

# Use of a Hybrid Metrology Approach to Develop Holistic Filtration Solutions in Hydrogen Peroxide

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## ABSTRACT

All semiconductor manufacturers are driving to advance their process efficiency and effectiveness to deliver improved performance. To achieve such improvements with each generation of new semiconductor devices while maintaining high reliability and yield, strict contamination control must be established for process chemicals and gas. Contaminants in these materials can be present in various forms, such as organics, gels, hard particles, anions, cations, polymers, etc., and is typically controlled using membrane-based filtration. To ensure that the appropriate filtration solutions are implemented, a two-step process is required. First, one must identify/characterize the contaminants present,<sup>1</sup> and then use that knowledge to optimize filtration schemes across the supply chain to ensure end to end impurity control.<sup>1</sup>

The goal of the study is to understand the contaminants natively present in semiconductor grade hydrogen peroxide ( $H_2O_2$ ) utilizing a hybrid metrology approach with techniques such as Inductively Coupled Plasma Mass Spectrometry (ICP-MS), Liquid Particle Counting (LPC), Scanning Mobility Particle Sizer (SMPS) and Time of Flight Mass Spectrometer (TOF-MS) to develop a profile of contaminants present. Once such a profile was developed, we evaluated the effectiveness of different filtration media on removal of these native contaminants and compared the results against the effectiveness of the membranes in retaining hard particles in Deionized Water (DIW), a prevalent method for characterizing a filter's retention efficiency.<sup>2</sup>

## INTRODUCTION

Semiconductor device manufacturers keep driving to improve the performance of their chips by increasing transistor density per unit area of chip, but this higher transistor count comes with a greater sensitivity for defectivity as there is continued shrinking of critical particle size.<sup>3</sup> To achieve such improvements with each generation while maintaining high reliability and yield, strict contamination control must be established for process materials. The numerous chemicals used in the manufacturing of a chip are a big source of contaminants and they can take a variety of forms such as particles, gels, and dissolved species such as cations,<sup>4</sup> anions, organics, etc.

For this work, we focused specifically on 30%  $H_2O_2$  due its use in several critical wet etch and clean (WEC) and chemical mechanical polishing (CMP) unit processes. The use of  $H_2O_2$  is projected to exceed 200,000 MT by 2024<sup>5</sup> and is primarily used in blended applications like SPM (Sulfuric Acid – Hydrogen Peroxide Mixture), SC1 (mix of ammonium hydroxide and hydrogen Peroxide), SC2 (mix of hydrochloric acid and hydrogen peroxide) and other proprietary blended formulations. Development of filter-based contamination control solutions traditionally have focused on using standard particles as a measure of contamination retention properties, made using materials such as gold (Au)<sup>4</sup> or polystyrene latex (PSL) beads.<sup>6</sup> Due to its strong oxidizing nature, metrology techniques capable of analyzing  $H_2O_2$  directly at higher concentrations (>15%) are limited. So, to develop a holistic understanding of contamination challenges present in the chemical and identifying performance of the filtration solutions, we need to take a step-by-step approach:

### Part 1: Identify the native contaminants present in the semiconductor grade 30% $H_2O_2$

To understand the quality variations that are a result of packaging used to store and transport the chemical, we tested 30%  $H_2O_2$  from the same lot of chemical but packaged in two different HDPE containers. We utilized techniques that are commonly used in the industry such as LPC and ICPMS to analyze the chemical along with newer techniques such as SMPS and TOF-MS to develop a profile the contaminants. The approach of utilizing multiple metrologies is particularly important so that we can gain a full understanding of the nature of these contaminants that are present in the chemical.

### Part 2: The effectiveness of traditional filtration solutions for contamination control

Traditionally, filter manufactures have utilized standard hard particles like Au and PSL to understand the retention efficacy of the filter membranes. However, as the contaminants are becoming more complex, retention testing with these standard particles is not enough to represent the challenge that the diverse contaminants present in chemical requiring filtration. By characterizing the different native contaminants present, it enables filter manufacturers to develop the appropriate filtration solutions.

