Application Note 122

High-Range Hardness APA 6000

Introduction

Water hardness is defined by the amount of divalent cations contained in a sample and is expressed in mg/L (ppm) as $CaCO_3$. Calcium and magnesium are normally the only ions present in significant concentrations. In water samples with a hardness level less than 10 mg/L, the hardness can be measured by direct colorimetric methods. Colorimetric methods rely on an indicator dye that changes color upon binding hardness. In these methods, the extent of color change of the dye gives a measure of hardness in the sample.

Titrimetric Method of Analysis

When hardness exceeds 10 mg/L, direct colorimetric methods fail. At these higher levels, it is necessary to use an alternate method such as a titration with a chelant in the presence of a colorimetric indicator. Methods such as these are appropriately called titrimetric methods.

The hardness titration is actually a back-titration. An indicator dye is added and is complexed with hardness. A chelant is added to remove the hardness from the indicator. After all the hardness present in the sample is bound to chelant, the indicator dye changes color. This color change is called the equivalence point. Therefore, in the back titration, the amount of added chelant necessary to reach the equivalence point gives a corresponding measure of hardness in the sample.

Conventional titrations are performed by adding aliquots of titrant to a buffered sample in the presence of an appropriate indicator until the equivalence point is met. An automated version of these titrations on an instrument platform would be time-consuming and expensive, as it would require the use of several pumps. Also, such an instrument would only be able to cover a limited range of concentrations.

Carrierless Sequential Injection Analysis Technology

The High-Range Hardness APA 6000 instrument uses CSIA technology (Carrierless Sequential Injection Analysis). Using CSIA, performing an automated titration is a simple task.

The High-Range Hardness APA 6000 instrument uses EDTA chelant as the titrant solution, Calmagite as the indicator dye, and AMP as the buffer at pH 10. The titration is performed in CSIA by first mixing precisely measured aliquots of sample and indicator, then “sandwiching” a plug of titrant solution between two plugs of a buffered sample-indicator mixture in a coil. As the solution moves through the reaction coil, the titrant plug disperses to create a concentration gradient at the interface where the titrant and sample-indicator solutions meet. The concentration gradient takes the shape of a peak. An equivalence point (where the concentration of titrant equals the sample concentration) exists on each side of the titrant plug. Therefore, it is the volume of solution between these equivalence points, also expressed as the peak width, which gives a measure of hardness in the sample.

A CSIA titration is a one-step titration because the plug of titrant is added all at once, rather than in portions, as with a traditional titration. Also, since the shape of the titrant gradient peak is of exponential character, the measured peak width correlates to the logarithm of sample concentration. Therefore the instrument can cover a wide concentration range, in this case 10 to 1000 mg/L as $CaCO_3$ of total hardness.

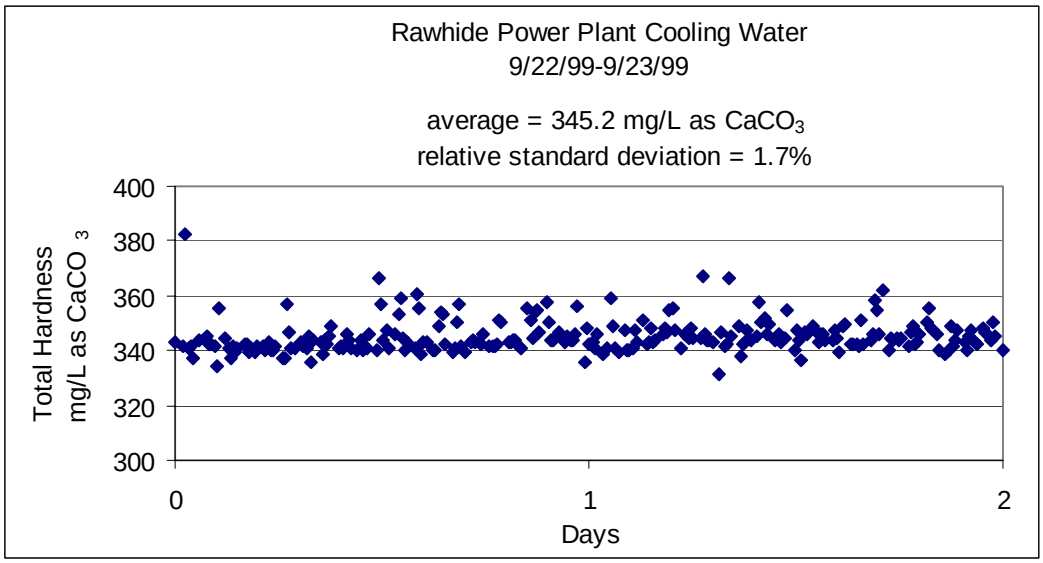
The technology of the APA 6000 platform provides high reproducibility in the dispensation and dispersion of the titrant plug. This reproducibility combined with a 4-point calibration, allows the instrument to deliver accurate and precise measurements over the entire operating range. Since the instrument software uses inflection points in the titration curve rather than a predetermined absorbance value, the measurements are not as sensitive to sample color and treatment chemicals.

