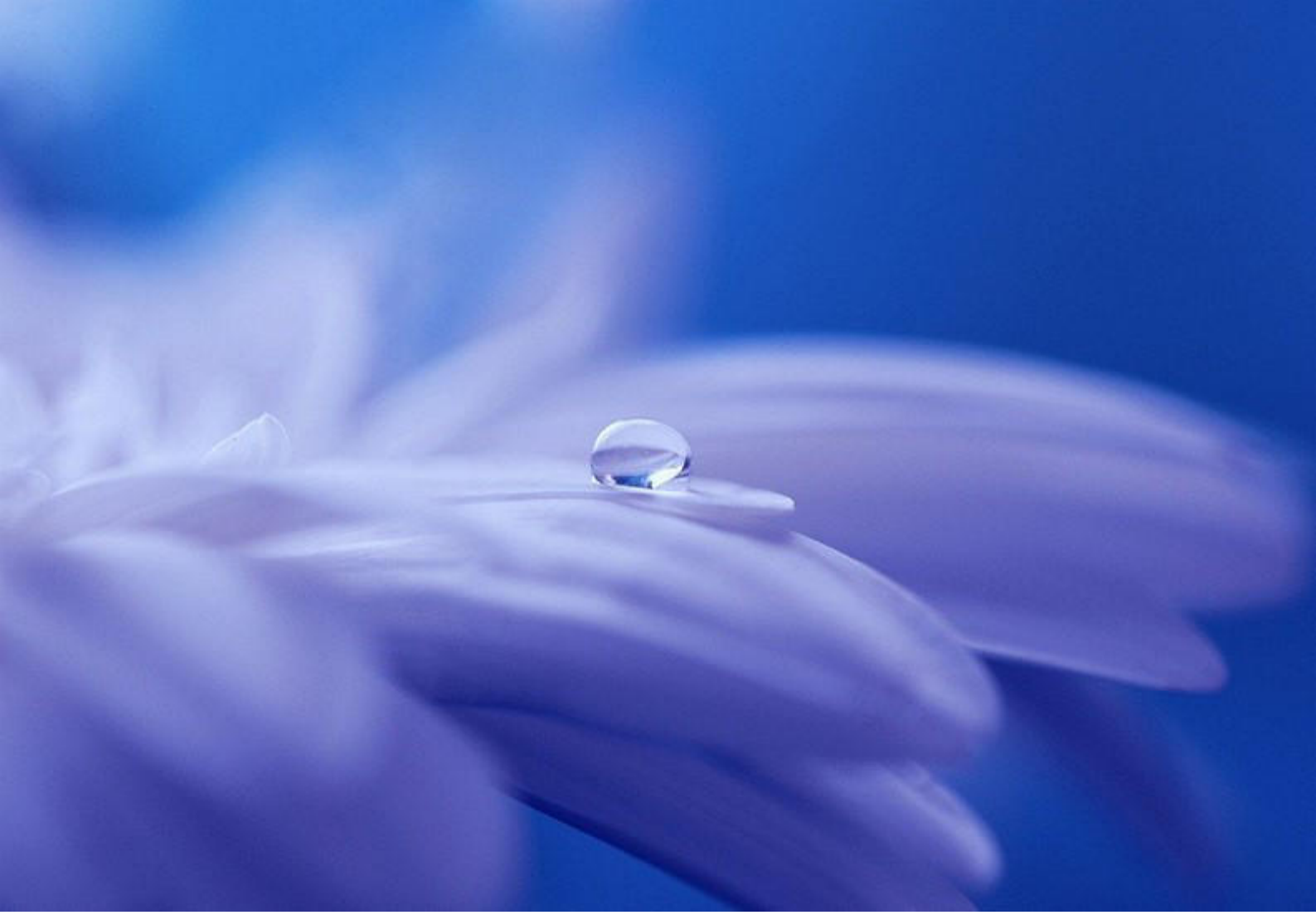

Application Note AN-T-131

Calcium, magnesium, and total hardness in water

Automated determination using the Cu-ISE and two different titrants

Water hardness is often determined photometrically using two different indicators and while performing the determination at two different pH values. This requires significant time to accurately adjust the pH. The determination itself is subjective, as the color change is determined by the analyst and not by an analytical device, which can cause differences between different analysts.

This application note introduces a more robust option to easily assess calcium, magnesium, and total hardness in water by using the Cu-ISE and two different titrants. Sample preparation is identical for both analyses and can therefore be automated without any issues. The Cu-ISE is also easy to handle. Additionally, the analysis is no longer subjective and both the precision and repeatability of the results are improved.

SAMPLE AND SAMPLE PREPARATION

This application is demonstrated on tap water from Herisau, Switzerland. It contains quite a high amount of calcium and magnesium ions naturally.

No sample preparation is required for this analysis. For the analysis itself, approximately 100 mL tap water is needed for each application.

EXPERIMENTAL

The analyses are carried out on an 815 Robotic USB Sample Processor XL in combination with a 907 Titrando and the *tiamo*™ software. For indication, a Cu-ISE in combination with a Long Life ISE reference electrode is used.

Two determinations need to be performed. During the first titration with EDTA, the sum of calcium and magnesium is measured, whereas with the second titration with EGTA, only the calcium is analyzed. From this difference, the magnesium hardness can be calculated. A small amount of either a Cu-EDTA or Cu-EGTA solution is added for the indication of the equivalence point in both titrations.