## EXPERIMENTAL DESIGN

### Materials and Instrumentation

**Materials:** Semiconductor Grade 30% Hydrogen Peroxide ( $\text{H}_2\text{O}_2$ ) in High Density Polyethylene (HDPE) containers, 90 mm Polytetrafluoroethylene (PTFE) membranes for  $\text{H}_2\text{O}_2$  filtration, Rion KZ-30W Syringe Sampler, Ultra-Pure Water (UPW), 2 Liter (L) Perfluoroalkoxy alkanes (PFA) tank, 25 nm Polystyrene Latex (PSL) nanoparticles, 5 nm Gold (Au) nanoparticles

**Instrumentation:** Rion KS-19F LPC, TSI SMPS 3938, Agilent 8900 ICP-MS, ESI Scout Carbon TOF-MS

### Experimental Setup

For part 1 of the experiment, we attempted to directly analyze the 30%  $\text{H}_2\text{O}_2$  in the two different HDPE containers using the LPC connected to the KZ-30W syringe sampling system, but the LPC reported coincidence errors in the reported data. The coincidence errors were due to extremely high particle counts ( $>100,000$  particles/milliliter [ml]) of chemical. To overcome this measurement challenge, we developed a dilution curve to accurately quantify the  $>30$  nm particles present in the respective 30%  $\text{H}_2\text{O}_2$  containers. The method involved diluting the  $\text{H}_2\text{O}_2$  with UPW at different dilution ratios that did not trigger coincidence errors on the LPC. The measured counts from these dilutions were used to create a concentration curve, that was then used to estimate the  $\geq 30$  nm particles present per ml of the 30% solution. We also grab sampled the liquid from different chemical bottles and analyzed it for additional metrology such as SMPS, ICP-MS and TOF-MS to profile for contaminants other than what LPC can detect.

For part 2 of the experiment, we ran the filtration test using two different PTFE membranes with similar surface properties, but with different pore sizes for the filtration test with membrane B having a smaller pore size than A. Figure 1 represents the test system used to run part 2 of our experiment. For the test, native 30%  $\text{H}_2\text{O}_2$  was poured into a 2 L pre-cleaned PFA tank, and the chemical was filtered dynamically

through a 90 mm coupon holder containing selected PTFE membranes using a centrifugal pump. The chemical downstream of the coupon holder was analyzed (i) in-line, using a slipstream of the filtered chemical directed into a KS-19F at a fixed 10 ml/minute flow rate, and (ii) offline, by collecting samples of the filtered chemical in PFA bottles and testing with SMPS, ICP-MS and TOF-MS.

Additionally, we used a similar set up to run the standard particle retention to calculate the retention efficacy of our membranes in DIW (Figure 2). This is a traditional approach used in the industry where feed is prepared by spiking a known concentration of Au or PSL in DIW which is pressurized using  $\text{N}_2$  gas. The solution is dynamically passed through a 90 mm coupon holder with membranes installed. The filtrate is either analyzed using ICPMS or Spectrometer to calculate the filtration efficiency of the membrane.

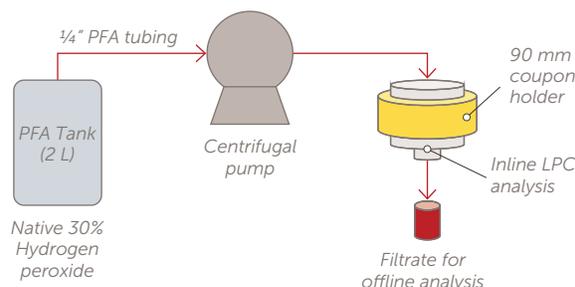


Figure 1. Schematic diagram of the experimental system used for the filtration test.

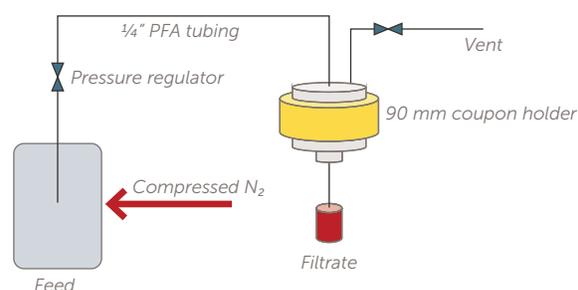


Figure 2. Schematic diagram of the experimental system used for the filtration test.

