On-line Measurement of Sub-ppb level Hydrogen Peroxide in Ultrapure Water Production Process

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Abstract

An on-line H₂O₂ analyzer was developed for application to the ultrapure water production process, using a gasometric method. The analyzer consists of a dissolved oxygen (DO) sensor and analyzer, a catalyst that converts H₂O₂ to O₂, and a computer that stores the DO data. H₂O₂ concentrations were calculated by measuring the change in DO concentration before and after the catalyst and using the calculation formula presented in this study. In order to accurately analyze a sub-ppb level of H₂O₂, a DO meter which can correctly measure the DO concentration at the ppb level was applied. An ion exchange resin with Pd, was selected as an appropriate catalyst since it could decompose 99% of H₂O₂ to O₂ at a space velocity of 120/h. The minimum analysis time was 20 min, and the detection limit was observed to be 0.27 ppb. When the DO concentration of the sample was 1.5 ppb or lower, an H₂O₂ concentration of 1 ppb or lower was successfully measured. Good correlation, with an R² value of 0.99, was observed between the measured and calculated H₂O₂ concentrations.
Introduction

Hydrogen peroxide (H₂O₂) is known to be a strong oxidant and is used for various purposes in industrial applications, including as a disinfection agent in food industry, a bleaching chemical in textile industry, and a cleaning solution in semiconductor manufacturing industry¹,². In addition, H₂O₂ has also been widely applied to wastewater treatment facilities, as a trigger chemical for advanced oxidation processes, which degrade various organic materials³. Because of the strong oxidizing potential of H₂O₂, H₂O₂ concentrations have been regulated in ultrapure water (UPW), which is used in semiconductor manufacturing processes. According to the International Roadmap for Devices and Systems (IRDS), announced in 2019, the concentration of H₂O₂ in the UPW used during the semiconductor production process should be maintained below 3 part per billion (ppb)⁴. Therefore, trace H₂O₂ concentrations must be monitored, in real-time, in the UPW that is supplied to semiconductor manufacturing facilities.

Several analytical methods exist for the measurement of H₂O₂ concentrations in water samples, such as titrimetric methods, spectrometric methods, fluorometric methods, gasometric methods, chemiluminescent methods, and electrochemical methods. The titrimetry, spectrometry, fluorescence, and electrochemical methods for analyzing H₂O₂ concentrations have been extensively studied and are widely used in the field. The detection limits of these methods are known to range from tens to hundreds of ppb⁵-⁹. The chemiluminescence method quantifies H₂O₂ concentrations by detecting the luminescence when H₂O₂ reacts with luminol, in the presence of an appropriate catalyst. Several studies have reported that chemiluminescence is a suitable method for measuring trace amounts of H₂O₂, in the range of 1 ppb or lower⁸,¹⁰,¹¹. However, because this method requires the use of
an expensive luminometer, it is considered to be an inappropriate technique for the on-line analysis of H₂O₂ concentrations from a single location.

Guwy et al.¹ reported a good correlation between O₂ evolution and H₂O₂ concentrations, in the range of less than 1.5%, for on-line analyses. Also, Vigil et al.¹² used the evolution of O₂ from H₂O₂ decomposition to characterize the synthesis of manganese oxide nanoparticles. Another advantage of applying the gasometric method as an on-line measuring method is the lack of any chemical requirement, which eliminates the necessity of periodic chemical exchanges and removes the possibility of measurement errors due to chemical shortages when installed in the field. However, the gasometric method has been utilized to measure H₂O₂ concentrations at the parts per million (ppm) level. Because O₂ in the atmosphere can be a source of error, it is difficult to analyze ppb level H₂O₂ under conditions where the sample is exposed to the atmosphere. In contrast, the UPW production process in the semiconductor industry has been designed to remove O₂ from the water and to maintain the O₂ level as low as possible, using a vacuum degasifier or membrane degasifier (MDG).

