Application Note

ULR CL17sc success at a semiconductors manufacturing facility in TX

Introduction

Ultrapure water for semiconductor, pharmaceutical, chemical, or beverage production has strict limits on presence of contaminants including oxidants or reducers. Incoming source water is usually chlorinated and undergoes dechlorination with either granulated activated carbon (GAC) or chemicals such as sodium bisulfite (SBS). Dechlorinated water flows through additional treatment, frequently involving RO filtration when the operators should maintain low levels of disinfectant, while not allow excess of oxidants to damage the membranes. It has been shown that prolonged exposure of RO filters to chlorine above 38 ppb (based on 1000 ppm-hr over 3 years) is detrimental to the membrane structure and integrity, while absence of the disinfectant promotes biogrowth and causes loss of recovery. To maintain this delicate balance, the operators must be able to accurately monitor chlorine concentration and addition of dechlorinating chemicals.

Problem

Dechlorination is used in the UPW preparation cycle for electronics, as well as other industries. The effects of GAC channeling and the issues related to underfeeding/overfeeding dechlorinating agents are well-known in the industry. The channeling and underfeeding SBS will manifest in creating an excess of chlorine attacking the RO membrane's polymeric structure and causing irreversible damage. The overfeeding SBS leads to increase in biofilm formation due to the lack of biocide in the water. Besides the added cost and increase in biofouling, excess of sulfites leads to depletion of dissolved oxygen and proliferation of sulfur-reducing bacteria (SRB) in the water. SRB can cause microbially influenced corrosion, rotten egg smell due to formation of hydrogen sulfide (H_2S), slimy coatings, and brown foaming. All these factors driving either excess, or lack of chlorine will diminish the RO membranes performance (flux) necessitating better monitoring and process optimization. Currently, RO feedwater monitoring and proportional addition of SBS is done with either grab sample analysis alone, or in its combination with continuous measurement of redox potential (ORP). Well known deficiencies of this approach do not make it the method of choice and such monitoring cannot provide effective optimization. There is a need for a simple and reliable instrumentation measuring chlorine directly, accurately and in a substantially continuous manner; able to monitor the exposure of the RO filters to chlorine to understand its impact on the membrane efficiency and life span.

Solution

The need to maintain disinfectant residual to keep biofilm from growing excessively while at/below 38 ppb to ensure life expectancy of the RO membranes dictates the necessity to monitor residual chlorine accurately at such low levels. The Ultra-Low Range (ULR) CL17sc chlorine analyzer uses colorimetric method to measure total chlorine residual with unparalleled accuracy provided by the low limit of detection (LOD) of 8 ppb. Accurate chlorine readings reported every 150 seconds will show a complete picture of dechlorination process, detect any excursions of chlorine above the set limit, and help to manage RO membranes properly. The Cumulative Chlorine Counter™ function of the analyzer calculates and shows on the screen how much chlorine has passed through the membrane at any given time. All this helps to ensure specified quality of RO feedwater of produced UPW, and by extension the quality of the manufactured products ranging from semiconductors to drinking water.

Case Study

A study conducted at a semiconductor facility in Texas was to help optimize their SBS feed control in the UPW preparation cycle. At the time of test, the UPW personnel relied on a standard CL17 analyzer and an ORP sensor to monitor and control dechlorination. The analysis of the time-stamped data showed that such correlation could not be used for process control. As follows from the data presented in Figure 1, logged extremums of the ORP readings did not match the max/min chlorine concentrations registered at the same time. ORP readings implied chlorine concentrations were between 25 and 42 ppb for the duration of the test whereas direct DPD chlorine analysis revealed an actual concentration range of 7 to 609 ppb between minimum and maximum. The latter correlation showed that the ORP probe was likely dysfunctional, given the reversed Min and Max correlated values (Figure 1). This observation highlights how dangerous it can be to rely solely on ORP readings to control dechlorination process.

