Application Note

ULR CL17sc vs standard CL17sc and ORP at a semiconductor manufacturing facility

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) further contributing to membrane fouling. 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. 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 chlorine presence 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 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 microprocessor manufacturer was to compare performance of the ULR CL17sc against the existing combination of the legacy CL17 analyzer and ORP sensor. In this trial the test showed that the ORP sensor did not adequately reflect the magnitude of the chlorine concentration changes measured by the two colorimetric chlorine analyzers (Figure 1). It is clearly seen during chlorine excursions and at the end of the test when chlorine concentration was steadily growing (Figure 1 and 2). The data analysis allowed to establish the validity of the results in terms of accuracy. To understand this, the readings were compared to the LOD of the corresponding analyzers (Figure 2).

The comparison of the collected data presented in Table 1 and reflects each analyzer's LOD & LOQ to determine how frequently chlorine levels fall within the established target range (30 ppb). The results of the legacy CL17 showed that while chlorine was at the safe levels, the amount of SBS was excessive almost all the time (Table 1). The results of the ULR CL17sc showed that chlorine was indeed at the safe levels >99% of the time and SBS was likely in excess in about 38% of the time (Table 1). Therefore, the SBS feed was optimal in >60% of the time maintaining chlorine at the safe level for the membranes, while enough to prevent excessive biogrowth. At the same time, the ORP readings were very arbitrary

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and could never provide the expected level of process optimization (Table 1).

The data generated by the ULR CL17sc provided assurance that the site was consistently dechlorinating to safe chlorine levels while maintaining it at the right amount to prevent excessive biofouling. A potential overfeed of SBS was also indicated, providing an opportunity for further cost savings.

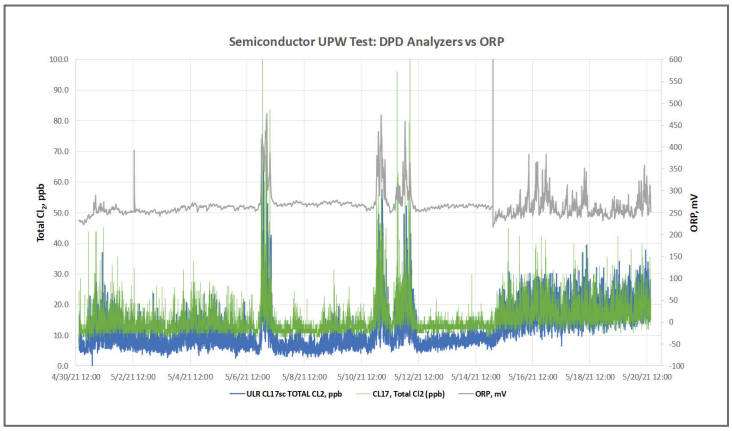

Figure 1. Comparison of direct total chlorine readings gbenerated by two colorimetric analyzers vs. ORP.

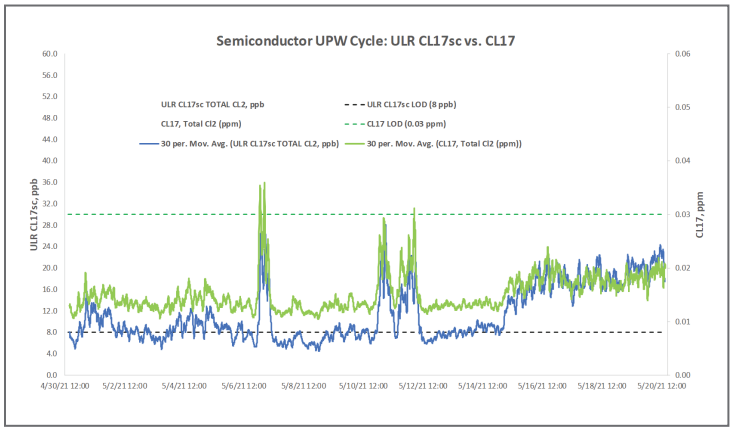

Figure 2. Comparison between two colorimetric analyzers vs. their respective LOD. Moving averages are used for illustration purpose only, not for any calculations presented in Table 2.

Table 1: Comparison of the data collected during the test regarding LOD & LOQ demonstrating credibility of the results.

Sensor	LOD (ppb)	Customer Set Chlorine Threshold (30 ppb)	Safe Chlorine level (< 30 ppb)	Unsafe Chlorine Level (> 30 ppb)	Optimal Chlorine Levels (>LOD to <30 ppb)	Potential SBS Overfeed (Cl2 < LOD)
CL17	30	At LOD (presence/absence)	98.7 %	1.3 %	0.0 %	98.7 %
ULR CL17sc	8	Above LOQ (24 ppb) accurate determination	99.3 %	0.7 %	61.0 %	38.3 %
ORP	NA	300 mV*	93.7 %	6.3 %	NA	NA
		266 mV**	62.5 %	37.5 %	NA	NA

* General industry recommendation ** Derived from actual chlorine readings (ULR CL17sc)

Outcomes

Application of the ULR CL17sc helps to keep the SBS feed under tighter control and can provide enough direct chemical costs reduction 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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