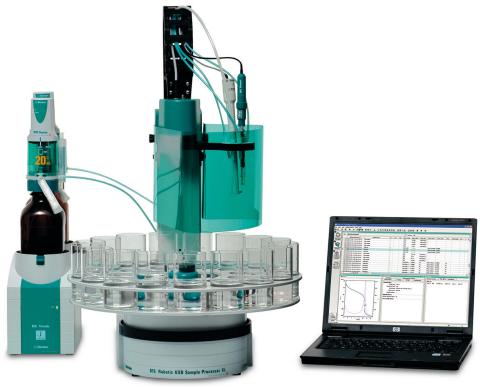

Figure 1. Titrando system consisting of an 815 Robotic USB Sample Processor XL in combination with a 907 Titrando.

RESULTS

Sharp titration curves with a large potential difference are obtained for both analyses. The results are reproducible as displayed in Table 1.

Table 1. Results of the determination of the total, the calcium and the magnesium hardness (n = 5).

	Mean value / mmol/L	SD(abs)/ mmol/L	SD(rel) in %
Total hardness	3.517	0.020	0.57
Ca hardness	2.547	0.012	0.47
Mg hardness	0.971	0.009	0.94

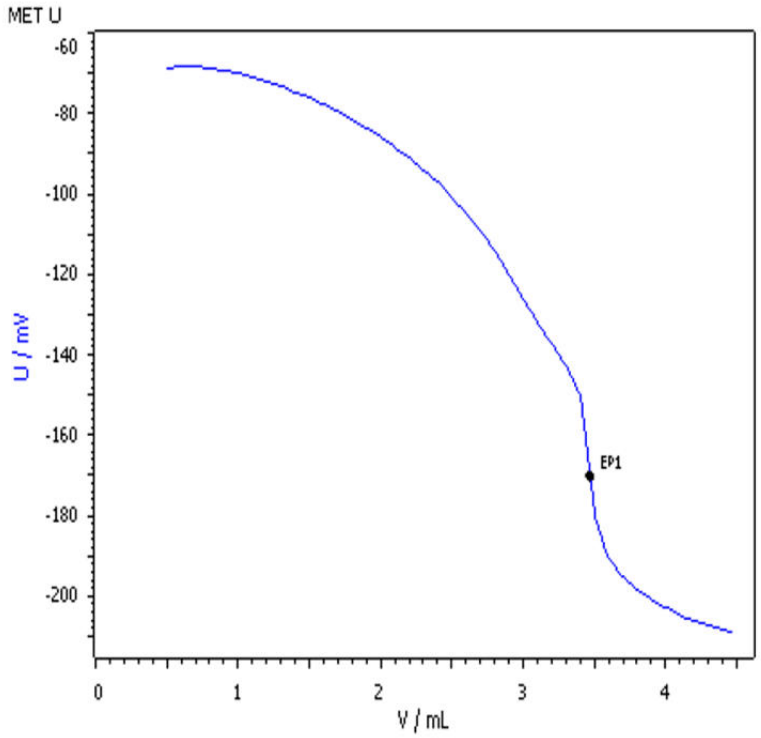

Figure 2. Example titration curve with EDTA for the total hardness determination in a sample of Herisau tap water.

CONCLUSION

This application shows the possibility of an objective, fast and reliable determination using the Cu-ISE. The Cu-ISE is easy to handle, and its surface can be easily polished as soon as performance decreases, resulting in a refreshed surface.

As both analyses are performed with the same instruments and electrodes, they are easily automated. The automation leads to precise and reproducible results. Even more time can be saved if the analyses are carried out on an OMNIS sample robot where parallel analyses are possible.

Internal reference: AW TI CH1-1163-022014

CONTACT

Metrohm Nederland
Bijdorpplein 13-15
2992 LB Barendrecht
info@metrohm.nl

CONFIGURATION

907 Titrando

High-end titrator for potentiometric and volumetric Karl Fischer titration with two measuring interfaces and Dosino dosing units.

- up to four dosing device systems of the 800 Dosino type
- dynamic (DET), monotonic (MET) and endpoint titration (SET), enzymatic and pH-STAT titrations (STAT), Karl Fischer titration (KFT)
- "iTrode" intelligent electrodes
- Measurement with ion-selective electrodes (MEAS CONC)
- Dosing functions with monitoring, liquid handling
- four MSB connectors for additional stirrers or dosing device systems
- USB connector
- For use with OMNIS Software, *tiamo* software, or Touch Control
- Complies with GMP/GLP and FDA regulations such as 21 CFR Part 11, if required

815 Robotic USB Sample Processor XL (1T/2P)

Robotic USB Sample Processor XL with one workstation and two built-in membrane pumps for the automatic processing of routine samples in series with large quantities and for complex sample preparation or parallel runs. Up to three dosing devices for Liquid Handling tasks can be connected.

Because of the multitude of application variants, rack, stirrer, titration head, robotic arm, Swing Head and sample vessels must be tailored to the application and ordered separately.

The control is "stand alone" using Touch Control. The following software products can be selected for the PC control: tiamoTM titration software, MagIC Net chromatography software, viva voltammetry software, or OMNIS.

Ion-selective electrode, Cu

Copper-selective electrode with crystal membrane.
This ISE has to be used in combination with a reference electrode and is suitable for:

- ion measurements of Cu2+
- ion measurements in small sample volumes (minimum immersion depth 1 mm)
- Complexometric titrations with CuEDTA

Thanks to the robust/break-proof plastic shaft made of EP, this sensor is mechanically very resistant.
The polishing set supplied enables easy cleaning and renewing of the electrode surface.

LL ISE reference electrode

Silver / silver chloride reference electrode with double junction system.
This reference electrode is well suited for:

- automated applications
- ion measurements
- surfactant titrations

The ground-joint diaphragm, which is insensitive to contamination, offers a constant and reproducible electrolyte outflow. Additionally, the reference electrolyte is gelified for even better signal stability. The sensor is delivered with c(KCl) = 3 mol/L as bridge electrolyte, which can be freely selected and exchanged as needed.