

Use of on-line UV/Vis-spectrometry in the measurement of dissolved ozone and AOC concentrations in drinking water treatment

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Abstract The concentration of dissolved ozone and Assimilable Organic Carbon (AOC) are important performance parameters in drinking water production. For the measurement of ozone, a spectral algorithm was developed that allows quantification insitu using a UV/Vis spectrometer probe. Furthermore, a strong correlation between the change in the absorption spectrum after individual treatment steps and the formation or removal of AOC in that treatment step was observed. This allowed the development of a spectral algorithm that predicts AOC formation during ozonation and subsequent removal in further treatment steps. This method has been verified at one pilot plant of the Amsterdam drinking water supply.

Keywords UV/Vis, spectrometry, on-line, AOC, ozone, drinking water

INTRODUCTION

Oxidation of organic materials for drinking water disinfection, as well as improving organoleptic characteristics, is a commonly applied treatment step. During oxidation of the natural organic substances in the source water, for example using ozone, large molecules, such as humic and fulvic acids, are cracked into smaller ones (Hammes et al, 2006). A side-effect of this procedure is the increased availability of microbiologically assimilable organic carbon; Whereas the original large molecules are not readily accessible to micro-organisms, the smaller oxidation products can be digested and thus can stimulate bacterial regrowth in the distribution network (Van der Kooij, 1992). The fraction available for uptake by micro-organisms is classified as AOC. This is an important parameter especially in drinking water networks where no residual disinfectant is present in the water. The measurement of AOC is performed using cell cultures, which is a lengthy procedure. A more rapid assessment of the AOC levels produced during treatment would be very valuable, as it can allow the optimisation of treatment for the actual water quality.

Online UV/Vis spectroscopy has proven itself as a tool that allows the collection of specific information on the removal efficiency for and subsequent concentrations of (organic) substances in water. For example, the parameters total suspended solids and chemical oxygen demand (COD) and nitrate can be readily monitored readily with UV/Vis spectral measurements (Langergraber, 2004). Other examples are the prediction of disinfection by-product formation by chlorination (Korshin, 1997) and chlorine demand (Chow et al., 2006). The use of two on-line spectrometer instruments, placed before and after a treatment step, and the calculation of the differential spectrum between these two sites could open up a further area in water quality monitoring and process control as it allows calculation and prediction of water quality parameters previously unavailable. A major benefit in process control of such a setup would be the high measurement frequency. Grab sampling and laboratory analysis are still the most widely used tools for providing data, by because of its non-continuous nature and the delay in obtaining laboratory results, it is totally unsuitable for process control. Furthermore, the actual water quality upon entering the distribution network is therefore poorly defined.

In the study presented herein the simultaneous application of two on-line UV/Vis spectrophotometer for the monitoring of dissolved ozone concentrations as well as AOC formation during oxidation and subsequent AOC removal in further treatment steps was investigated.

MATERIALS AND METHODS

UV/Vis spectrometer

On-line UV/Vis measurements were performed using a submersible, two beam spectrophotometer, spectro:lyser™, from scan Messtechnik. The probes installed were equipped with a 35mm measuring cell, and measured absorbance between 200 and 750 nm, with a resolution of 2.5 nm. The instrument is built as a compact submersible sensor enabling measurement of UV/Vis spectra directly in liquid media with a detector precision of 0.004 extinction units, which corresponds to 0.10 abs/M for the instrument used. Signal drift is < 0.01 extinction units in 30 days both in water and in air. The linear range of the instrument in absorption measurements is between 0 - 70 abs/M.

Development of spectral algorithms

The spectro:lyser™ is equipped with calibration algorithms that allow the measurement of turbidity, nitrate and TOC and also perform automatic turbidity compensation of the spectrum. The latter allows the subsequent calculation of DOC. These calibrations were developed using multivariate statistical analysis of large datasets of absorption spectra of different waters. In this analysis, the entire spectrum has been used in the search for concentration - spectral relationships. Full spectral analysis was required, as the overlapping spectra of the substances present in the water produce a complex background. Linear relations between single determinants and absorptions at single wavelengths are often impossible to find, or are strongly affected by cross-sensitivities. The model applied, Principle Component Analysis followed by Partial Least Squares regression (PLS), combines full spectral analysis with various validation procedures and outlier tests, to reach both high correlation quality and robustness (Otto, 1999), even in complicated mixtures of substances. A more detailed description of the methods applied can be found in Langergraber (2003).