Therefore, the quantification of low H₂O₂ levels in UPW can be achieved because the DO concentration in sample can be maintained as low as possible. Based on this specific information, we developed a modified gasometric method to determine H₂O₂ concentrations below 1 ppb by analyzing quantitatively the O₂ concentrations generated during the decomposition of H₂O₂ into water using catalyst. In order to the quantification of trace H₂O₂ levels (equal to 1 ppb or lower) in UPW, an O₂ analyzer equipped with a catalyst for H₂O₂ decomposition and a data acquisition method were first evaluated. Second, studies were performed to determine the detection limits of the on-line H₂O₂ analyzer and the effects of background O₂ concentrations. Finally, the developed H₂O₂ analyzer was verified by comparing values between measured and calculated data.
Experimental

Materials

In this study, an H$_2$O$_2$ solution (≥ 30%, Sigma-Aldrich) was used to prepare a standard. Three types of H$_2$O$_2$ decomposition catalysts were tested. The first was a catalyst with a MnO$_2$ content of 94 mol% or higher (Purelyst MD-400, Puresphere co., Ltd, Korea), with a diameter of 3–5 mm, and a specific surface area of 300 m$^2$/g or larger. The second catalyst was a strong basic anion exchange resin with hydroxide form (Amberjet UP6040, DOW chemical, USA). The third catalyst was a palladium-doped polymer-based resin (Lewatit K 7333, Lanxess, Germany).

All experiments were conducted using UPW, which was produced by a UPW production facility that was continuously operated for 24 h each day. The unit processes comprising the UPW production process were described, in detail, in our previous study$^{13}$. The quality of the produced water and the measurement equipment for the UPW production facility were as follows: 0.4–5.0 ppb total organic carbon (TOC; Siverse 500 RLe, GE), 18.2 M·cm resistivity (M300, Mettler Toledo), and 0.3–0.5 ppb dissolved oxygen (DO; Orbisphere 510, Hach).

Apparatus

A schematic of the on-line H$_2$O$_2$ analyzer that was used in this study is shown in Figure 1. Because this analyzer can only be operated in on-line mode, the point of measurement and the analyzer must be connected with a tube, and a minimum water pressure of 1 atm is necessary at the measuring point. The analyzer consists of a DO analyzer (Orbisphere 410, Hach), with a sensor, a column that contains the H$_2$O decomposition catalyst, a flow meter, and valves. A DO analyzer was equipped with a luminescent DO sensor which measures DO concentration by detecting the decreased amount of luminescence in the reaction between
oxygen in solution and light emitted from the sensor. The measuring range of a DO analyzer was 0 to 20,000 ppb. One DO meter was used instead of two, to reduce the uncertainty that may occur if the two DO meters showed different values at the same sampling point. The H$_2$O$_2$ analyzer flowrate was fixed at 0.2 L/min, which was the manufacturer's recommended flowrate for a DO sensor. Therefore, the volume of the column varied from 0.1 L to 0.3 L, to adjust the space velocity (SV) of the catalyst from 40/h to 120/h. Automatic valves were used, controlled by a program, to create a flow path allowing the column to be passed or bypassed over a certain time interval. The measurement was divided into two steps, and each step was fixed at 10 minutes. The first step consisted of monitoring the DO concentration in the sample. During this step, the DO concentration was measured after passing the sample through the H$_2$O$_2$ decomposition catalyst.

In the verification of analyzer by comparing measured and calculated H$_2$O$_2$, the H$_2$O$_2$ concentration in a sample was controlled by adding a stock solution of H$_2$O$_2$ into a sample stream using a piston pump, as shown in Figure 1. The concentration of the stock solution and the flowrate of the stock solution were varied to ensure the appropriate H$_2$O$_2$ concentration in the sample flow.

Results and discussion

Principal of hydrogen peroxide measurement

This study developed a method for measuring trace concentrations of H$_2$O$_2$, in a semiconductor-grade UPW production facility. Generally, the H$_2$O$_2$ concentration of raw water in UPW production processes is approximately 1 ppb. However, the H$_2$O$_2$ concentration increased rapidly after TOC reduction UV which is installed to degrade organic materials in UPW production process$^{13}$, despite the presence of an H$_2$O$_2$ decomposition unit to remove H$_2$O$_2$ after TOC-reduction UV. Monitoring the H$_2$O$_2$ level in UPW is necessary
because H₂O₂ can cause defects of semiconductor during the production of the semiconductor.

