

Simulation of the online determination of the TOC content with uniTOC of media containing boric acid as cooling water, used in circuits of plants



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Introduction

In this application we will show how the uniTOC can be used for TOC detection of water mixed with boric acid. This type of mixture is used as cooling media in circuits of plants. Usually the TOC values in this media are in a range of 500 - 1000 ppb. Therefore it was decided to include an upper limit value of 1000 ppb sucrose in the final measurements of the simulation

Sample Preparation and Analysis

- a) Each solution was freshly prepared (except the reagent) before analysis. The dilution medium ultra pure water was tapped freshly directly before using from our own in-house production line to avoid cross contaminations with TOC.
- b) The reagent was freshly prepared and stirred for > 24 h at room temperature to decompose the self-containing TOC content. For the reagent 100 g Sodium peroxodisulfate (min. 99 %) and 30 mL ortho-Phosphoric acid (85 %) were diluted in 1000 mL ultra pure water.



Figure 1: TOC Analyzer uniTOC

Experimental conditions

For the TOC analysis an uniTOC (2 ppb to 5000 ppb measurement range) device was used at room temperature and normal pressure. The uniTOC performs the full oxidation by UV, based on NDIR detection of carbon dioxide and calculates the TOC content from the peak area. Because uniTOC is able to enhance the oxidation process by dosage of reagent (phosphoric acid/ sodium peroxodisulfate), the experiments were run with and without reagent to compare the oxidation performance.

Results & Discussion

Profile of the TOC degradation of the reagent itself

Before starting the measurement series, the TOC content of the reagent was validated. The reagent was measured three times every three hours in a range of about 48 hours. The

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minimum of TOC value was almost reached after 20 hours.

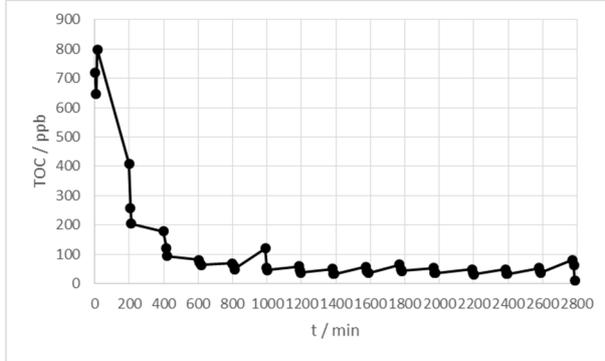


Figure 2: Profile of the TOC degradation of the reagent itself. The minimum of TOC value was reached after 20 hours.

Analysis of ultra pure water of in-house pipeline of membraPure

For further investigations, the blank TOC value was firstly determined, in the locally produced ultra pure water. Within a time range of 30 min and 8 measurement points, an average of 9 ppb has been identified.

Table 1: TOC values as Blank in ultra pure water.

min	ppb
0	13.1
5	9.2
8	8.1
13	7.1
17	8.7
22	8.1
27	9.8
31	9.9
average	9.25

Analysis of solutions with a TOC level of 1000 ppb Sucrose

To investigate the effect of reagent a solution with 1000 ppb Sucrose was analysed, with and without the dosage of the reagent Phosphoric Acid/ Sodium Peroxodisulfate. Because of the reproducibility, a series of 8 measurements were performed. Figure 3 shows the recovery rate for the TOC value with and without the use of reagent.

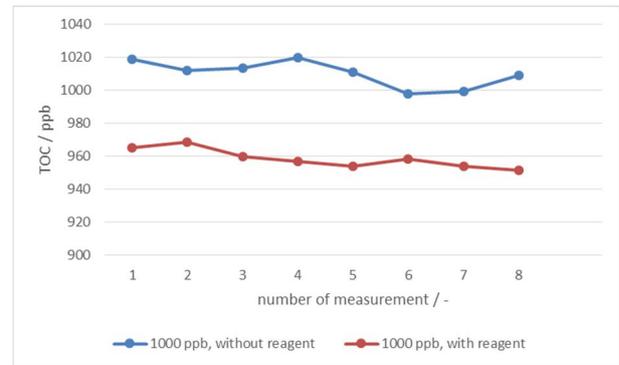


Figure 3: Analysis of 1000 ppb Sucrose solution without (blue line) and with (red line) reagent is shown the recovery rate of 1000 ppb Sucrose.