Pilot plant

Two on-line spectrometers probes were installed in the pilot plant of Amsterdam waterworks (Waternet), location Weesperkarspel. In this pilot plant, the full treatment train of the waterworks is represented. The source is an artificial lake with high concentrations of natural organic matter. In the pilot plant it is sub sequentially treated in an ozone reactor (4 bubble columns), pellet softening reactor, biological activated carbon (BAC) filtration reactor and finally a slow sand filter.

A parallel BAC reactor was fed with water from the full scale treatment plant, which uses identical raw water, to be able to verify the effects of the changes in the ozone settings on water quality. On-line data and grab samples were collected from 6 points in the process (figure 1). For on-line measurements, one spectrometer was installed in a by-pass setup before the ozone reactor (point 1). The second one was installed in by-pass setup directly after the ozone reactor (point 2) and was connected to sample lines from points 2 - 6, using a time controlled switch to cycle the feed between all five lines. Using the spectrometers a full spectrum was recorded every 2 minutes.

Grab samples were analysed for AOC (LOQ = 1 µg/L +/- 0.5 µg/L) and UV absorbance (LOQ = 0.1 abs/m, σ = 0.095 abs/m) at 230, 254, 280 and 350 nm by an accredited laboratory using standard procedures (APHA, 2005). Ozone concentrations were analysed immediately after sampling using the Indigo procedure described in APHA (2005) with LOQ = 0.02 mg/L and σ = 0.005 mg/L.

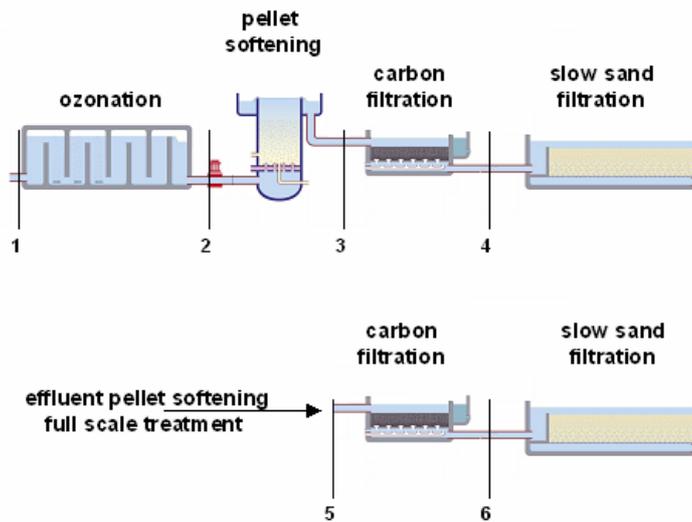


Figure 1. Scheme of pilot plant. Sampling points indicated with 1- 6.

Ozone measurements

The half life of ozone in water is very short, to be measured in minutes. This makes ozone concentration measurements, especially using grab sampling, difficult. Therefore, a different approach was used in the development of the ozone calibration algorithm. A reliable ozone spectrum (Molina, 1986) was used to simulate the presence of ozone in water. The advantage of this method is that it can be performed without the need for sampling and analytical chemistry. Not only does this save time and expenses, it also avoids errors associated with grab sampling, an important source of inaccuracy especially when measuring instable substances (Gy, 1998).

The absorption spectra for ozone concentrations between 0 and 5 mg/L were calculated and combined with sets of spectra representing four different types of drinking waters. For each type, to a series of 500 spectra, reflecting natural fluctuations in water quality, the ozone spectra were added. For each of the four waters, 40 samples reflecting the dynamics of the water as well as the full concentration range of ozone were selected for use in the statistical analysis. Typical matrix variance between 230 and 280 nm, where the ozone absorption peak is located, was observed to be in the order of 0 - 10 abs/M. This is the same order of magnitude as the absorption resulting from 1 mg/L O₃, which is approximately 6 abs/M. Using the PCA/PLS method, a linear combination of wavelengths was obtained that provides a robust correlation between the ozone concentration and the turbidity compensated UV-absorbance. This calibration was validated by measuring 8 concentrations equally distributed between 0 and 4 mg/L in drinking water of a type not included in the development dataset, and checking the ozone values against the readings obtained with a calibrated EBARA EL-2001. A correlation between the two instruments of (R^2) 0.998 was obtained.

