WHITE PAPER

# Automated water hardness determination according to ASTM D8192

Water hardness is one of the most popular analyses when it comes to water quality determination. Each bottle of mineral or sparkling water provides information about its calcium and magnesium content. Calcium is essential for the human body, especially for the skeletal system, and is required to be consumed in high amounts. The highest uptake of Ca for humans is via milk and other dairy products. In second place comes mineral water, which also contains high levels of magnesium, indispensable for life.

However, calcium and magnesium naturally present in water are the primary cause of tubes and pipes clogging which can lead to failures and loss of efficiency for several kinds of processes. Due to these reasons, water hardness (calcium and magnesium) must be determined frequently to ensure that a sufficient amount of nutrients are contained while avoiding frequent pipeline issues and shutdown of any affected processes or utilities.

Generally, this is performed manually with visual indication (e.g., ASTM D1126, ASTM D511, EPA 130.2, EPA 215.5, APHA 130.2, and APHA 2000), an unreliable method with less reproducible results, prone to human error. A new norm (ASTM D8192) solves these issues and allows the measurement of water hardness objectively without the disadvantages of using visual endpoint determination.

Metrohm

## MANUAL TITRATION

Calcium and magnesium ions in various substances are often determined by manual titration, as it is mentioned in several international norms and standards. The reason for this is the simple and easy to use apparatus. Only a buret, a titrant, and a flask is needed (**Figure 1**).

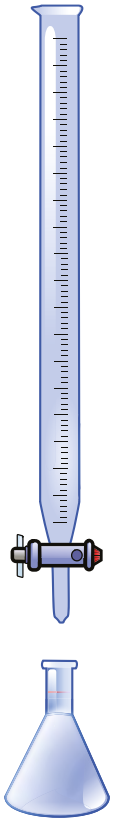

**Figure 1.** Typical setup for a manual titration. The buret is filled with titrant, and the Erlenmeyer flask contains the sample solution which includes the analyte to be measured.

Every laboratory can perform this kind of analysis as very little investment cost is required. However, the money needed for the setup is not the only thing that needs to be considered.

## DISADVANTAGES OF MANUAL TITRATION

### – VISUAL PERCEPTION OF THE ENDPOINT

Every individual perceives colors and color intensity differently. This leads to some deviations or bias depending on the individual analyst performing a manual titration. **Figure 2** illustrates this point and the difficulty in determining an endpoint visually.

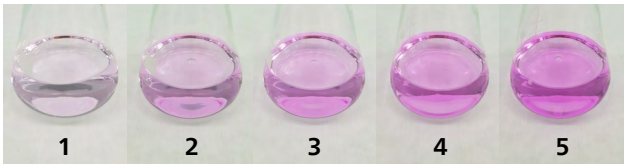


**Figure 2.** Titration of c(HCl) = 1 mol/L with c(NaOH) = 1 mol/L and phenolphthalein as the indicator. Each of these images differs only in the addition of a single drop of the NaOH titrant.

The intensity of the colors obtained in **Figure 2** differ by only approximately 50 µL NaOH titrant from each flask to the next. The question arises regarding where the «correct» endpoint should be chosen – is it image 1 or image 5, or somewhere in between? If this is not handled in exactly the same manner by different analysts, then the precision of the measurement will suffer.

### – DROP SIZE

When using manual titration, results can only be as accurate as the smallest drop size given by the buret. In the pharmaceutical industry, one drop is defined to be **50 µL**. This means that a maximum accuracy regarding a drop size of 50 µL can be achieved. Assuming a consumption of about 5 mL titrant, this may lead to an error of up to 1%.

### – ERROR OF BURET

As with all glassware, the buret itself has a specific tolerance. As an example, the allowed tolerance with a 50 mL buret is 50 µL. However, this is not the only error source resulting from handling a buret.

The parallax error occurs if the analyst does not view the meniscus horizontally, but from an angle. Meniscus readings differ depending on the viewing angle, as shown in the illustration in **Figure 3**.

