

Colorimetric vs Amperometric Technologies

Introduction

Like Oxidation-Reduction Potential (ORP or RedOx), another electrochemical instrumentation used by some utilities to control chlorination/dechlorination is amperometric sensors. Unlike ORP, amperometric method provides a better correlation to chlorine concentration, being more selective. However, there are other issues in applying it successfully, especially to control the absence, intermittent, or very low concentrations of chlorine. This becomes a problem because amperometric sensors must see oxidants in sample to provide sustainable operation. Therefore, at intermittent sample flow or chlorine feed, or in a consistent absence of chlorine, amperometric probes can lose their sensitivity to chlorine and require more frequent interactions. This happens due to various factors, from simple fouling of the probe's surface to the development of layers of organic or inorganic coatings on the electrodes preventing the necessary electrochemical reactions.

The main benefits provided by any electrochemical technology, e.g. amperometric sensors, are reagentless operation and fast response to rising chlorine levels based on continuous nature of the measurements. When amperometric sensors are fully functional, their performance and accuracy depend on other parameters of the sample, such as pH, sample flow, pressure, as well as the sensor-related aspects – zero/slope calibration accuracy and stability, electrolyte longevity, membrane, or electrode fouling, to name a few. Some membrane-less (bare electrode) amperometric systems feature automatic cleaning, which is useful, while such systems much more pH-dependent and must compensate it using constant pH measurements correlated to chlorine concentration mathematically. Otherwise, amperometric sensors rely on either external buffer feed then losing the reagentless appeal, or on internal buffering of the electrolyte inside the membrane cap, then losing the membrane-less appeal.

On the other hand, the colorimetric technology is based on a batch analysis and its cyclic nature that involves taking a sample, adding chemical reagents, and measuring light absorbance. Such analysis usually takes one to two minutes to complete. Therefore, the initial response of an amperometric sensor is reported immediately and can help to reflect change in the chlorine concentration earlier on, while colorimetric methods provide uncompromised accuracy, Figure 1.

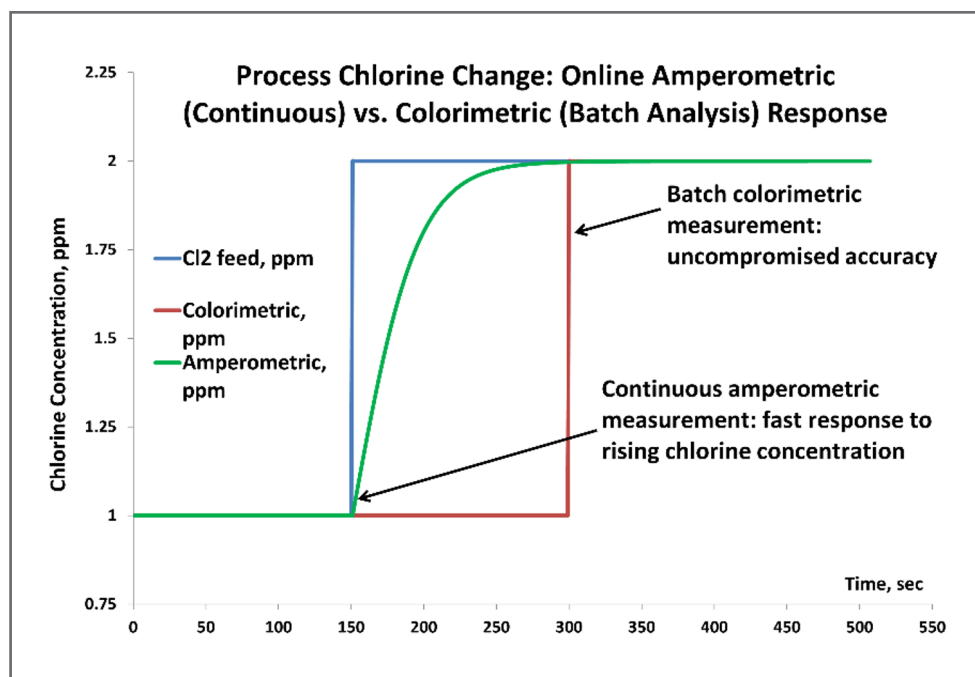


Figure 1: Response of colorimetric (batch) and amperometric (continuous) analyzers to rising chlorine concentration.

As seen from the diagram in Figure 1, full accuracy of the measurement is achieved in approximately the same time for both methods. Any continuous measurement is characterized by the sensor's response time, e.g., T_{90} or T_{95} , which represents the time to achieve 90% or 95% of the maximum signal level, or accuracy. This characteristic, usually specified between 60 s and 120 s, varies from sensor to sensor and depends on the sensor's design and sample conditions. For comparison,

batch analysis of chlorine based on the standard DPD method achieves >95% accuracy in 100–150 s and is independent of sample pH being major contributor to the uncertainty. Sample temperature and flow should be within the specified range and there are known interferences to the DPD colorimetric method to consider. Main point of such comparison is that while amperometric sensors respond to rising chlorine faster, both methods achieve fully accurate reading in about the same time!

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When it comes to accuracy of these compared methods, we must remember that amperometric sensors are as accurate as the reference method for their calibration. With this, amperometric sensing technology is based on consumption of the electrodes and therefore such sensors must be calibrated to maintain adequate accuracy. Since the electrodes and electrolyte wear out during normal operation, calibration of the sensors is a routine reality that may become a maintenance headache depending on the sample conditions. For instance, calibration stability depends on how stable the sample pH, temperature, and chlorine concentration. The larger the swings in those parameters, and/or the higher the chlorine concentration, the more frequently amperometric system will need calibration. In low-chlorine conditions the maintenance requirements may add chemical zero calibration, and in UPW conditions too low conductivity may be

detrimental to adequate performance of amperometric sensors. Therefore, the amperometric sensor's specifications published by the manufacturer should be well understood in the context of all these aspects.

On the other hand, colorimetric technology provides a very stable calibration based on the Lambert-Beer's physical law and may need to be only verified using a reference analysis. Usually, colorimetric analyzers require no recalibration regardless of sample conditions, as long as they are within the manufacturer's specifications. From the specifications standpoint, the Hach Ultra-Low Range CL17sc analyzer has the lowest proven Limit of Detection among the competition – 8 µg/L (ppb). This specification is based on extremely stable calibration at the low end and the design providing high precision and resulting accuracy of chlorine measurements.

Summary

In summary, both colorimetric and amperometric methods for monitoring and controlling chlorination/dechlorination in water treatment offer distinct advantages and drawbacks.

- The colorimetric method, employing batch analysis, boasts higher accuracy and independence from other parameters such as pH, flow, pressure.
- On the flip side, the amperometric method is reagent free, offers continuous readings, but prone to interference from sample parameters such as pH, flow, pressure and temperature.
- Implementing amperometric technology requires much better understanding of the nature of the sample to be tested and the application realities, making it difficult to perform consistently without significant initial evaluation. Hence, utilities must carefully evaluate their specific application and the pros and cons of each monitoring method.



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