Application Note AN-T-084

Total, calcium, and magnesium hardness in water samples

Fully automated determination in colored and colorless water samples by photometric titration according to ASTM D8192

Water hardness is mainly caused by calcium and magnesium ions. Over time, excessively high water hardness can negatively affect water systems and pipes. Accurate and reliable monitoring of water hardness is important for protecting company assets. Controlling the water hardness can decrease the risk of clogging and improve heat transfer.

ASTM D8192 describes the photometric titration of the total, calcium, and magnesium hardness in water with an optical sensor for objective endpoint indication, increasing precision and reliability. The method is suitable for both colored and colorless samples such as groundwater, surface water, wastewater, and drinking water. Using a fully automated OMNIS system equipped with an Optrode ensures that the sample preparation and analysis are repeatable. This increases the precision and reliability, allowing accurate determination of these parameters.

SAMPLE AND SAMPLE PREPARATION

This application is demonstrated on wastewater (moderate yellow hue), tap water, and leachate. No sample preparation is required.

EXPERIMENTAL

The determination is carried out on an automated system consisting of an OMNIS Sample Robot S, OMNIS Dosing Modules, and an OMNIS Advanced Titrator equipped with an Optrode (Figure 1).

Figure 1. Fully automated system consisting of an OMNIS Sample Robot S, OMNIS Dosing Modules, and an OMNIS Advanced Titrator equipped with an Optrode.

In the first titration, the total hardness is determined. The calcium hardness is determined in a separate titration. The magnesium hardness is subsequently calculated from the difference of the two titration results.

An appropriate amount of water sample is pipetted into the titration beaker. For the total hardness determination, Eriochrome Black T indicator solution and a buffer solution (pH 10) consisting of sodium tetraborate and sodium hydroxide are added to the sample. For the calcium hardness determination, sodium hydroxide and hydroxyl naphthol blue indicator solution are added to the sample. The prepared samples are then titrated with standardized EDTA until after the equivalence point.

RESULTS

Results are summarized in Table 1. Example titration curves are displayed in Figures 2 and 3.

Table 1. Results for the total, calcium, and magnesium hardness according to ASTM D8192 on a fully automated OMNIS system. TH = Total hardness, CaH = Calcium hardness, and MgH = Magnesium hardness, all expressed as mg/L CaCO3.

Sample (n = 6)	TH (mg/L $CaCO_3$)	CaH (mg/L $CaCO_3$)	MgH (mg/L $CaCO_3$)
Wastewater	261.5 ± 0.2	202.9 ± 0.2	58.6 ± 0.3
Tap water	351.6 ± 0.1	267.1 ± 0.1	84.5 ± 0.1
Leachate	87.8 ± 0.2	75.4 ± 0.3	12.5 ± 0.3

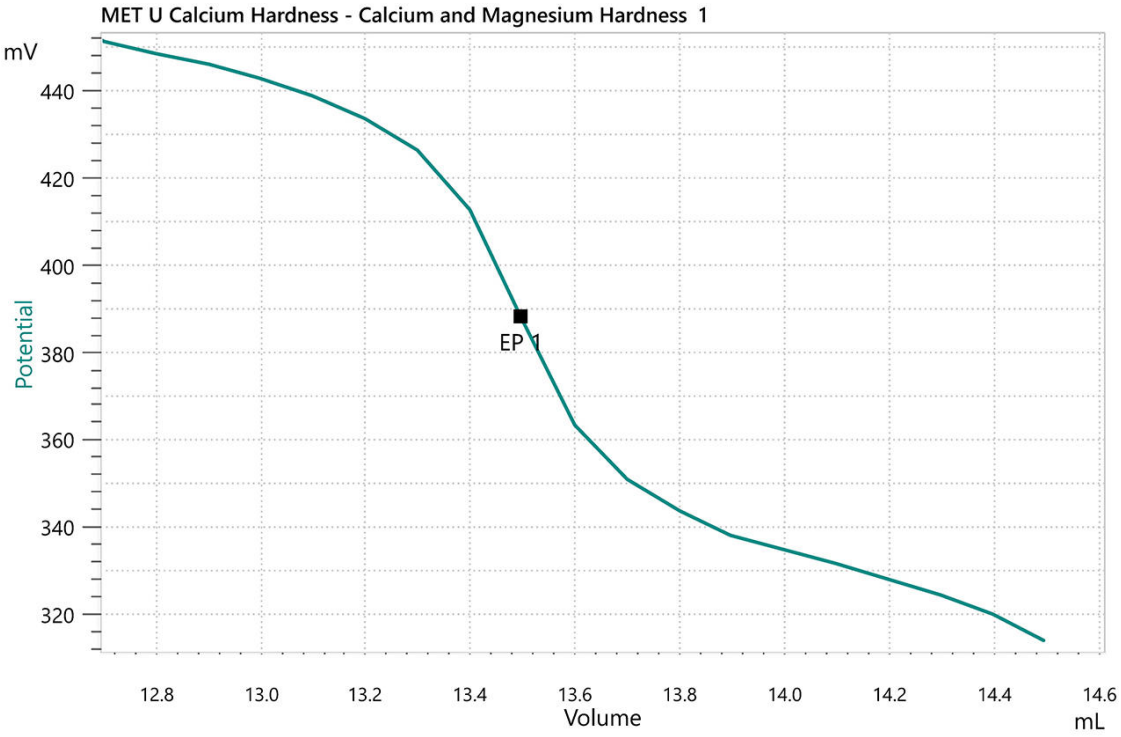

Figure 2. Titration curve of the determination of the calcium hardness (CaH) in tap water.

