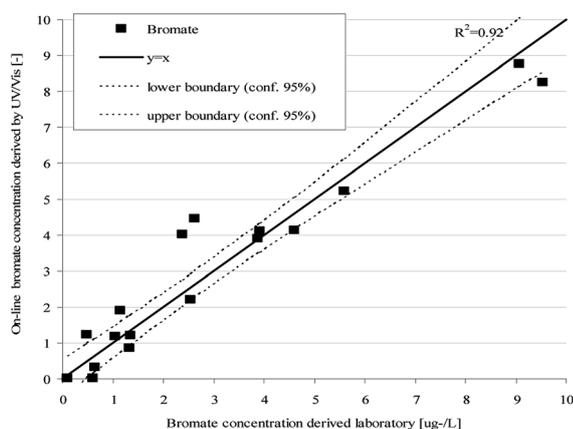


Fig. 4 Correlation between the bromate formation measured by the laboratory (X-axis) and from the change in UV absorbance (Y-axis).

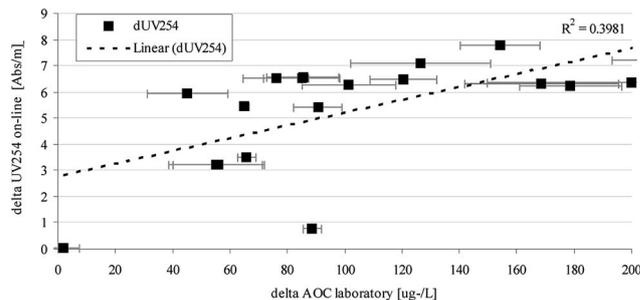


Fig. 5 Correlation between AOC formation during ozonation and the change in  $UV_{254}$ .

It can be observed that the found correlation using multiple wavelengths shows a much better correlation with the amount of AOC formed during ozonation than only using the single wavelength at 254 nm. The algorithm was developed based on a wide variation in AOC concentrations formed as a result of different applied ozone dosages, varying temperatures and raw water compositions as can be seen based on the  $UV_{254}$  values (Table 1). The wavelengths used for the algorithm range between 320 and 435 nm. The first two wavelengths  $UV_{320}$  and  $UV_{347.5}$  are located within the area defined as the area organic matter is typically detected.<sup>34</sup> The other two wavelengths are in the area colour and turbidity are normally detected. These wavelengths might well be related to other processes going on, but did turn out to be statistically significant contributing to the amount of AOC formed. This algorithm makes it possible to estimate on-line the amount of AOC formed during ozonation.

The AOC concentrations were measured in duplicate, indicated by the error bars. It can be seen that for some sample quite a wide spread in AOC concentration was measured

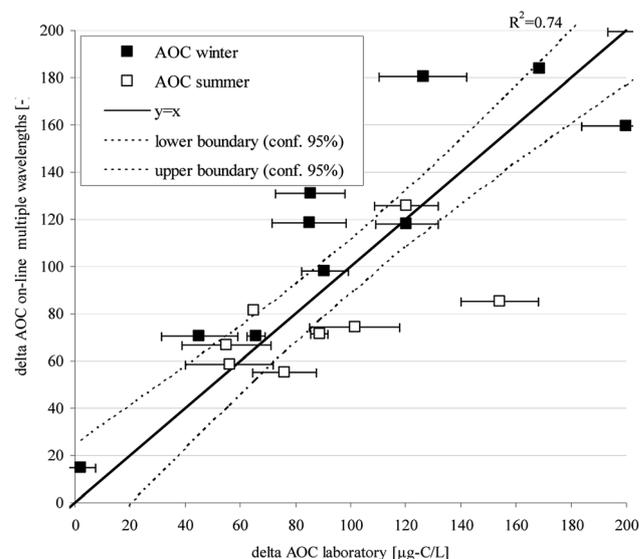


Fig. 6 Correlation between AOC formations during ozonation measured by the laboratory and predicted AOC formations based on change in UV/Vis absorbance using eqn (5).

between the duplicate samples. For the algorithm development the average values were taken. The variations in laboratory results affect the strength of the found correlation.

## Conclusions

The objective of this study was the development of algorithms that make on-line monitoring of the ozonation process in water treatment possible through a real-time estimation of AOC formation and *Ct* value based on UV/Vis spectra collected in process. The results show that it was possible to use differential UV/Vis spectroscopy to produce surrogate parameters for the on-line estimation of AOC formation and the *Ct* value achieved during ozonation. Based on these results it will be possible to optimise the ozone dosage at the Weesperkarspel plant and give a direct indication of the amount of AOC formed during ozonation by only using UV/Vis spectrometers. This information enables operators to better control the subsequent treatment steps such as BAC filtration. On-line monitoring of the *Ct* values during ozonation gives the operators certainty on the performance of an important disinfection step. Besides, monitoring of the *Ct* value helps in optimizing the ozone dose, leading to less overdosing of ozone, and subsequently less harmful by-products formed. Direct control of the harmful by-products, such as bromate, might result in limiting the applicable ozone dosage to ensure the bromate formation does not exceed the allowed threshold values. Nevertheless, the conventional ways of controlling the ozone dose through the measurement of bromate and determination of indicator organisms in large volume samples should be continued to crosscheck the sensitivity of the developed algorithms.

The algorithms were developed for a certain type of water relatively high in NOM content with DOC values fluctuating between 5.9 and 6.5 mg-C L<sup>-1</sup> and undergoing seasonal changes, such as algal blooms and temperature fluctuations. When wanting to apply this algorithm to different water types it must be tested if the coefficients match the local situation or if a new calibration needs to be developed. Nevertheless this study shows that it is possible to develop an algorithm for the on-line estimation of *Ct* value, bromate and AOC formation based on UV/Vis spectra.

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