

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

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Abstract

The application of ozone in water treatment serves many purposes, such as disinfection, degradation of organic micro-pollutants and oxidation of taste, odour and colour producing compounds. A commonly used method to determine the disinfection capacity of ozonation is calculating the exposure of pathogens to ozone, this capacity is expressed as the Ct value, a product of the residual concentration of the disinfectant (C) and contact time (t). Ozone reacts with natural organic matter (NOM), breaking high molecular weight compounds down into smaller fractions, resulting in an increase in carbon readily available for bacterial uptake. To estimate the regrowth potential of micro-organisms in (non-chlorinated) distribution systems, the assimilable organic carbon (AOC) concentration can be used as an indicator parameter. To optimise the applied ozone dosage by on-line control, real-time information on the actual Ct value and the AOC formation is necessary. Using in process UV/Vis spectroscopy, algorithms have been developed for the on-line determination of the Ct-value and the formation of AOC formation 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 AOC formed.

Keywords: AOC, biological stability, Ct, differential UV/Vis spectrometry, disinfection, drinking water, ozonation

Introduction

The use of ozonation in water treatment serves a number of purposes, such as degradation of organic micro-pollutants, oxidation of taste, odour and colour producing compounds and the oxidation of organic matter. The primary use of ozonation in water treatment plants, however, remains disinfection (2003).

A commonly used method to determine the disinfection capacity of ozonation is calculating the exposure of pathogens to ozone, this capacity is expressed as the Ct value (WHO 2008). 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. In the U.S. EPA guidelines (USEPA 1989) an overview of required Ct values for ozonation for achieving sufficient log inactivation per pathogen is given. Based on this overview the minimal required Ct value can be determined. In order to be able to calculate the Ct value, the ozone concentration in water should be determined together with the hydraulic residence time. Bader and Hoigne (1982) developed the indigo method for the determination of ozone concentration in water. Since then several researchers have developed on-line methods for the estimation of ozone concentration in air (Molina, *et al.* 1986) and in water (van den Broeke, *et al.* 2008) by means of UV/Vis spectrometry. 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. The second phase of ozone decomposition (minutes range) follows an empirical first-order rate law, while the initial phase of ozone decomposition ($t < \sim 20$ seconds) follows higher-order kinetics (Buffle, *et al.* 2006a, Buffle, *et al.* 2006b, van der Helm, *et al.* 2008). The ozone decomposition in the initial phase is mainly due to reactions with natural organic matter (NOM).

Organic matter present in surface water bodies originates from run off, vegetative debris and humic substances. Besides, the organic matter can originate from in situ sources such as algae, consisting of extracellular and intracellular algal organic matter (Amy 2008). This natural organic matter (NOM) gives the water a yellowish to brownish colour (Zepp, *et al.* 1981). The NOM in water reacts with ozone and the high molecular weight compounds are broken down into smaller fractions, resulting in an increase in readily available carbon for bacterial growth. This can negatively influence the biological stability of the water, an important criterion in distribution systems where no residual disinfectant is used (van der Kooij, *et al.* 1999). The nature and concentration of the NOM determine which reaction products are formed (Von Gunten 2003).

To be able to quantify the amount of NOM present in water, originally, the total organic carbon (TOC) concentration was measured, developed by van Hall *et al.* (1963). If the water sample is pre-treated by filtration over $0.45\ \mu\text{m}$, the dissolved organic carbon (DOC) concentration is determined. Since the development of the TOC/DOC measurement, researchers have studied surrogate methods that are simple, rapid and can be applied on-line to allow for monitoring of the operation and performance of a treatment plant (Dobbs, *et al.* 1972, Edzwald, *et al.* 1985). Many of these surrogate methods are based on the characteristic that NOM absorbs light across a broad range of wavelengths. The absorption spectra, however, are characterless, the absence of distinct peaks being due to the broad and overlapping absorption bands of a multitude of organic compounds that constitute NOM (Liu, *et al.* 2010). This is also reflected in the numerous correlations found between the organic matter in the water and UV absorbance at different wavelengths. Foster and Morris (1971) described the noticeable influence of variations in the dissolved organic content on the UV absorption spectrum between the wavelengths of 250 - 350 nanometres (nm) in sea water. Maes (1982) observed a correlation between the TOC concentration and the UV absorbance at a wavelength of 260 nm (UV260) for a wide range of samples and selected UV260 to rule out the interference of inorganic substances that might be present in water. Chin *et al.* (1994) found a good

correlation between the absorption at a wavelength of 280 nm, the molecular weight and the aromaticity of aquatic humic substances, while Edzwald et al. (1985) and Dobbs et al. (1972) described a relationship between the UV254 and TOC concentration. Later, Edzwald and Tobiasson (1999) developed the specific UV absorbance (SUVA) as an operational indicator for the nature of NOM, where the SUVA is defined as the UV254 per unit dissolved organic carbon (DOC) in mg/L.