RESULTS AND DISCUSSION

Ozone measurements

The spectral algorithm for ozone concentrations was employed to determine ozone in the Waternet pilot plant. Using 36 sampling points available, a concentration profile of ozone throughout the reactor could be measured. Of the 36 measurements, 35 could be used for spectral analysis. One point was removed from the dataset because the by-pass setup was not properly filled during measurement of the spectrum. Furthermore, bubbles were observed in the sample cell due to convection of ozone gas from the bubble columns into the bypass of the spectrometer and due to

gas formation caused by a drop in pressure at the sampling point. These bubbles were registered both visually and by the spectrometer probe and caused scattering of the absorbance values. However, as the effect on the spectrum of the bubbles is identical to turbidity, the spectral turbidity compensation fully corrected the spectrum (Huber, 1998; Latimer 1962), allowing unhampered measurement of dissolved components in the water.

After removal of outliers, (10% outlier removal, i.e. 3 measurements removed) a correlation coefficient (R^2) of 0.97 between lab and online measurements, and a precision of 0,005 mg/L were obtained (figure 2). A small bias in the on-line results, with high concentrations being underestimated by approximately 0.2 mg/L, was corrected by a 2-point calibration that adjusted the slope of the calibration curve. The multi-wavelength algorithm shows a significantly better correlation with the ozone concentration than the best single wavelength measurement (figure 2).

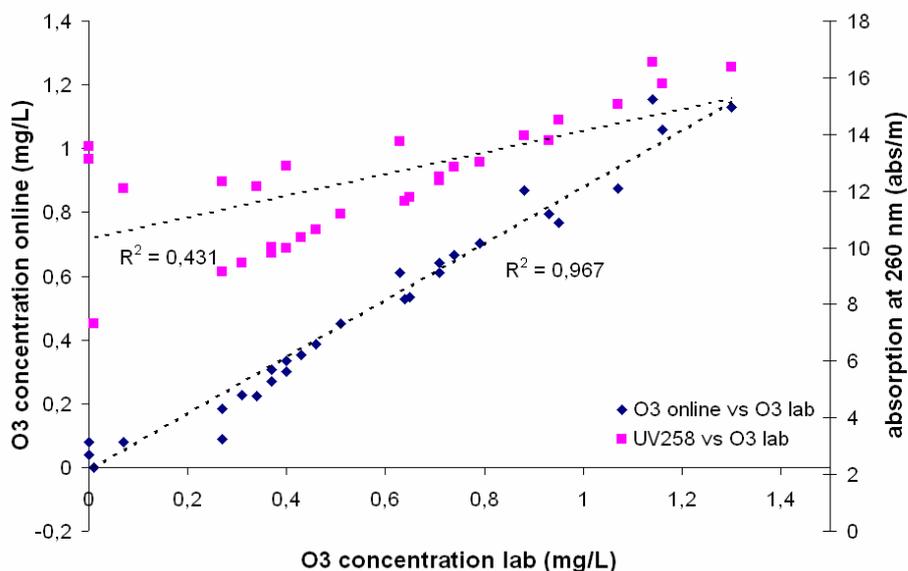


Figure 2. Correlation of on-line and laboratory ozone measurements and correlation of laboratory ozone measurements against single wavelength measurements at 258 nm. Correlation between O_3 and other single wavelengths was lower.

Change in organics during oxidation

Besides measuring the ozone concentration profile across the reactor, the spectrometer probe also allowed the measurement of the change in composition of the organics during oxidation. This is classically followed at single wavelengths, and is measured before and after the oxidation reaction. Using an on-line instrument, however, the change in absorption can be followed across the reaction. As the presence of ozone complicates the UV measurements, it absorbs light in the same region as organics, a single wavelength photometer will always measure a sum of absorptions from ozone and the organics. The full spectral method, with ozone measurement at multiple wavelengths, allows removal of the ozone contribution from the spectrum and thus a more accurate assessment of the organics. Using this approach, the corrected UV-absorbance curves found at 3 indicator wavelengths are presented in figure 3. The shape of the curves approaches an exponential, which correlates well with known kinetics of ozonation reactions (Hoigné, 1994). The correspondence with earlier results indicates that the ozone compensation is reliable.