In this study, an analyzer was developed, based on the mechanism in which 2 moles of H₂O₂ are converted into 2 moles of H₂O and 1 mole of O₂, on the surface of a catalyst (Eq. 1)¹⁰.

\[
2\text{H}_2\text{O}_2 \xrightarrow{\text{Catalyst}} 2\text{H}_2\text{O} + \text{O}_2 \tag{1}
\]

Therefore, this study hypothesized that DO concentrations, if accurately measured before and after contacting the H₂O₂ removal catalyst, can be used to calculate accurate H₂O₂ concentrations, based on Eq. 1. The H₂O₂ concentration can be calculated using Eq. 2.

\[
\text{H}_2\text{O}_2 \text{ concentration (ppb)} = \left[\text{DO concentration after catalyst (ppb)} - \text{DO concentration before catalyst (ppb)}\right] \times 2.125 \tag{2}
\]

where, 2.125 was obtained by dividing 1 mole of H₂O₂ molecular weight by 0.5 mole of O₂ molecular weight. The selected DO analyzer must be able to accurately measure DO in water. In this study, the DO analyzer (Orbisphere 410, Hach) was used. This analyzer was developed to measure on-line DO concentrations at the end of the UPW production process, and the analyzer has a measurement range from 0 to 20,000 ppb. During this study, we first investigated whether the DO analyzer was sufficiently stable to be used for H₂O₂ analysis. The DO concentrations of the UPW being produced by the UPW production facility, which was operated by the author’s facility, was adjusted to a range of 0.1 to 20 ppb, and DO concentrations were measured for 10 minutes. The DO concentrations were controlled by controlling the removal efficiency of the MDG, which removes O₂ during the UPW production process. Because the DO analyzer produces 1 data point every 10 seconds, the arithmetic means and standard deviations for a total of 60 data points were calculated, as
shown in Table 1.

The standard deviation of the measured value for each measurement concentration was observed to range from 0.8% to 24%. In particular, the standard deviation was determined to be 5% or lower for measurements performed for concentrations of 2 ppb or more. It indicates that the DO analyzer can reliably measure DO concentrations in UPW for at least 10 minutes, when unaffected by external variables during the measurement period. Therefore, the DO concentration can be measured accurately and consistently, indicating that these measurements can be applied to the development of an H$_2$O$_2$ analyzer.

Selection of a catalyst for hydrogen peroxide decomposition

H$_2$O$_2$ is a thermodynamically unstable chemical, naturally decomposing into water and O$_2$. H$_2$O$_2$ decomposition is known to increase under conditions of high temperature or high pH or when it interacts with a catalyst, such as transition metals$^{14,15}$. In this study, a solid catalyst was determined to be a suitable method for an on-line analyzer, to decompose 100% of H$_2$O$_2$ into water and O$_2$, because it requires only a short contact time and can be used for long operational periods, without replacement. In this study, an experiment was conducted to identify a suitable catalyst for use in the on-line analyzer, from among a strongly basic anion (SBA) exchange resin, a MnO$_2$ pellet, and a Pd-supported ion-exchange resin. An SBA exchange resin, containing OH functional groups, has a pH of 12 or high on the resin surface, which allows the ion exchange resin to decompose H$_2$O$_2$ into H$_2$O and O$_2$$^{16}$. Catalysts containing transition metals or noble metals can also be effective for H$_2$O$_2$ decomposition. Many studies have reported the effectiveness of Mn for catalyzing H$_2$O$_2$ decomposition$^{17-19}$. Catalysts that are composed of Pd are also frequently used in during the H$_2$O$_2$ production processes but are also known to cause a reaction that decomposes H$_2$O$_2$ into O$_2$ and H$_2$O, and
its reaction rate was relatively quicker than those reported for Mn or ion exchange resin\textsuperscript{20}.

The abilities of the three catalysts to trigger H\textsubscript{2}O\textsubscript{2} decomposition were tested, using a column reactor. The concentration of O\textsubscript{2} produced was analyzed in the solution, which was passed through a reactor filled with each catalyst, at SVs of 40, 80, and 120/h. The H\textsubscript{2}O\textsubscript{2} concentration in the feed water was 40 ppb. The decomposition efficiency of H\textsubscript{2}O\textsubscript{2}, as shown in Figure 2, was calculated based on the measured O\textsubscript{2} concentration, divided by the expected O\textsubscript{2} concentration of 85 ppb, which is the expected O\textsubscript{2} concentration if 100\% of 40 ppb H\textsubscript{2}O\textsubscript{2} were successfully transformed into O\textsubscript{2}.

