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Should you install an online hardness analyzer?

Manufacturers have improved the reliability of online hardness analyzers, increasing the feasibility to automate many water treatment units. The most common applications are boiler feedwater quality and cation softener end-of-run length. Proper selection and implementation of online hardness analyzers is critical to maximize return on investment.

As shown in Table 1, there are two types of analyzers: ion specific electrode (ISE) and spectrophotometric. Both analyzers use an EDTA-based titration;* however, the detector technology is different.

TABLE 1. Summary of hardness analyzers

Parameter	ISE analyzer	Spectrophotometric analyzer
Measurement	Calcium	Total hardness
Interferences	High alkalinity, high sulfite, filming amines, iron	Suspended solids, highly colored species
Optimal sample configuration	Dedicated sample	Dedicated or sequenced samples

ISE unit. Ion selective electrodes use a polyvinyl chloride membrane that is selectively permeable to specific ions in solution. The most commonly used ISE is a pH probe. ISE uses the same principal of the galvanic cell—measuring the electrochemical potential across the membrane and comparing it to a reference electrode. The strength of the net electrochemical potential is directly proportional to the concentration of the selected ion.

For calcium hardness measurements, calcium ions selectively transfer across the membrane to the measurement chamber and complex with EDTA—thus changing the electrochemical potential of the solution. The difference between the electrochemical potential of this solution and reference solution is directly proportional to the calcium concentration.

Primary sources of error for the ISE are sample temperature and total ionic strength of a sample. To minimize these errors, the sample alkalinity must be below 250 ppm as $CaCO_3$, and the sample temperature should be 41°F–104°F (5°C–40°C). Strict sample flow control eliminates streaming current effects. Other interferences include materials that can physically foul the probe, such as filming amines, and chemicals that poison the electrode, such as sulfite.

This unit is best suited for continuous measurement of a single stream due to the requirement for equilibration time between sample streams. The typical probe life is six months. Also, the unit requires monthly replenishment of one reagent and periodic pump refurbishment.

Spectrophotometric method. This method uses two reagents, EDTA and an indicator to conduct a titration using a spectrophotometric detector. EDTA complexes both calcium and magnesium ions, yielding a measurement of total hardness. The spectrophotometric method is more accurate than the visual colorimetric method to detect the color change at the endpoint of the titration.

The primary source of error for this method is sample temperature. To minimize these errors, the temperature must be 41°F–104°F (5°C–40°C). Other interferences include suspended solids or highly colored materials.

This unit analyzes using a batch method and is well suited to alternately sampling two different sample streams. Likewise, it requires monthly replenishment of five reagents and quarterly pump refurbishment. The newest units can alternately sample two streams.

Applications engineering. Online analyzers do not substitute for routine manual measurement. More important, the manual measurement becomes a confirmation of the online measurement. Online hardness analyzers require more maintenance than online pH meters due to replenishing reagents, refurbishing pumps, replacing tubing and recalibrating.

To ensure reliable operation, operators often outsource the maintenance for these analyzers. Matching the objective of the online measurement with selection of the proper sample stream is critical to a successful application. For example, the ISE-based analyzer is the best choice to monitor the endpoint of a softener due to the advantage of continuous measurement of the gradually increasing hardness concentration.

Conversely, the spectrophotometric unit is the best choice to sequentially monitor more than one softener effluent stream, even though the unit generates fewer data points. An example of a misapplication is surface condenser condensate. Although an online hardness analyzer will provide a confirmation of a cooling water leak, an online conductivity meter provides a more robust and economical detection method.

The decision to install an online hardness analyzer requires a careful assessment of the objective, sample location and maintenance resources. Improper assessment or implementation efforts are costly, resulting in poor performance or abandoned instruments. HP

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* Ethyl-diamine tetra-acetic acid.