All of the previously discussed points show that manual titration is easy to perform but is quite prone to human error and user bias. Also, manual titration is not very advantageous resource-wise due to the excessive amount of time needed for cleaning, refilling the buret, as well as manually calculating the results. Safety of the lab personnel is not guaranteed, as chemicals can easily be spilled while refilling the buret.

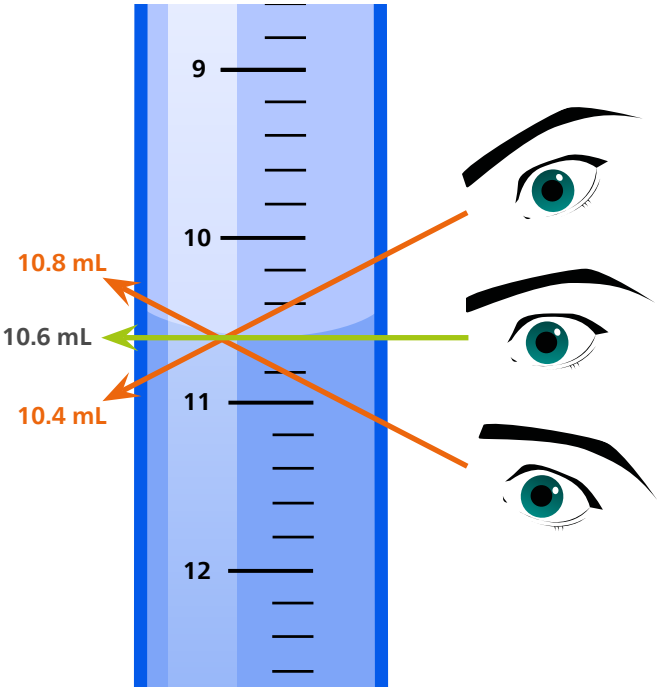


**Figure 3.** Parallax error occurs if the user reads the meniscus values from different visual angles.

## DATA INTEGRITY AND AUTOMATED EVALUATION

Data integrity is another negative point to consider for manual titrations, since all data must be transferred manually into a notebook or into software. The resulting calculations are not carried out automatically, further increasing the risk for errors. Human error is a likely possibility in this situation. Besides the lack of data integrity, visual methods cannot be automated and are difficult to validate.

All of these errors are cumulative and result in an error of approximately 0.1–0.3 mL depending on the parallax error, which corresponds to a relative error of 2–6% in the case of 5 mL titrant consumption up to the endpoint.

## SWITCHING TO AUTOMATED TITRATION

The aforementioned challenges have resulted in a paradigm shift by laboratories to switch to using automated titrations whenever possible.

This is also the case for ASTM D8192, which transferred the previously recommended manual titration for hardness to an automated one. Because of this change, the limited accuracy and precision of manual titrations are overcome.

Devices used in automated titration consist of a motor-driven spindle and a glass cylinder that is filled with titrant. Furthermore, recent generations are equipped with a built-in stirrer and allow the user to carry out calculations automatically and save the results on a storage device (e.g., USB stick or PC), or print the results directly after analysis.

### – VISUAL PERCEPTION NO LONGER MATTERS

Automated titration could not have been established without the development of sensors. In 1909, the first glass electrode for potentiometric titration was built. Potentiometric sensors allow reproducible endpoint determination independent from a color change or bias from an analyst. As various samples require different electrode properties, there are currently a large number of sensors available. One sensor in particular must be mentioned when discussing automating colorimetric titrations: the Optrode (**Figure 4**).

**Figure 4.** The Optrode sensor from Metrohm is used for the automatic unbiased detection of the endpoint if color indicators are used for endpoint indication.

As titrations with color indications are still common, the Optrode was developed, which is a sensor that is able to detect minor color differences by determining the change in absorbance at a specific wavelength, then converting the absorption into a measureable potential. In this way, colorimetric titrations become more accurate and precise, as they no longer depend on the visual perception of laboratory analysts.