Among the three catalysts, the ion exchange resin with Pd showed more than 99\% H\textsubscript{2}O\textsubscript{2} degradation efficiency, whereas the H\textsubscript{2}O\textsubscript{2} resolution of SBA was the smallest. The H\textsubscript{2}O\textsubscript{2} decomposition efficiency decreased with increasing SVs for all three catalysts. To accurately measure the H\textsubscript{2}O\textsubscript{2} concentration using an on-line H\textsubscript{2}O\textsubscript{2} analyzer, the complete decomposition of H\textsubscript{2}O\textsubscript{2} in the solution is necessary. Therefore, the Pd resin was determined to be the best catalyst in this study. Although the H\textsubscript{2}O\textsubscript{2} decomposition efficiency decreased slightly, by approximately 1\%, with increasing SVs, the optimal SV for the analyzer was determined to be 120/h, based on the high cost of Pd resin.

The H\textsubscript{2}O\textsubscript{2} decomposition pathway and efficiency of the Pd catalyst can be adjusted by changing the ion concentrations, pH, and dissolved H\textsubscript{2} concentration in the solution. The decomposition efficiency of H\textsubscript{2}O\textsubscript{2} may be reduced in samples containing large amounts of halide anions or when the pH of an aqueous solution is low\textsuperscript{15}. Additionally, dissolved H\textsubscript{2} concentrations can inversely affect the accurate measurement of H\textsubscript{2}O\textsubscript{2} concentrations. Under the Pd catalyst, there is a possibility of a side reaction to occur. Dissolved H\textsubscript{2} could react with H\textsubscript{2}O\textsubscript{2} and be converted into H\textsubscript{2}O, which would result in the calculated H\textsubscript{2}O\textsubscript{2} concentration being lower than the actual concentration\textsuperscript{21,22}. Therefore, if dissolved H\textsubscript{2} is present in the solution, the H\textsubscript{2}O\textsubscript{2} concentration measurement must be adjusted, based on Eq. 3 which was
developed based on the reaction in which 1 mole of H₂ can react with 1 mole of H₂O₂.

However, Eq. 3 is only valid when the dissolved H₂ concentration is lower than the H₂O₂ concentration and assumes that all dissolved H₂ reacts with H₂O₂ and is oxidized into H₂O.

\[
\text{H}_2\text{O}_2 \text{ concentration (ppb)} = \text{Difference in DO concentration after and before a catalyst (ppb)} \\
\times 2.125 + \text{Dissolved H}_2 \text{ concentration in feed water (ppb)} \times 17
\]  

(3)

where, 17 was obtained by dividing 1 mole of H₂O₂ molecular weight by 1 mole of H₂ molecular weight.

**Data analysis of DO measurements**

The development of an H₂O₂ analyzer using the gasometric method requires the accurate measurement of DO concentrations, both before and after the H₂O₂ removal catalyst. Because the H₂O₂ analyzer developed in this study is intended for on-line operation, the dissolved DO concentrations of samples that are continuously flowing into the analyzer must be accurately measured. To reduce errors caused by differences among multiple DO analyzers, the DO concentration was sequentially measured before and after the catalyst, using the same DO measurement equipment.

The operational logic of the on-line analyzer that was used in this study could be divided into two stages. During the first step, the DO concentration of the sample was measured before the catalyst, and in the second step, the DO concentration of the sample that passed through the catalyst was measured. During this process, a large change in the DO measurement data was observed immediately after switching the flow path, due to stagnant water samples in the unmeasured piping entering the DO analyzer. Therefore, the accurate extraction of DO
concentrations from all measured data is necessary after changing the flow path. Because fluctuations in measured data are the greatest immediately after valve switching, the averages and standard deviations summarized in Table 2 were calculated after excluding data for 0, 1, 2, and 3 minutes at the beginning of the measurement period.

As shown in Table 2, the standard deviations for all DO concentrations measured over the entire measurement period were larger than those that were associated with the initial measurement exclusion, for all DO concentrations. However, no large differences in deviation were observed when using different exclusion times, indicating that the use of a 1-minute exclusion period following valve switching is sufficient for the accurate detection of DO values and the accurate calculation of H₂O₂ concentrations. Therefore, in this study, data were used after excluding the initial 2-minute period, to secure the maximum amount of data while allowing sufficient time for stabilization.