## RESULTS AND DISCUSSION

### Part 1: Native contaminants present in the semiconductor grade 30% H<sub>2</sub>O<sub>2</sub>

Using the LPC, the 30% H<sub>2</sub>O<sub>2</sub> from the same lot of chemical but packaged in different HDPE bottle were analyzed using the dilution model. Using the model, we were able to observe significant differences in the ≥30 nm particles/ml present between bottle 1 and bottle 2. This difference would not have been observable if the chemical was measured directly at its full concentration due to the high particle counts causing coincidence errors during particle counting. When there are too many particles present in the chemical, the measurement cell within the LPC gets saturated with particles, resulting in the system measuring counting multiple particles as a single large particle, and giving lower counts than the actual real values and alerting the tool user that there is a measurement error.

Figure 3 shows the cumulative counts of particles ≥30 nm that were measured on the LPC. While Bottle 1 had ~500k particles/ml present in it, bottle 2 has ~900k particles/ml, roughly around 40% higher count in particles between the bottles. The data highlights that even though the H<sub>2</sub>O<sub>2</sub> was from packaged using the same lot or batch of chemical, there is a notable difference in the particle counts from each bottle, highlighting the impact packaging container has on final chemical quality.

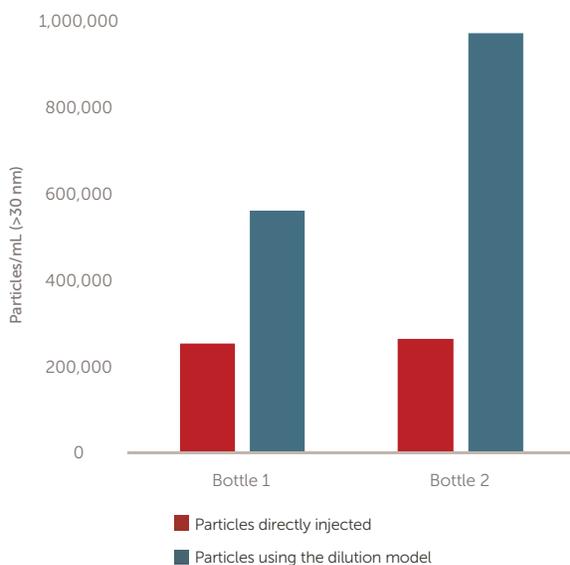


Figure 3. Impact of coincidence errors for estimation of real particle counts in 30% H<sub>2</sub>O<sub>2</sub>.

For the offline analysis of 30% H<sub>2</sub>O<sub>2</sub>, Figure 4 shows the measured concentrations of 30 individual elements, common elements of concern for semiconductor manufacturing<sup>5</sup> from ICP-MS. The data shows that both bottles having similar low (<200 part per trillion [ppt]) metal profile with comparable levels of elemental contaminants with Na, K, Ca, Cr at highest concentration for both the bottles.

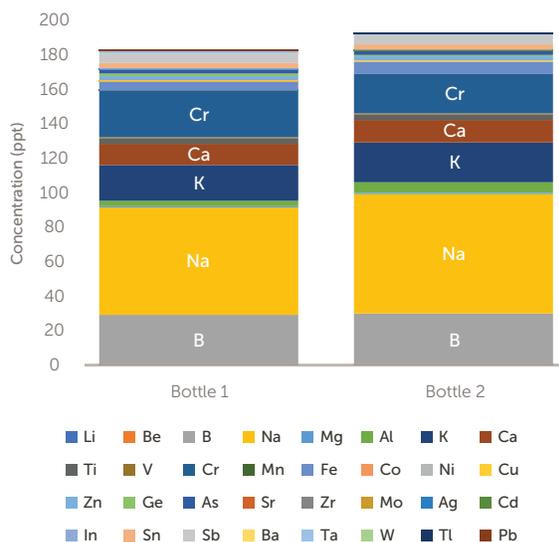


Figure 4. Total metals in 2 different grades of 30% H<sub>2</sub>O<sub>2</sub>.