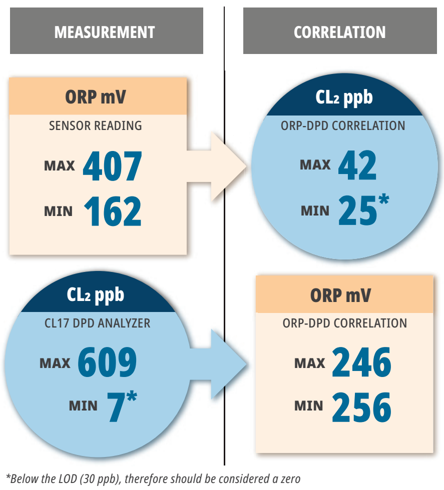

Figure 1. Attempt to correlate ORP and chlorine concentration readings: top row - Min and Max ORP readings vs. corresponding results of DPD chlorine analysis; bottom row – Min and Max DPD readings vs. corresponding ORP values (reversed correlation).

The personnel knew they were overfeeding SBS, however could not quantify it using standard instrumentation, therefore used a Hach DR1300 FL handheld using fluorometric method to verify ULR chlorine and sulfite concentrations. A test involving ULR CL17sc process analyzer was conducted to quantify chlorine response and optimize the SBS feed. The test results (Figure 2) showed that optimal SBS feed to maintain ~40 ppb residual chlorine would be at 60-70% of the current rate, which would provide significant chemical cost savings justifying implementation of the ULR CL17sc analyzer.

After the test, the UPW facility management decided to halve the SBS feed rate (Figure 3) and purchased the analyzer.

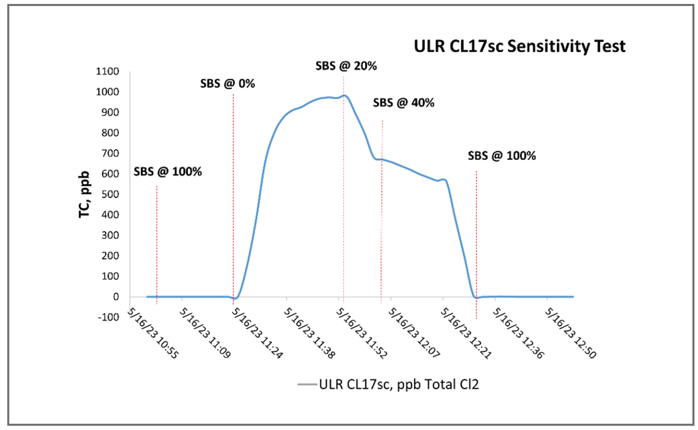

Figure 2 – Dechlorination optimization test demonstrated that SBS feed could be safely cut in half and even more.

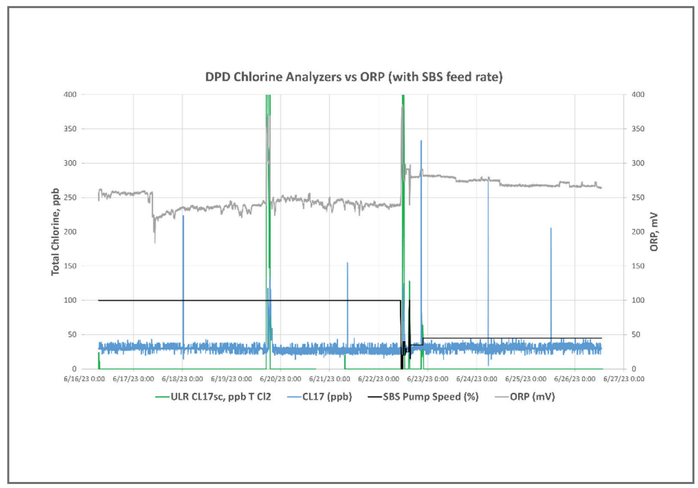

Figure 3. Trend demonstrating ULR CL17sc readings vs ORP and reduction in SBS feed.

Outcomes

Application of the ULR CL17sc in combination with DR1300 FL handheld fluorometer helped to keep the SBS feed under tighter control. As demonstrated by the conducted field testing, implementation of ULR CL17sc for monitoring of RO feedwater dechlorinated with SBS can save enough money only on the chemicals to justify purchase of the analyzer.

The indirect cost saving encompassing prolonged life of the RO membranes, assurance of produced water quality, overall decrease of maintenance efforts would provide additional reasons to adopt new analytical instrumentation for process optimization in UPW production.

The ULR CL17sc instrument will provide highly accurate direct chlorine measurements at minimal maintenance efforts supporting all chemical and labor cost savings and projecting the full ROI in one to two years on average.

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