Detection limit of H₂O₂ measurements

The H₂O₂ concentration was monitored, using an on-line H₂O₂ analyzer, installed at the point where low concentration H₂O₂ is expected in the UPW production facility. In UPW production facilities, 10 to 20 ppb of H₂O₂ is generated in TOC reduction UV, and more than 99% of the generated H₂O₂ is removed by the following H₂O₂ removal catalyst. At this time, the removal catalyst installed in UPW production process was a product that was developed and commercialized by Samsung Engineering, and the removal reaction mechanism is shown in Eq 4, where, SBA-SO₃ represents the strong basic anion exchange resin with SO₃⁻.

\[
\text{SBA-SO}_3 + \text{H}_2\text{O}_2 \rightarrow \text{SBA-SO}_4 + \text{H}_2\text{O}
\] (4)
Figure 3 shows the results of H$_2$O$_2$ concentration measurements, using an on-line analyzer for 3 days, for the H$_2$O$_2$ removal catalyst (AR- SO$_3$) effluent, which is expected to have the lowest H$_2$O$_2$ concentration throughout the UPW production facility. The measured H$_2$O$_2$ concentration for 3 days was observed to fluctuate within the range of 0 to 0.25 ppb.

Assuming that the H$_2$O$_2$ concentration of the analyzed sample remains constant, the H$_2$O$_2$ analyzer has difficulty accurately analyze concentrations below 0.25 ppb using DO concentrations. In this study, the data in Figure 3 were defined as background noise, and the average concentration and standard deviation of these data were calculated to be $0.13 \pm 0.048$ ppb. Therefore, the detection limit of the analyzer developed in this study was calculated to be 0.27 ppb, using Eq. 5\(^{11}\).

$$\text{Instrument detection limit} = \text{average of noise} + 3 \times \text{standard deviation of noise} \quad (5)$$

The observed detection limit for the on-line H$_2$O$_2$ analyzer in this study was analogous to that for performing H$_2$O$_2$ measurements using chemiluminescence, which is known to measure sub-ppb levels of H$_2$O$_2$. Yamashiro et al. reported 0.3 ppb as being the lowest detectable limit for the development of on-line H$_2$O$_2$ analyzers based on chemiluminescence\(^{10}\).

Figure 4 shows the results of investigating the effects of background DO concentrations in the H$_2$O$_2$ analyzer on the H$_2$O$_2$ analysis. Because the H$_2$O$_2$ concentration is calculated based on the difference between DO concentrations before and after the H$_2$O$_2$ decomposition catalyst, the probability of inaccurate H$_2$O$_2$ measurement results increases when background DO concentrations in the sample solution are high, which are likely to have greater effects on low concentrations of H$_2$O$_2$. To verify this phenomenon, low concentrations of H$_2$O$_2$ (0.32 and 0.39 ppb) were measured using the on-line H$_2$O$_2$ analyzer developed in this study while
simultaneously changing the sample DO concentration from 0.3 to 1.5 ppb.

The deviations among the measurements for 0.32 and 0.39 ppb H\(_2\)O\(_2\) were calculated to be 2.5% and 1.4%, respectively. When the background DO concentration was greater than 1 ppb, the deviation among H\(_2\)O\(_2\) measurements for the 0.32 ppb sample was 2.5%, which was similar to the deviation observed when the DO concentration was less than 1 ppb. For the H\(_2\)O\(_2\) measurements of the 0.39 ppb sample, the measured deviations for DO concentrations ranging from 0.3 ppb to 1 ppb and from 1 ppb to 1.5 ppb were 1.2% and 1.4%, respectively. Therefore, when the DO concentration in the sample is 1.5 ppb or less, the measurement of low H\(_2\)O\(_2\) concentrations was not affected.

**Verification of H\(_2\)O\(_2\) measurements**

The ability of the developed H\(_2\)O\(_2\) analyzer to accurately measure the H\(_2\)O\(_2\) concentration was verified at several H\(_2\)O concentrations. The H\(_2\)O\(_2\) concentration of the sample was by continuously injecting a trace H\(_2\)O\(_2\) stock solution into the UPW. The prepared H\(_2\)O\(_2\) concentrations ranged between 0.5 and 50 ppb. More than 60 repeated analyses were conducted for each concentration, and the results are shown in Figure 5. At concentrations below 1 ppb, the deviation was measured at 8%, but at concentrations greater than 1 ppb, deviations were less than 2%. In addition, the correlation between the measured and expected values within the measurement range was investigated, as shown in Figure 6. As shown in the figure, the measurement was approximately 7% below the expected value; however, a linear correlation was confirmed between the two values, and the R\(^2\) value was 0.99.