UV254 has been widely adopted by researchers as an on-line characterization of the organic content of the water. However, collection and interpretation of absorbance data at only a single wavelength fails to take advantage of the substantial information that is embedded in the full UV spectral data (Korshin, *et al.* 1997a).

Korshin et al. (1997b) found a distinct relation between the formation of trihalometanes (THMs) and haloacetic acids (HAAs), well known disinfection by-products (DBPs) during chlorination and the change in absorbance at a wavelength of 272 nm (Δ UV272). The Δ UV272 parameter has successfully been used as an indicator for the formation of disinfection by-product species as well as chlorine decay in water of varying types and temperatures by Roccaro et al. (2008).

With respect to regrowth in (non-chlorinated) distribution systems, the assimilable organic carbon (AOC) concentration is often used as an indicator parameter (van der Kooij 1992). Water without residual chlorine is considered biologically stable if the AOC concentration is below 10 μ g Acetate-C/L, whereas water with residual chlorine is defined biologically stable for AOC concentrations below 50 μ g Acetate-C/L (Escobar, *et al.* 2001, van der Kooij 1992). Determination of the AOC concentration is a labour intensive procedure, requiring up to 15-30 days. 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. (1989) found a linear relationship between the increase in AOC and the decrease in UV254 absorbance of water after ozonation. Van den Broeke et al. (2008) found a correlation between the change in absorbance, using multiple wavelengths, and the change in AOC concentration in water during the treatment processes ozonation, pellet softening and biological granular activated carbon (BGAC) filtration. This algorithm was developed based on a wide spread in AOC data, AOC formation during ozonation, biodegradation of AOC during pellet softening and biodegradation and adsorption during BGAC filtration were all combined for the development of the algorithm.

Besides the temperature and the pH, the origin of NOM and concentration in the water, determine the required ozone dose to reach the desired Ct value and subsequently the amount of AOC formed (Von Gunten, 2003). To be able to come to an effective on-line control of the ozone dose, on-line information on the Ct value and the AOC formation is necessary. In this research algorithms were developed for the on-line monitoring of ozonation through estimation of Ct-value and AOC formation during ozonation by using UV/Vis spectrometers.

Material and Methods

Origin of samples

Samples were taken at an ozonation pilot plant located 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. The water is pre-treated by coagulation and sedimentation, followed by about 100 days retention in a reservoir. Subsequently it is filtered over rapid sand filters. The pre-treated water is transported to the Weesperkarspel treatment plant, which comprises of ozonation, pellet softening, biological granular activated carbon filtration and slow sand filtration.

The pilot plant is a physical model of the full-scale plant. The flow through the pilot plant ranged from 4 to 15 m³/h. The ozone bubble columns were operated in counter-current mode. The ozone was dosed in 2 subsequent bubble columns; the concentration was equally divided over both columns. The DOC concentration varied between 5.6 – 6.6 mg-C/L and the applied ozone dosages between 1.0 – 4.0 mg O₃/L. The ozone dosages per DOC varied from 0.08 to 1.10 (mg-O₃/L)/(mg-C/L), depending on the conducted experiment. A total of 4 series of experiments were conducted during a period of 4 years in different seasons, taking into account seasonal effects such as fluctuating water temperatures (between 2-22 °C) and different NOM compositions.

Analysis

Grab samples were collected from sampling points at the influent and effluent of the ozonation reactor. The grab samples were analysed for; AOC (duplicate measurement) applying the simultaneous incubation of strains P17 and NOX (van der Kooij et al., 1982); DOC, measured according to the standard methods procedure using a Shimadzu TOC5000a; UV254 expressed as the absorbance per meter of cell length was determined using standard procedures described in Standard Methods (Eaton, *et al.* 2005). Ozone concentration in water was determined using the indigo method described by Bader and Hoigne (1982). In process UV/Vis absorption measurements were performed using two on-line spectrometers of the type spectro::lyserTM, from scan Messtechnik that were equipped with a 35 mm measuring cell. This instrument measures absorbance of ultraviolet and visible light from 200 to 750 nm (Rieger, *et al.* 2004).