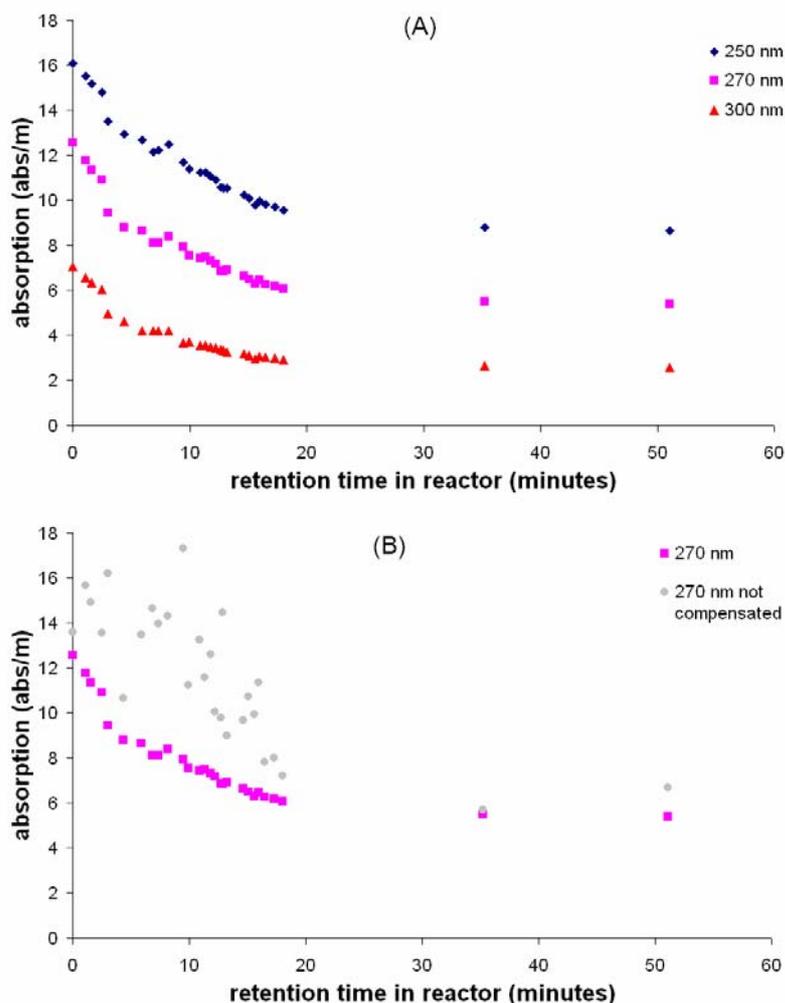


Figure 3. Change in UV-absorption across the ozonation reactor. Absorption was corrected for turbidity and ozone concentration (a). Effect of the correction is demonstrated in (b), where the non-corrected signal at 270nm is shown.

AOC

During oxidation the high molecular weight organic molecules are converted into smaller organic molecules. The total amount of organics in the water, however, does not change significantly. As a result, classical spectroscopically measurable sum parameters such as DOC are not very well suited to assess AOC concentrations. For measurement of AOC a new spectral algorithm was required.

Using the PLS method 39 laboratory results for AOC, sampled from all 6 sampling points in the plant, were matched with the full spectra recorded at these points at the time of sampling. First the combination best correlating wavelengths were obtained using PCA. A total of 8 wavelengths was required to find satisfactory correlation ($R^2 > 0.8$). A set of coefficients that calculates the AOC concentration from these wavelengths was then obtained from the PLS procedure. In the development of this calibration, 75% of the available measurements were used. The remaining 25% were used for checking the obtained calibration, which showed a similar correlation between the laboratory results and the spectral AOC values (R^2 0.86, figure 4).