Figure 3 shows that the expected TOC values of 1000 ppb are almost reached. The deviations can be explained by the sample preparation. With a measured mean value of 1010 ppb, the deviation is 1 %, which is in the range of acceptance.

If reagent is used, the recovered TOC value is 958 ppb with an average deviation of 4.2 %. This can be explained by the fact that the addition of reagent causes oxidation to start before the analysis begins, so that not all carbon dioxide is detected.

These observations are consistent with the recommendation to use the reagent only at higher TOC concentrations above 2000 ppb.

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Analysos of ultra pure water containing boric acid with/without 1000 ppb Sucrose

This situation was simulated by the corresponding customer request, in which firstly 40 g/L boric acid (> 99.8 %) was dissolved in ultrapure water. The measured conductivity of approx. 45 µS/cm is irrelevant for the uniTOC measuring method and the measurements can be continued. The prepared solution was measured using the same method with and without reagent and the recovered TOC values were evaluated. The results are summarised in Figure 4. In the next step the solution containing 40 g/L boric acid was spiked with 1000 ppb Sucrose. Again, the same method was used with and without reagent. The results are shown in Figure 5.

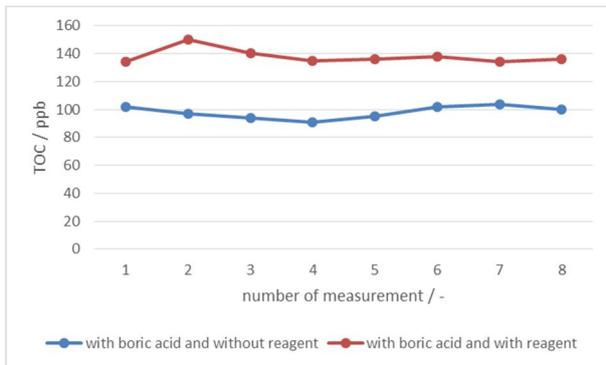


Figure 4: Analysis of boric acid solution without (blue line) and with (red line) reagent.

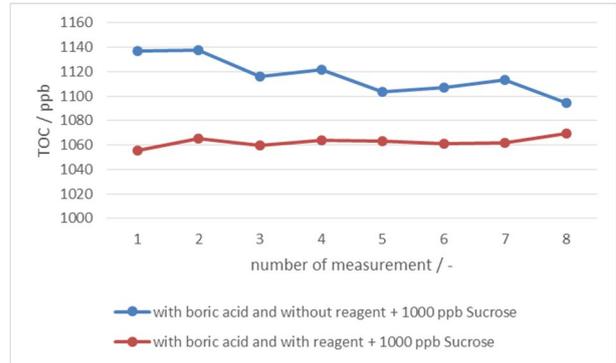


Figure 5: Analysis of boric acid solution and 1000 ppb Sucrose without (blue line) and with (red line) reagent is shown the recovery rate of 1000 ppb Sucrose.

Figure 4 shows that the dissolved boric acid has no significant effect on the reagent. By determining the blank value for the ultrapure water of approx. 9 ppb, it can be seen that the boric acid used has an inherent 130 ppb TOC. This content increases further if the TOC value is determined by adding reagent. This leads to the conclusion that the boric acid contains organic components that are more difficult to decompose and that can only be completely converted by the use of reagent.

The results in Figure 5 are consistent with the observations made so far in Figure 3: The use of a reagent leads to an upstream degradation of sucrose (ca. 40 ppb) and the amount analysed is slightly below the amount used. Added to this is the TOC content of boric acid with approx. 130 ppb. Compared to the average of specified quantity with 1062 ppb the deviation is 2.6 % and is within the range of acceptance.

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Conclusions

The results of the stepwise approach and the coordinated experiments have shown that uniTOC is a suitable device for this kind of application. The boric acid has no influence on the TOC content and the added amounts of sucrose could be confirmed by analysis with the uniTOC. How the medium of dissolved boric acid affects the fluidics of uniTOC has to be investigated in long-term studies. Only 8 measuring points are not sufficient for this. However, it has already been observed that after switching off uniTOC device, the first deposits of boric acid appear in the remaining residues after a short time. This effect can easily be avoided by rinsing with ultrapure water after finishing the analysis.

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