Ct value determination

The Ct value was calculated based on the ozone concentration in the water and the contact time, according to equation 1 (van der Helm, *et al.* 2007):

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

Where *Ct* is the ozone exposure ((mg-O₃/L)*min), *n_{sp}* is the number of sampling points (-), *c_{O3}* is the ozone concentration in water (mg-O₃/L) and *t* is the time (s).

Spectral algorithms

Multiple linear regression (MLR) analysis was carried out using the statistical toolbox in Matlab[®] (Matlab 2009). A linear combination of parameters was used to express the response (e.g. change in AOC concentration) and the statistical dependency of each wavelength to the response was evaluated. The changes in UV absorbance were obtained by subtraction of the effluent ozonation UV absorbance spectra from influent ozonation UV absorbance spectra. The algorithm for estimation of AOC formation was developed based on the turbidity-compensated differential spectra and the change in AOC concentration determined by the laboratory. The algorithm for estimation of Ct value was developed based on the turbidity-compensated differential spectra and the measured Ct values. The turbidity compensation was performed using the s::can software ana::pro Version 5.9c. Because of the precision of the instruments, only spectra with more than 0.2 Abs/M were considered (van den Broeke et al., 2008).

Results

Ozone concentration and Ct value

At the ozonation pilot plant a total of 24 sampling points were available for sampling and determination of the ozone concentration in water. In Figure 1, the measured ozone concentration in water is displayed for 3 settings (a low ozone in water dosage 1.0 mg-O₃/l, average dosage 2.5 mg-O₃/l and the highest dosage 4 mg-O₃/l for a DOC concentration of approximately 6 mg-C/l).

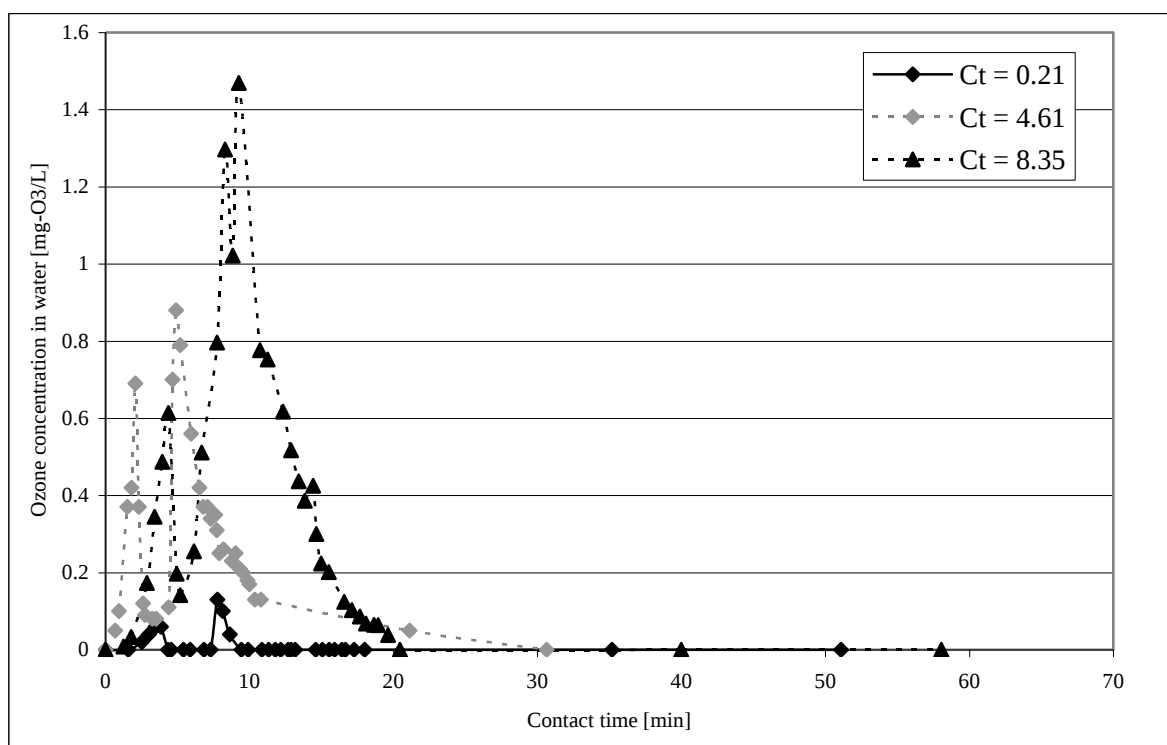


Figure 1. Dissolved ozone concentration measured at 33 sampling points

In Figure 1, the ozone dosage points can be distinguished by the increase in ozone concentration in water. 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. Figure 2 displays the corresponding cumulative Ct values, also plotted against time.