The AOC calibration obtained in this way is a surrogate parameter (Korshin, 1997; Li, 1998), in the sense that the AOC concentrations in the water are far below the concentrations that can be distinguished using a UV/Vis spectrophotometer without sample pre-concentration. Therefore, the correlation observed is between not between the AOC itself and the spectrum, but between other properties of the spectrum that are linearly related with AOC. Because of this, changes occurring in

the matrix that are not proportional to the amount of AOC present in the water can directly lead to deviations between the developed model and the actual composition of the water. As this matrix is known to change seasonally and as well as between different sites, a second approach was used to establish a more robust correlation between the absorption spectra and AOC.

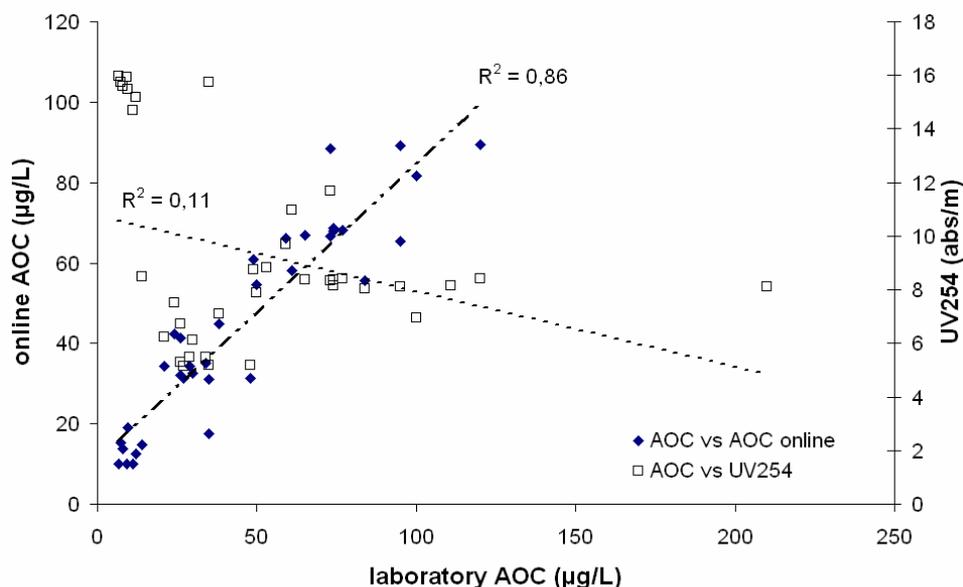


Figure 4. Correlation between laboratory AOC and surrogate on-line AOC. For comparison, the best correlation between AOC and a single wavelength is displayed as well.

It has been described that differential spectroscopy allows predictions of for example disinfection by-product formation, although the formed substances themselves are not visible. In these cases, the change in the spectrum is directly related to the process employed, and is largely independent of the composition of the raw water (Li, 1998). A similar approach was used here to predict the change in AOC concentrations for the treatment steps in the pilot plant. To do this, both the differential concentrations ($\Delta\text{AOC} = [\text{AOC}_{\text{before}}] - [\text{AOC}_{\text{after}}]$), as well as the differential spectra ($\Delta\text{Abs} = \text{Abs}_{\lambda,\text{before}} - \text{Abs}_{\lambda,\text{after}}$) were calculated. In total 25 differential ΔAOC and differential spectra were available for development of a calibration algorithm using the PLS method. Because of the precision of the instruments, only spectra with a differential value of more than 0.2 abs/M were considered in these procedures. The resulting linear combination of 6 wavelengths shows a strong overall correlation with the ΔAOC for all three treatment steps considered in this study (table 1). Furthermore, it also shows significant to strong correlation when applied to the single treatment steps (figure 5).

Table 1: Calibration results.

Parameter	Ozone	AOC	delta AOC
correlation coefficient single wavelength	0,43 ¹	0,11 ²	0,58 ²
correlation coefficient multivariate calibration	0,97	0,86	0,91
Detailed results of multivariate calibration			
concentration range	0 - 5 mg/L	1 - 200 µg/L	7 - 200 µg/L
accuracy (95% confidence)	+/- 0,06 mg/L	+/- 18 µg/L	+/- 18 µg/L
precision of measurement	+/- 5 µg/L	+/- 1 µg/L	+/- 7 µg/L

¹: best single wavelength correlation at 258 nm. ²: standard indicator wavelength at 254 nm.

