Application Note AN-T-076

Conductivity, pH value, alkalinity, hardness, and chloride in tap water

Fully automated determination including sample preparation

The analysis of tap water plays an important role to assess the water quality or to identify possible contaminants. Parameters such as conductivity, pH value, alkalinity, water hardness, and chloride content are routinely analyzed.

In this application note, a fully automated system is presented which allows the determination of several parameters according to various standards within one analysis. These include conductivity (ISO 7888, EN 27888, ASTM D1125, EPA 120.1), pH value (EN ISO 10523, ASTM D1293, EPA 150.1), alkalinity (EN ISO 9963, ASTM D1067, EPA 310.1), Ca/Mg (ISO 6059, ASTM D1126, EPA 130.2), and chloride (ISO 9297, ASTM D512, EPA 325.3). Additionally the system transfers the required volume of sample into external titration vessels for the different analyses, reducing manual sample preparation. Furthermore, all sensors can be automatically calibrated and the titer of each titrant can also be determined.

This high degree of automation minimizes errors and guarantees outstanding reproducibility by freeing up valuable time for operators.

SAMPLE AND SAMPLE PREPARATION

The method is demonstrated for a tap water sample. No sample preparation is required as the system automatically transfers the defined sample volume to external titration vessels after conductivity measurement.

EXPERIMENTAL

This analysis is carried out automatically on an 815 Robotic USB Sample Processor XL equipped with two external titration vessels. One is set up with an iAquatrode plus and a combined Ca-ISE, and the second vessel is set up with an iAg-Titrode.

The samples are poured into beakers and then placed onto the rack. First, the conductivity measurement is directly performed in the beaker with a 5-ring conductivity measuring cell with integrated temperature sensor. Afterwards, a sample aliquot is transferred into the first external titration vessel to perform the pH measurement and then the alkalinity titration (using standardized HCl solution). Next, the pH value is adjusted by the addition of TRIS buffer, and the sample is titrated with standardized EDTA titrant until after the second equivalence point is reached. A second portion of the sample is transferred into the second titration vessel for the chloride determination with standardized silver nitrate titrant (after an acidification step). Finally, cleaning of both titration vessels and sensors is carried out automatically.

The pH electrode and the conductivity measuring cell are calibrated prior to the analysis.

Figure 1. Example setup of a 815 Robotic USB Sample Processor XL with one external titration vessel, a 905 Titrando and 856 Conductivity Module equipped with iAquatrode plus, combined Ca-ISE, iAg-Titrode, and 5-ring conductivity measuring cell for the analysis of tap water.

RESULTS

The system enables reproducible results for all analyzed parameters. The overall analysis time for one sample is less than 15 minutes. All results are summarized in Table 1 and exemplary titration curves are given in Figures 2, 3, and 4.

Table 1. Analyzed parameters for tap water (n = 10).

Parameter	Mean	SD(rel) in %
Conductivity	567.4 µS/cm	0.84
pH value	7.83	0.32
p-value	N/A	N/A
m-value	5.44 mmol/L	0.09
Calcium	84.57 mg/L	0.50
Magnesium	19.66 mg/L	1.74
Total hardness	2.92 mmol/L	0.62
Chloride	10.87 mg/L	1.51