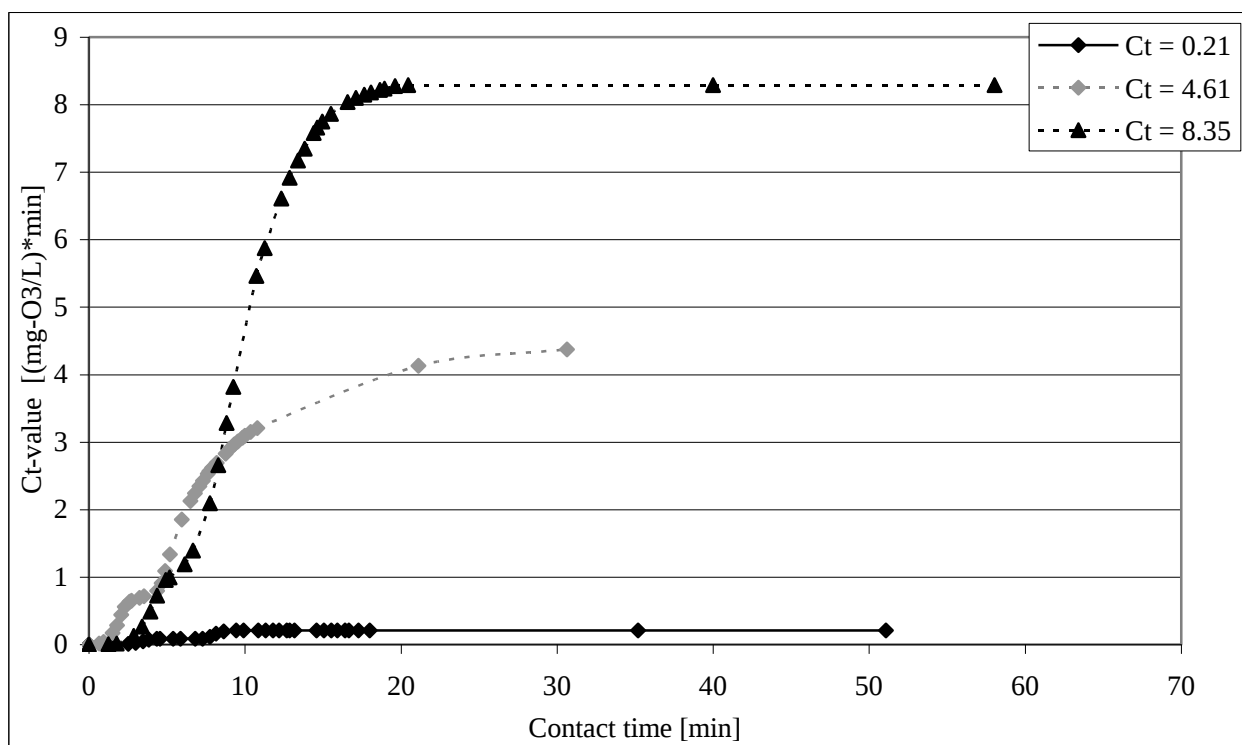


Figure 2. Cumulative Ct value for 3 runs (low, average and high ozone dosage)

A low ozone concentration in water with a long contact time can still have a significant effect on the Ct value. This can be seen in Figure 2, for the Ct = 4.61 (mg-O₃/L)*min line, where the last three sampling points contribute to approximately 25% of the Ct value.

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

It was shown in the literature that it is possible to estimate on-line the ozone concentration in water by using UV/Vis spectrometers (van den Broeke et al., 2008). However, in a full-scale plant the amount of sampling points where the ozone concentration in water can be determined is usually limited. Therefore it was investigated whether it was possible to find a direct relation between the change in UV/Vis absorbance and the Ct value. MLR was applied on the Δ UV/Vis absorbance spectra and the Ct values. The following relationship was derived, described by equation 2:

$$Ct_{est} = -2.38 - 193.447 \cdot \Delta UV_{265} \quad (\text{eq. 2})$$

The best correlation ($R^2 = 0.88$) was observed using the absorbance at 265 nm (ΔUV_{265}). The Ct values derived using Equation 2 are shown in Figure 3.