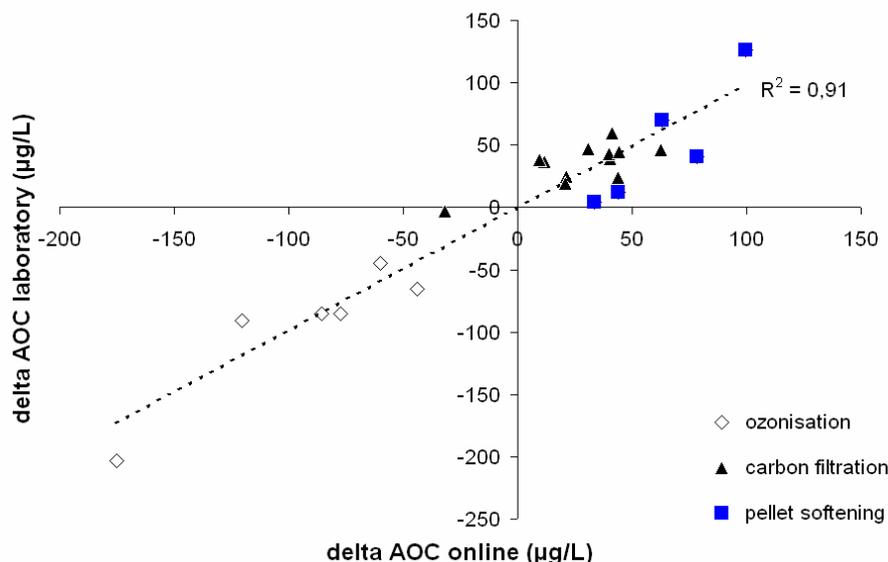


Figure 5. Correlation between AOC changes over individual process steps and predicted AOC change based on differential spectra.

The fact that the calibration also performs well in determining the AOC changes in the individual treatment steps, demonstrates the robustness of the correlation in this particular application. The correlation coefficients for the treatment steps are: ozonation 0.85; pellet softening 0.81; carbon filtration 0.66 (after removal of 1 outlier). The lower correlation of the spectral calibration for AOC in the biologically active carbon reactors is most likely caused by the complexity of the processes in this treatment step; the concentrations of the organic substances change due to physical absorption as well as biological degradation. These processes have a different effect on each type of substance, for example the amount of biological degradation will depend strongly on the composition of the AOC. In the pilot plant, this mixture of organic material was constantly changing due to changes in the settings of the ozone reactor. The full scale plant, however, operated with constant settings and a better correlation for the AOC calibration over the BAC reactors could be expected when only the delta AOC between sample points 5 and 6 is considered. Indeed, the correlation between the change in AOC recorded with the laboratory analyses and the online calculations for these two sample points shows an R^2 of 0.98, whereas it is 0.48 for the delta AOC between 3 and 4. Of course, these coefficients are just rough indications, as only 6 measurements were available for calculation each of these correlations, which is insufficient for a reliable assessment.

CONCLUSIONS

A method that allows the building of reliable calibration models for dissolved ozone and AOC concentrations with very good coefficients of determination has been presented. The described approach is based on the PLS method, and produced robust calibrations in the particular application reported, despite the presence of background signals from a mixture of natural substances, changes in background signal and changing absorption signals due to gas bubbles.

The development of such a calibration does not necessarily require sampling and laboratory measurement but can be performed using historical data and spectra available in literature as well, as demonstrated for ozone. Development of calibration models in this way is cheaper and faster, as no additional sampling and analytical chemistry are necessary.

The developed calibration, in combination with the on-line spectrometer probe, allows for on-line and in-situ measurement of dissolved ozone concentrations. The use of two instruments

simultaneously, required to perform on-line differential measurements, allows the prediction of the changes in AOC levels in individual treatment steps in real-time, demonstrated here for ozonation, pellet softening and biologically active carbon filtration.

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