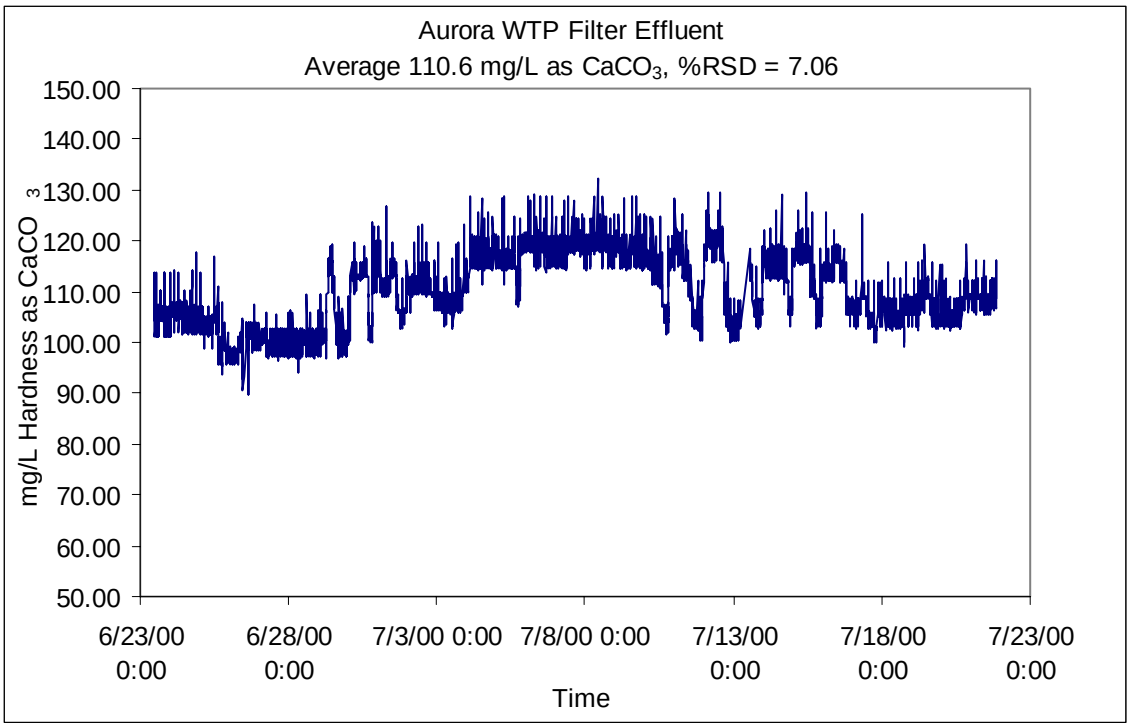
Applications

In addition to variable levels of hardness, many raw waters also contain heavy metals that interfere even at trace levels. Even though heavy metals contribute to the total hardness and therefore should be measured, they cause problems because they also interfere with the indicator dye. The High-Range Hardness APA 6000 uses a masking agent (Magnesium-CDTA reagent) prior to the titration step. Under the proper reaction conditions, the CDTA chelant removes all bound heavy metals from the indicator that were present in the sample, exchanging one magnesium for each bound heavy metal. This allows the heavy metals to contribute to the total hardness measurement due to the additional magnesium added (calcium, magnesium, heavy metals) without interfering with the measurement value.

Many ground waters also contain high levels of carbonate alkalinity. An acid digestion is performed in the High-Range Hardness APA 6000 prior to the titration step to remove carbonates in the sample that would precipitate with hardness at the pH of the titration. After digestion, the strong buffering capacity of the reagents brings the sample to the proper pH for the titration.

The graphs below illustrate the use of the High Range Hardness APA at a power plant and a drinking water facility. Total hardness was determined for the cooling water at the power plant and the final effluent at the drinking water facility.





Conclusion

In summary, the High-Range Hardness APA 6000 instrument is well suited for measurements in both raw and finished waters. It is free of heavy metal and carbonate interferences and covers a wide range of concentrations. Two sample streams can be connected to one instrument, allowing the end-user to collect hardness information on both the raw and finished waters. Combined with its networking capabilities, the High-Range Hardness APA 6000 is ideal for the monitoring of water softening processes, cooling water in power plants and raw water and final effluent from drinking water facilities.

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