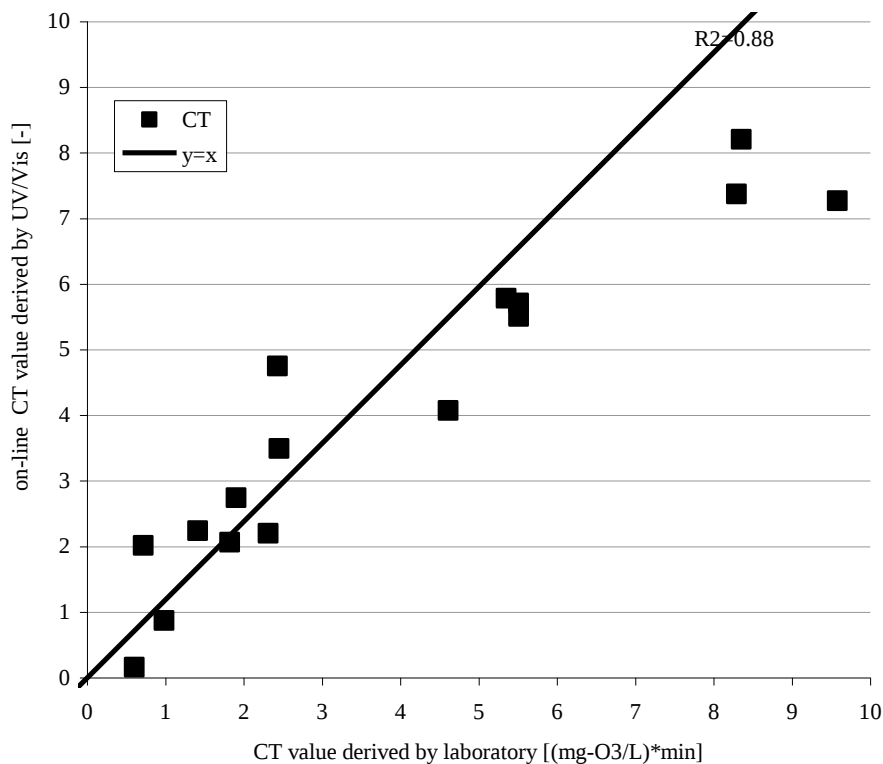


Figure 3. Correlation between the Ct value during ozonation determined by product of ozone concentration in water, measured by the laboratory, and residence time and the change in UV absorbance

This algorithm makes it possible to estimate on-line the Ct value and determine the log removal of pathogens.

Algorithm for on-line estimation of AOC formation during ozonation

Besides the on-line determination of the disinfection capacity, the formation of AOC is also important, since the AOC concentration affects the biological stability of the water produced. In literature it was shown that a correlation existed between the change in UV254 and the AOC formation during ozonation (van der Kooij, *et al.* 1989). In Figure 4, the change in UV254 was plotted against the amount of AOC formed.