Next, we looked at the results from the analysis of the chemical using the SMPS, the technique allows us to get an insight into the contaminants (particles or residues) present in the chemical sized between <30 nm, not visible using the LPC. But similar to the results from the LPC, SMPS results shown in Figure 5 show higher signal of contaminants in bottle 2 in comparison to bottle 1 with the difference most evident in the counts for contaminants sized between 5 – 15 nm.

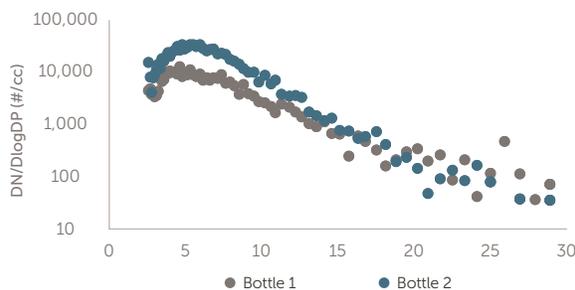


Figure 5. Difference in particles <15 nm between Bottle 1 and 2 using SMPS.

Finally, we collaborated with Elemental Scientific to analyze the  $H_2O_2$  using their SCOUT Carbon which analyzes the 30%  $H_2O_2$  using electrospray ionization for sample introduction followed by analysis using a TOF-MS. The system provided a semi-quantitative report for different classes of compounds present in the peroxide as shown in Figure 6. The results show a relatively higher concentration of Nitrogen (N), Phosphorous (P), and Carbon Hydrogen Oxygen (CHO) compounds in Bottle 2 while Bottle 1 has a higher signal for Sulfur (S) class compounds.

The results from the TOF-MS analysis of the chemical correlates with the results from the LPC and SMPS. When we review the results from all the analysis done, the data indicates that while particle analysis, especially in smaller sizes <40 nm is important – additional analysis of the chemicals helps develop a better understanding of these contaminants. In this case, the data would indicate that the higher particle signal from Bottle 2 is potentially due to N and CHO class organics seen by TOF-MS as the elemental analysis by ICP-MS indicated equivalent cleanliness for the samples.

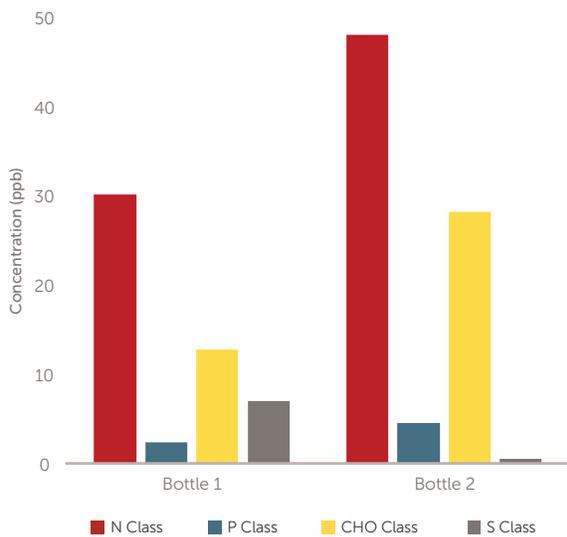
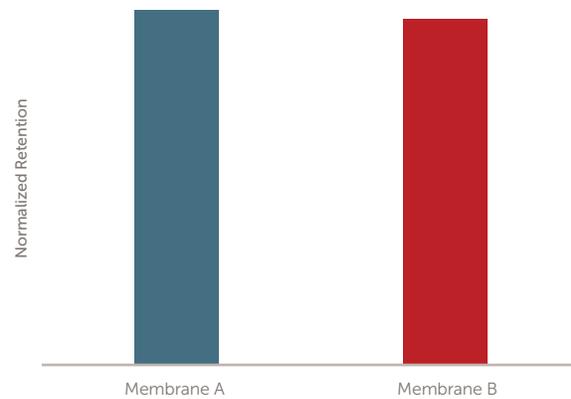


Figure 6. prepFAST Carbon Organics in native  $H_2O_2$ .