## – TRACEABLE RESULTS FOR DATA INTEGRITY

During manual titration procedures, all results are read from the buret and transcribed into a lab journal or manually typed into software. This process is error-prone, with a high likelihood that some of the values are transferred incorrectly. To solve this issue, automated titrations record the measured values and the result calculation is performed automatically on the device. These results can be exported as a PDF file or printed with date and time stamp. Therefore, human error is kept to a minimum.

## – ASTM D8192

ASTM D8192 was specifically developed to increase the grade of automation and therefore the precision of the analysis. Color changes where the endpoints are hardly detected visually can now be detected easily and objectively with the Optrode. Results obtained by automated titration are comparable to the manually obtained data.

In the case of magnesium and calcium ions, the total hardness is determined by titration with EDTA at pH 10 with Eriochrome black T as the indicator, leading to a color change from red to blue. The calcium hardness is determined by titration with EDTA at pH 12 with hydroxynaphthol blue as indicator, which also leads to a color change from red to blue. An example of these two determinations is shown in **Figure 5**. Though not shown here, magnesium hardness is calculated from the difference between the total hardness and the calcium hardness.

Both color changes can be detected at the same wavelength (610 nm), avoiding the need to switch the measurement wavelengths between analyses and reducing the waiting time until the light has reached its full intensity after changing sensor wavelengths. All determinations showed a steep and smooth titration curve.

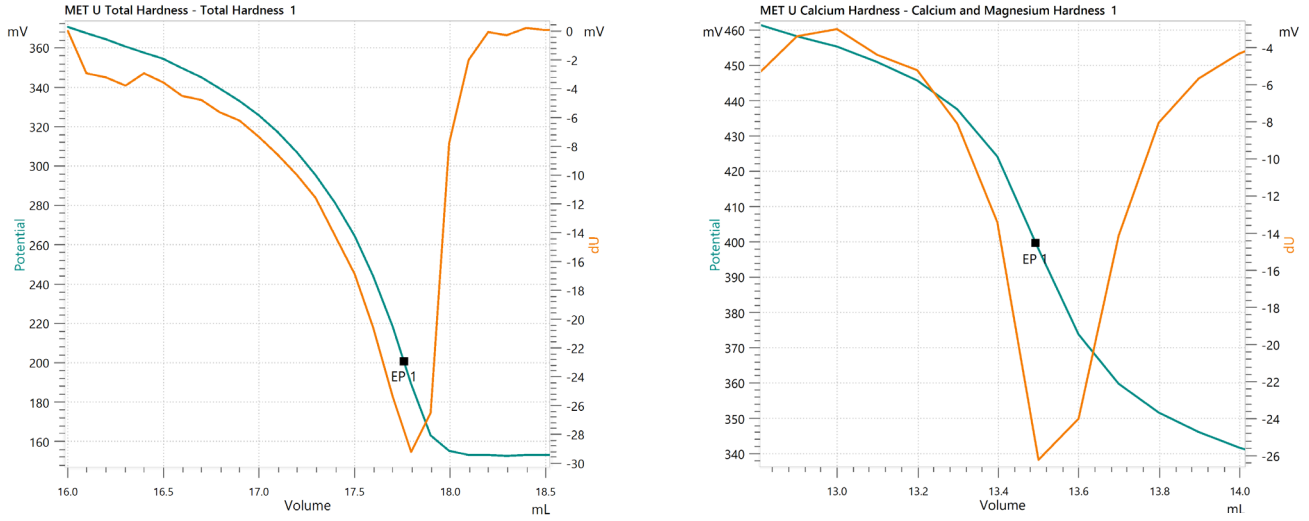


**Figure 5.** Titration curves obtained with OMNIS software and the Optrode sensor. Left: titration curve for the total hardness determination. Right: titration curve for the calcium hardness determination.

**Tables 1–6** show summaries of the results of total hardness (TH), calcium hardness (CaH), and magnesium hardness (MgH) expressed as $CaCO_3$ in mmol/L and mg/L. All results were within the limit of the precision calculation given by ASTM D8192. SD(abs) must not exceed the calculated value of precision.