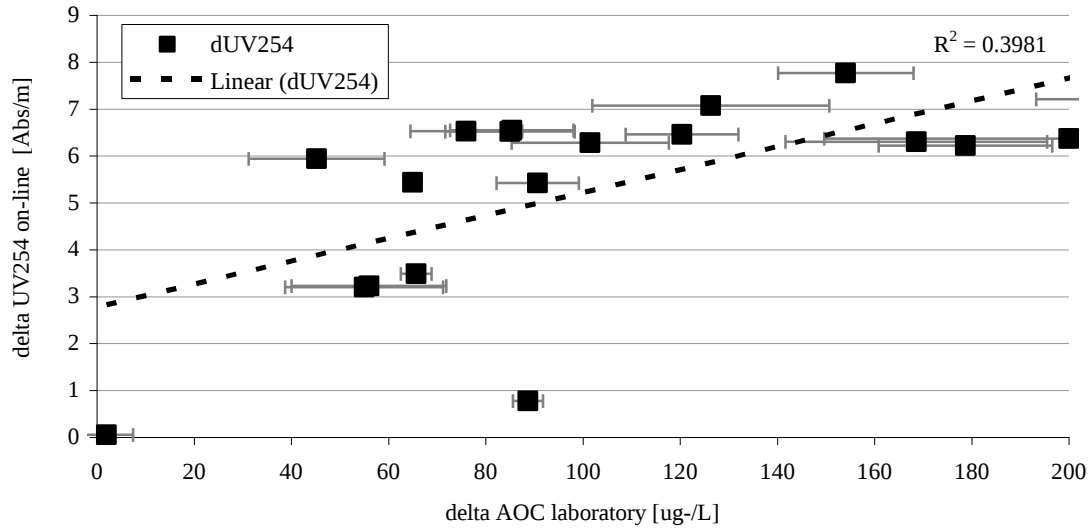


Figure 4. Correlation between AOC formation during ozonation and the change in UV₂₅₄.

It can be seen that for this research the correlation between the AOC formation and ΔUV_{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. It was shown by van den Broeke et al. (2008) that the use of multiple wavelengths resulted in a better correlation with the change in AOC concentration. A total of 30 data points were available to calibrate the algorithm on. The calibration resulted in an algorithm developed based on a total of 4 wavelengths and a $R^2=0.74$ (Figure 5 and equation 3):

$$\Delta AOC_{est} = 37.5677 + 7467.54 \cdot \Delta UV_{320} - 17533.3 \cdot \Delta UV_{347.5} + 7558.3 \cdot \Delta UV_{427.5} + 16028.2 \cdot \Delta UV_{435} \quad (\text{eq 3})$$

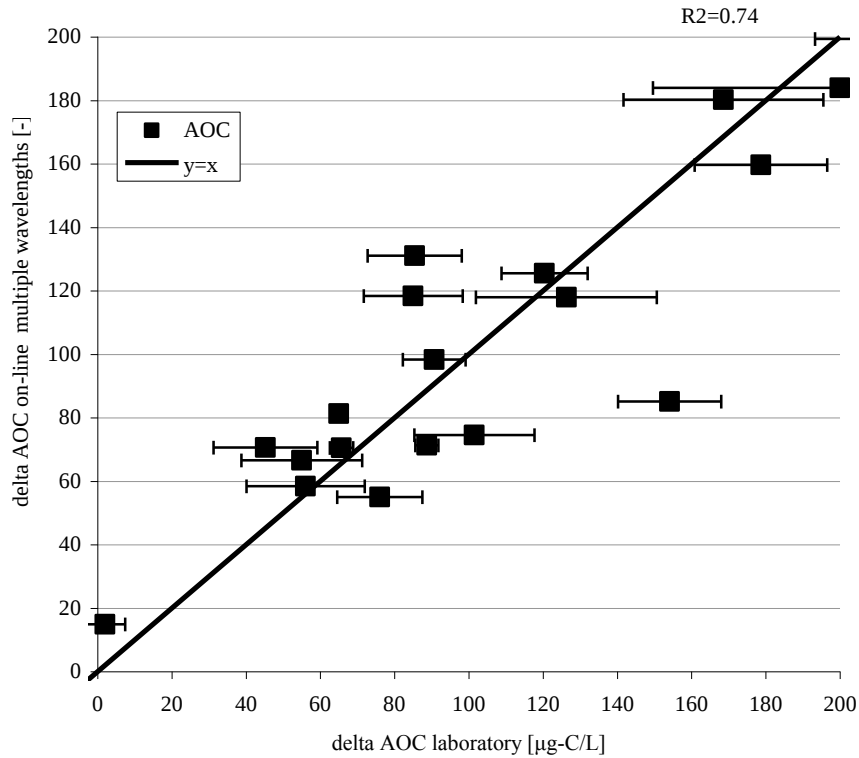


Figure 5. Correlation between AOC formation during ozonation measured by the laboratory and predicted AOC formation based on change in UV/Vis absorbance using equation 2.

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. This algorithm makes it possible to estimate on-line the amount of AOC formed during ozonation.

Conclusions

The objective of this study was to develop algorithms that make it possible to monitor on-line the ozonation step through the estimation of AOC formation and Ct value with UV/Vis spectrometers. The results showed that it is possible to use differential UV/Vis spectrometers as a surrogate parameter for the on-line estimation of AOC formation and achieved Ct value during ozonation. Based on these results it is possible to determine the optimal ozone dosage directly and give a direct indication of the amount of AOC present in the water by only using UV/Vis spectrometers.

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