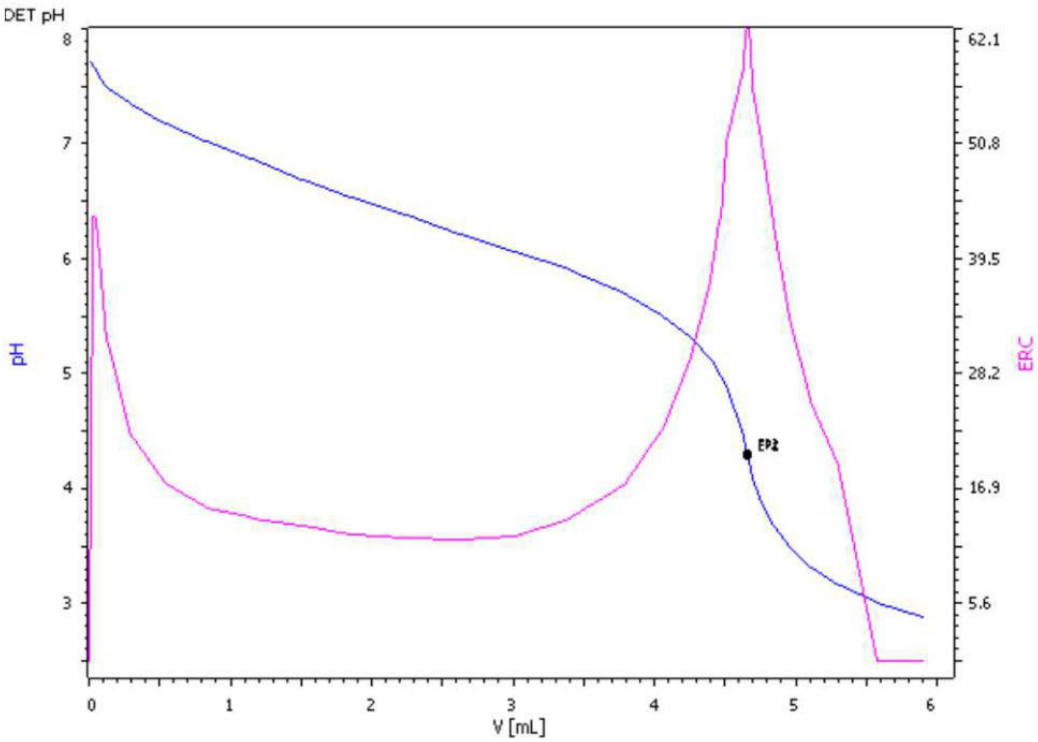

Figure 2. Example of a titration curve for alkalinity measurement in tap water.

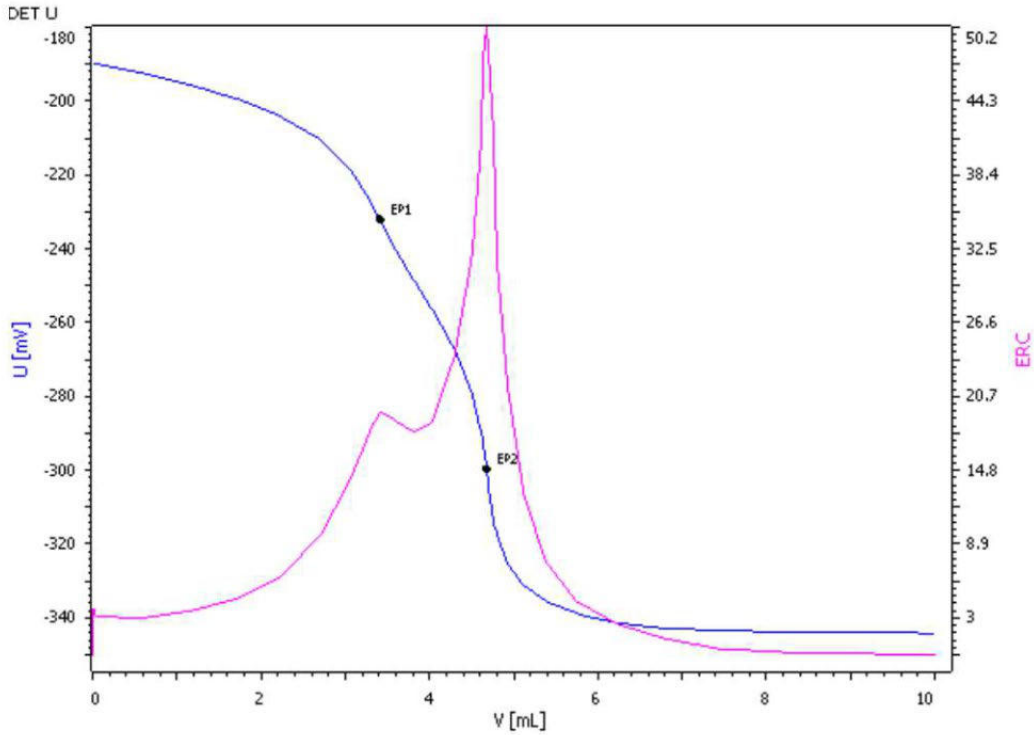

Figure 3. Titration curve for the determination of water hardness, the first EP corresponds to the Ca content and the difference obtained by EP2-EP1 corresponds to the Mg content.