## Part 2: Retention with different Filter Media in Native Peroxide – Standard Particle Retention

We selected two PTFE membranes with similar surface energies but different pore sizes to understand their relative effectiveness in filtering the 30%  $H_2O_2$ . First, we evaluated the efficiency of both the membranes in retaining standard test particles in DIW with challenged 25 nm PSL and 5 nm Au. Figure 7 shows the results from the tests, with the larger PSL particle retention test showing equivalent levels of retention, whereas with the smaller 5 nm Au nanoparticles, we see a difference between the membranes in retention efficiency with membrane B retaining ~22% more Au particles than membrane A.

### 25 nm PSL Retention



### 5 nm Au Retention

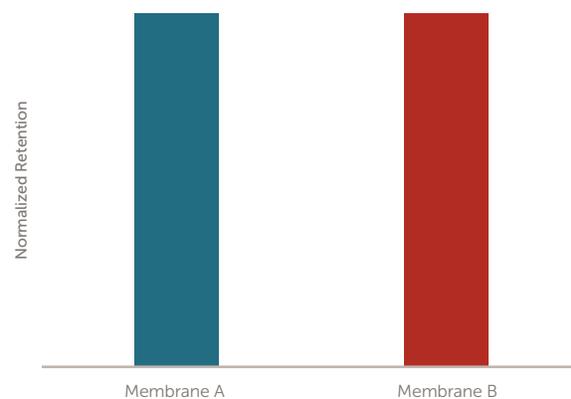
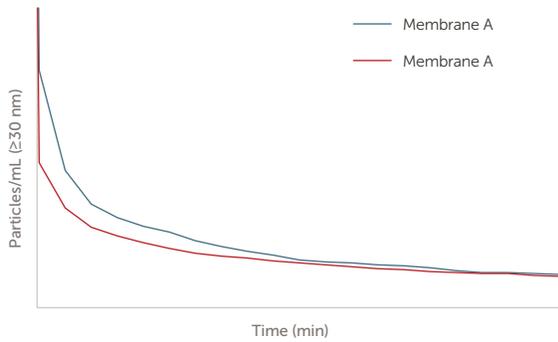


Figure 7. Standard Particle retention between 2 different membranes

The filtrate from both membrane A and B were analyzed in-line using the LPC ( $\geq 30$  nm) as seen in Figure 8. The graphs show the particle shedding and baseline behavior between the 2 membranes. Membrane B was cleaner in start-up and showed significantly better retention performance than membrane A.

### Particle Shedding Using Inline LPC



### Particle Baseline Using Inline LPC



Figure 8.  $\geq 30$  nm particles measured in the 30%  $H_2O_2$  filtrate.

During the filtration test, we also collected aliquots of the filtered chemical for analysis using offline tools. First, we evaluated the filtrate using ICP-MS to understand the elemental composition of the chemical and understand if the membranes had any capability for removal of metallic/elemental contaminants. We focused on metals that are of interest to the suppliers and pose a critical challenge in the semiconductor manufacturing process.<sup>5</sup> In Figure 9, the metal removal efficiency for the membranes, calculated by subtracting the concentrations

of the respective elements in filtrate from the respective feed, shows Membrane B does well in retaining elemental contaminants, especially compared to membrane A, with elements such as Sodium (Na), Aluminum (Al), Potassium (K), Iron (Fe), Nickel (Ni) and Zinc (Zn) removed more effectively than membrane A. Membrane A had a similar removal performance for Magnesium (Mg), while having better removal for Copper (Cu) and Silver (Ag).