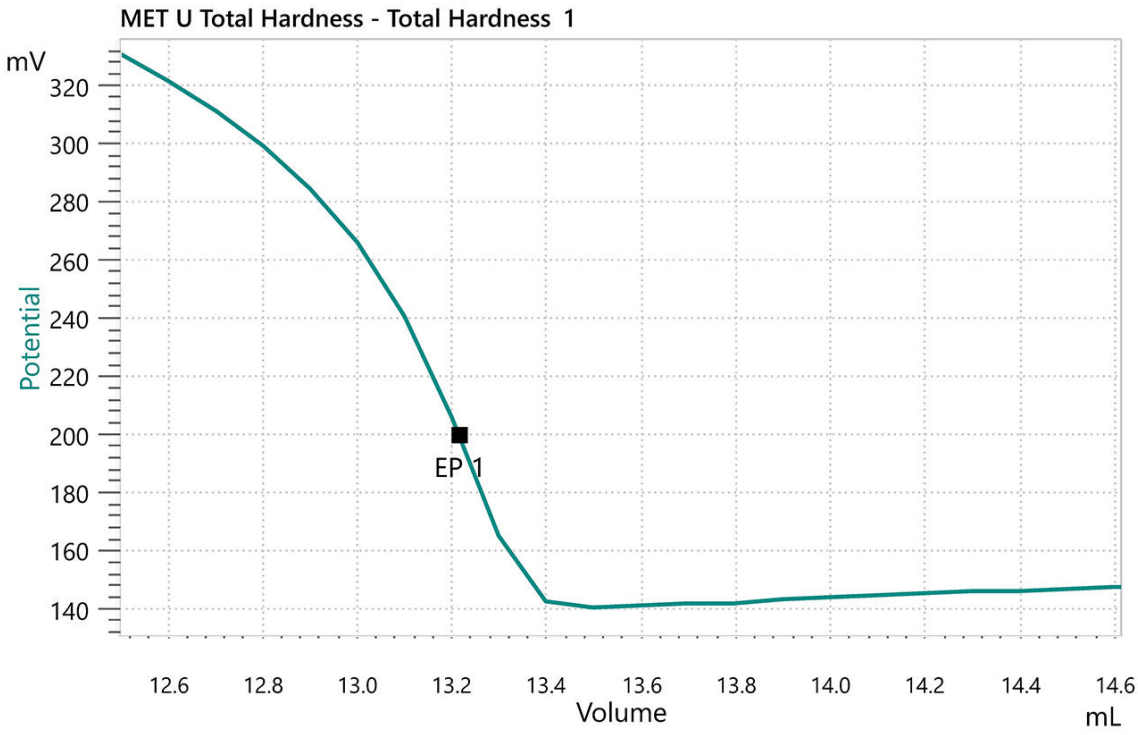

Figure 3. Titration curve of the determination of the total hardness (TH) in wastewater.

CONCLUSION

Determination of the water hardness according to ASTM D8192 using the Optrode ensures objectivity when determining the endpoint in comparison to the subjectivity of the human eye. This results in increased precision and reliability when monitoring water hardness in colored and colorless samples.

Thanks to its glass shaft, the Optrode is very easy to clean and 100% solvent resistant. Additionally, the Optrode is maintenance-free. Its space-saving design allows it to be used conveniently in automated systems.

Using a fully automated system further increases the precision and reliability of the determination as all sample preparation steps can be automated. Furthermore, the modularity of the OMNIS system allows the analysis of various other parameters, such as alkalinity or conductivity on one system. Efficiency can be even further improved with the ability to run up to four determinations in parallel on the same OMNIS system. This is regardless of whether it is the same parameter or different parameters.

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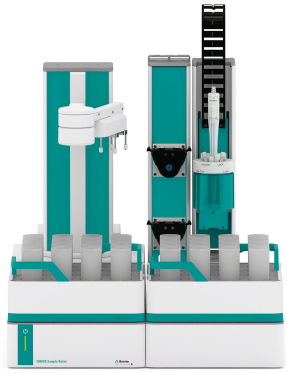
CONFIGURATION



OMNIS Sample Robot S Pick and Place

OMNIS Sample Robot S with a "Peristaltic" (2-channel) pump module and a Pick&Place module in addition to extensive accessories for the direct transition to fully automatic titration. The system provides space in two sample racks for 32 sample beakers of 120 mL each. This modular system is supplied completely installed and can thus be put into operation in a very short time.

The system can also be extended upon request to include two additional peristaltic pumps and another Pick&Place module, thus doubling the throughput. If additional workstations are required, then this Sample Robot is already able to be expanded to become an L-sized OMNIS Sample Robot, thus enabling samples from seven racks to be processed in parallel on up to four Pick&Place modules and quadrupling the sample throughput.