**Table 1.** Summary of results for total hardness (TH) expressed as $CaCO_3$ in mmol/L.

| Sample (n = 6) | TH in mmol/L | SD(abs) in mmol/L | SD(rel) in % | Precision in mmol/L |
|---|---|---|---|---|
| Wastewater | 2.61 | <0.1 | <0.1 | 0.41 |
| Tap water | 3.51 | <0.1 | <0.1 | 0.42 |
| Leachate | 0.88 | <0.1 | 0.2 | 0.40 |

**Table 2.** Summary of results for total hardness (TH) expressed as $CaCO_3$ in mg/L.

| Sample (n = 6) | TH in mg/L | SD(abs) in mg/L | SD(rel) in % | Precision in mg/L |
|---|---|---|---|---|
| Wastewater | 261.5 | 0.2 | <0.1 | 1.63 |
| Tap water | 351.6 | 0.1 | <0.1 | 2.05 |
| Leachate | 87.8 | 0.2 | 0.2 | 0.81 |

**Table 3.** Summary of results for calcium hardness (CaH) expressed as $CaCO_3$ in mmol/L.

| Sample (n = 6) | CaH in mmol/L | SD(abs) in mmol/L | SD(rel) in % | Precision in mmol/L |
|---|---|---|---|---|
| Wastewater | 2.03 | <0.1 | 0.4 | 0.41 |
| Tap water | 2.67 | <0.1 | <0.1 | 0.41 |
| Leachate | 0.75 | <0.1 | 0.3 | 0.40 |

**Table 4.** Summary of results for calcium hardness (CaH) expressed as $CaCO_3$ in mg/L.

| Sample (n = 6) | CaH in mg/L | SD(abs) in mg/L | SD(rel) in % | Precision in mg/L |
|---|---|---|---|---|
| Wastewater | 203.0 | 0.1 | <0.1 | 1.35 |
| Tap water | 267.1 | 0.1 | <0.1 | 1.66 |
| Leachate | 75.3 | 0.2 | 0.3 | 0.75 |

**Table 5.** Summary of results for magnesium hardness (MgH) expressed as $CaCO_3$ in mmol/L.

| Sample (n = 6) | MgH in mmol/L | SD(abs) in mmol/L | SD(rel) in % | Precision in mmol/L |
|---|---|---|---|---|
| Wastewater | 0.58 | <0.1 | 1.6 | 0.40 |
| Tap water | 0.84 | <0.1 | 0.1 | 0.40 |
| Leachate | 0.12 | <0.1 | 2.2 | 0.40 |

**Table 6.** Summary of results for magnesium hardness (MgH) expressed as $CaCO_3$ in mg/L.

| Sample (n = 6) | MgH in mg/L | SD(abs) in mg/L | SD(rel) in % | Precision in mg/L |
|---|---|---|---|---|
| Wastewater | 58.5 | 0.3 | 0.5 | 0.68 |
| Tap water | 84.5 | <0.1 | 0.1 | 0.80 |
| Leachate | 12.5 | 0.3 | 2.2 | 0.46 |

## – AUTOMATION FOR HIGHER EFFICIENCY

Automating the photometric titration of calcium and magnesium is possible using the OMNIS system from Metrohm. Using e.g., a Sample Robot S, the determinations can be carried out in parallel on two different towers (**Figure 6**). Expanding the system to a Sample Robot M or even Sample Robot L allows sample throughput to increase by roughly a **factor of four**.

**Figure 6.** OMNIS Sample Robot S with one titrator and three dosing units for automated parallel titration of the total and calcium hardness.

## SUMMARY

The new ASTM D8192 standard allows analysts the possibility to determine water hardness in different water matrices by complexometry with **automated photometric endpoint recognition**, increasing the reproducibility and the precision of the results. No more heated discussions about the color change are needed. Additionally, the time saved by laboratory personnel can be used for other more important tasks rather than observing color changes in solution, making the analysis more cost-effective than before. If even more efficiency is necessary, the titration itself can be also automated by using a corresponding sample robot (**Figure 6**). The Optrode (**Figure 4**) can be easily used with such automated systems.

## Contact

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