### Metal Removal Efficiency in 30% $H_2O_2$

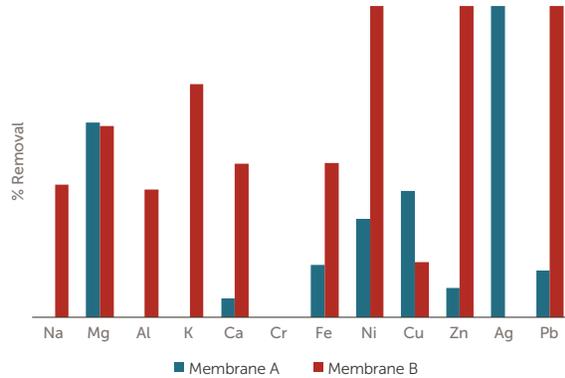
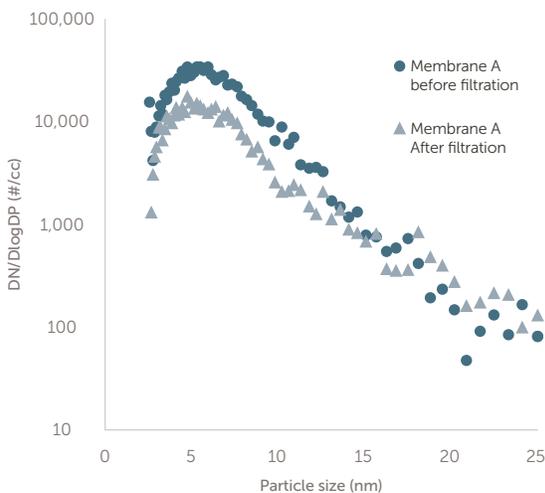


Figure 9. Metal Removal Efficiency in 30%  $H_2O_2$  – common metals of interest.

Similarly, the filtrate was also analyzed by SMPS to understand if the selected membranes can remove the  $< 30$  nm contaminants present in the 30%  $H_2O_2$ . We analyzed the samples pre filtration (directly from the feed) and the filtrate collected downstream of the membrane. In Figure 10, data from SMPS analysis shows that both filter membranes have removed contaminants from the chemical feed, improving its overall cleanliness and verifying the impact of filter media in removing contaminants sized  $< 30$  nm.

### Particle Size distribution of sample A before and after filtration



### Particle Size distribution of sample B before and after filtration

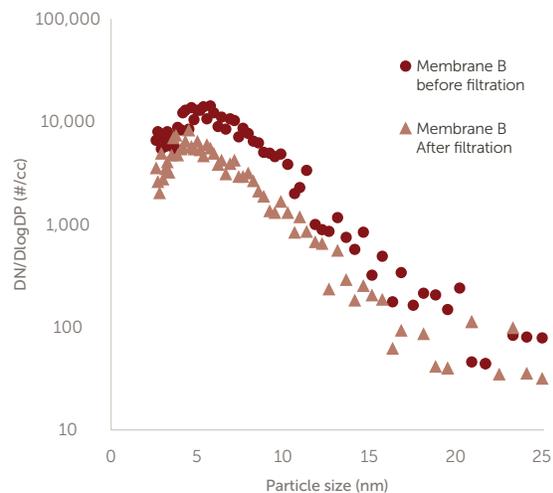


Figure 10. Particle Size distribution measured by SMPS showing results of before and after filtration of membrane A and B.

## CONCLUSION

In this paper, we first demonstrate the importance of utilizing multiple sensitive metrology techniques to understand the native contaminants present in the semiconductor grade H<sub>2</sub>O<sub>2</sub>. By analyzing all the collected data holistically, we are not only able to develop a profile of the type of contaminants present in this high purity semiconductor grade chemical, but also see differences in the quality of chemical in different containers even though they were sourced from the same batch at the supplier.

Once we were able to characterize the contaminants better, we used the same techniques to understand the retention efficacy of two different filter membranes, each with unique sieving and non-sieving properties, and develop an understanding of filtration beyond standard hard particle retention. This type of testing and data analysis will help in the development of optimal filtration solutions, that target specific classes of contaminants that are relevant to the chemical of interest and help provide effective micro contamination control.

## References

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This paper was first presented at the SPCC conference in 2024. <https://www.entegris.com/en/home/about-us/events/surface-preparation-and-cleaning-spcc-2024.html>

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