**Conclusions**

An on-line H\(_2\)O\(_2\) analyzer was developed for application in the UPW production process,
using a gasometric method, in which the O\textsubscript{2} concentration that was produced from the reaction between H\textsubscript{2}O\textsubscript{2} and a catalyst was measured and then converted into an H\textsubscript{2}O\textsubscript{2} concentration, using an appropriate redox equation. The DO analyzer that is normally used during UPW production processes was suitable for use as a detector for the H\textsubscript{2}O\textsubscript{2} analyzer, and an ion exchange resin with Pd was able to transform more than 99\% of H\textsubscript{2}O\textsubscript{2} into O\textsubscript{2}, in this study. The detection limit of this analyzer was 0.27 ppb. Low concentrations of H\textsubscript{2}O\textsubscript{2} (under 0.5 ppb) were also stably measured when the DO of the sample was under 1.5 ppb. The accuracy of the on-line analyzer was verified by comparing the measured and calculated H\textsubscript{2}O\textsubscript{2} concentrations, with a good correlation observed between the two values. The on-line H\textsubscript{2}O\textsubscript{2} analyzer that was developed in this study will be a useful instrument for monitoring the H\textsubscript{2}O\textsubscript{2} concentrations of UPW during semiconductor manufacturing processes and for evaluating the status of the H\textsubscript{2}O\textsubscript{2} removal catalyst that is installed in UPW production processes.

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Table 1. Investigations of DO measurements for 10 minutes, using a DO analyzer

| DO concentration (ppb) | Standard Deviation |
|------------------------|--------------------|
| 0.213                  | 0.050 (23.6%)      |
| 0.503                  | 0.049 (9.7%)       |
| 1.02                   | 0.053 (5.2%)       |
| 2.01                   | 0.045 (2.2%)       |
| 2.97                   | 0.050 (1.68%)      |
| 4.95                   | 0.15 (3.1%)        |
| 11.3                   | 0.17 (1.5%)        |
| 14.0                   | 0.11 (0.77%)       |
| 19.5                   | 0.21 (1.1%)        |
Table 2. Analysis of DO data, using various exception conditions

|                                | Expected DO concentration (ppb) (± standard deviation) |
|--------------------------------|-------------------------------------------------------|
|                                | 0.3         | 1           | 5           | 10          | 20          |
| Average DO concentration over  | 0.272 (±0.0691) | 1.12 (±0.376) | 4.57 (±0.820) | 9.50 (±2.58) | 18.7 (±4.83) |
| the entire measurement time    |                                                        |
| Average DO concentration except| 0.263 (±0.056) | 1.06 (±0.050) | 4.80 (±0.196) | 10.3 (±0.120) | 20.0 (±0.18) |
| initial 1 min data            |                                                        |
| Average DO concentration except| 0.267 (±0.0559) | 1.06 (±0.049) | 4.86 (±0.116) | 10.3 (±0.091) | 20.0 (±0.16) |
| initial 2 min data            |                                                        |
| Average DO concentration except| 0.264 (±0.0533) | 1.06 (±0.048) | 4.89 (±0.089) | 10.3 (±0.087) | 20.1 (±0.16) |
| initial 3 min data            |                                                        |
Figure Captions

Figure 1. Schematic diagram of the H$_2$O$_2$ analyzer

Figure 2. H$_2$O$_2$ decomposition capabilities of various catalysts.

Figure 3. Detection limits of H$_2$O$_2$ measurements

Figure 4. Effects of H$_2$O$_2$ measurement under various DO conditions. Orange circles mean 0.39 ppb H$_2$O$_2$ and blue diamonds means 0.32 ppb H$_2$O$_2$

Figure 5. Verification of H$_2$O$_2$ detection abilities using the on-line H$_2$O$_2$ analyzer

Figure 6. Comparison between the measured the calculated H$_2$O$_2$ values
Figure 1.
Figure 2.
Figure 3.
Figure 4.

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Figure 5.
Figure 6.

\[ y = 0.9371x \]

\[ R^2 = 0.9994 \]