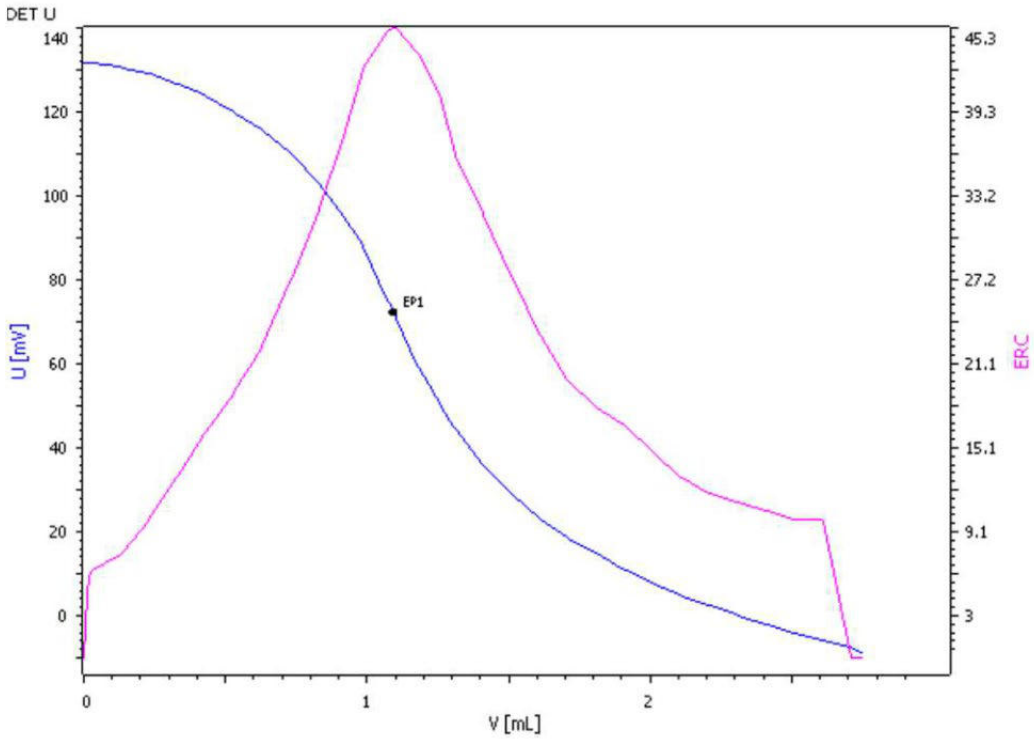

Figure 4. Titration curve for the determination of chloride in a tap water sample.

CONCLUSION

The high degree of automation for water analysis allows an increase in sample throughput, minimizes errors, and guarantees outstanding reproducibility. As the presented system includes sample preparation, the sample only needs to be placed in a beaker onto the rack and the system runs all analyses (conductivity, pH value, alkalinity, water hardness, and chloride) autonomously in one run. The automatic and accurate addition of the solutions combined with the automated system frees up valuable time of the operator and therefore increases the productivity in the lab.

Internal reference: AW TI CH1-1215-082011

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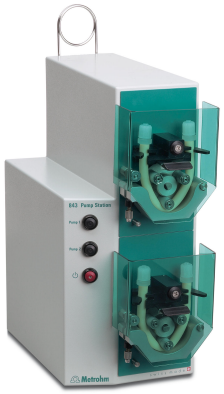
CONFIGURATION

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.



843 Pump Station (peristaltic)

The 843 Pump Station (peristaltic) has two built-in peristaltic pumps. These can be controlled directly via the interface using remote signals or manually by pressing a button.

856 Conductivity Module

Conductivity measuring module as supplement to an existing Titrando system or "stand-alone" in combination with a 900 Touch Control. With the 856 Conductivity Module, not only conductivity and temperature can be determined, but also TDS and salinity. It supports state-of-the-art conductivity measuring cells, i.e. 5-ring measuring cells.

The Conductivity Module is equipped with two USB interfaces for connecting printers, barcode readers, or sample changers and four MSB interfaces for stirrers or Dosinos.
For use with OMNIS Software, tiamo software, or Touch Control unit. Compliance with GMP/GLP and FDA regulations such as 21 CFR Part 11, if required.

905 Titrando

High-end titrator for potentiometric titration with two measuring interfaces for use with Dosino dosing systems.

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

5-ring conductivity measuring cell c = 0.7 cm-1 with Pt1000 (fixed cable)

5-ring conductivity measuring cell with cell constant c = 0.7 cm^{-1} (guide value), with integrated Pt1000 temperature sensor and with fixed cable (1.2 m) for connecting to an 856 Conductivity Module.

This sensor is suitable for measurements of medium conductivities, e.g., in:

- drinking water
- surface water
- wastewater

iAquatrode Plus with Pt1000

Intelligent, combined pH electrode with integrated memory chip for storing sensor data and with Pt1000 temperature sensor for pH measurements/titrations in ion-deficient aqueous media (e.g., drinking water, process water). This electrode shows a very short response time in these samples.

The fixed ground-joint diaphragm is insensitive to contamination.
When c(KCl) = 3 mol/L is used as bridge electrolyte, storage in storage solution is recommended.
The bridge electrolyte can be easily replaced with a chloride-free electrolyte (e.g., potassium nitrate $c(KNO_3)$ = 1 mol/L (6.2310.010)). Storage in the used bridge electrolyte.
iTrodes can be connected to Titrando, Ti-Touch, or 913/914 meters.

Combined polymer membrane electrode, Ca

Combined calcium-selective electrode with polymer membrane.
This ISE is suitable for:

- ion measurements of Ca2+ in aqueous solutions
- complexometric (back) titrations (e.g., determination of water hardness)

Thanks to a robust/break-proof plastic shaft made of propylene and an impact protection for the polymer membrane, this sensor is mechanically very resistant.
The reference electrolyte used is $c(NH_4NO_3)$ = 1 mol/L.

iAg Titrode

Intelligent, combined silver ring electrode with a pH glass membrane as reference electrode and integrated memory chip for storing sensor data.

This maintenance-free electrode is suitable for precipitation titrations when the pH value remains constant (titrant silver nitrate), for example of:

- Chloride, Bromide, Iodide
- Sulfides
- Hydrogen sulfide
- Mercaptans
- Cyanides

This electrode is stored in distilled water.

Depending on the application, we recommend using an Ag Titrode with Ag_2S coating, which can be ordered accordingly.

iTrodes can be used on Titrando, Ti-Touch or 913/914 meters.