Water analysis

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Metrohm

Ion analysis

Titration

Summary

A complete tap water analysis includes the determination of the pH value, the alkalinity and the total water hardness. Both the pH measurement and the pH titration by means of a standard pH electrode suffer from several drawbacks. First, the response time of several minutes is too long and, above all, the stirring rate significantly influences the measured pH value.

Unlike these standard pH electrodes, the Aquatrode Plus with its special glass membrane guarantees rapid, correct and very precise pH measurements and pH titrations in solutions that have a low ionic strength or are weakly buffered.

Total water hardness is ideally determined by a calcium ion-selective electrode (Ca ISE). In a complexometric titration, calcium and magnesium can be simultaneously determined up to a calcium/magnesium ratio of 10:1. Detection limits for both ions are in the range of 0.01 mmol/L.

Introduction

Since drinking water is absolutely essential for human beings, it is not surprising that the analysis of drinking, ground and surface water is continually increasing in importance. Among other things, a complete water analysis involves the determination of pH value, alkalinity and total hardness.

pH value

The most precise way to measure the pH is the potentiometric determination using a pH glass electrode. However, the pH measurement in poorly conducting or weakly buffered aqueous solutions such as drinking water places very high demands on a pH glass electrode. Additionally, the measured pH value often depends on the stirring speed.

Alkalinity

Alkalinity, that is the capacity of bases to neutralize acids, is a sum parameter comprising the water's carbonate, hydrogen carbonate, hydroxide, borate, silicate, phosphate, ammonium and sulfide concentrations. It is determined by titration with an acidic titrant. Drinking water and ground water generally contain only carbonates with trace amounts of the other bases.

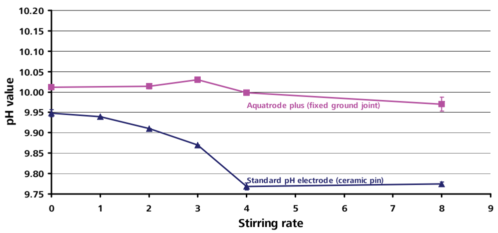
Total hardness

The total hardness is the sum of calcium, magnesium, barium and strontium ions. Since in drinking water only calcium and magnesium are present in significant amounts, the hardness is entirely determined by their content. The total hardness can be determined by potentiometric titration with ion-selective electrodes.

This presentation deals in detail with the determination of the pH value, the alkalinity and the total hardness of water samples. Moreover, it addresses some problems that can occur during these measurements and offers viable solutions.

pH value/alkalinity

For the determination of the carbonate alkalinity, EN ISO 9963-2 (1996-02) prescribes a SET titration with the titrant c(HCl) = 0.05 mol/L to pH = 5.4. A prerequisite for a correct titration is a rapid response of the glass membrane and an accurately measured pH value at the start and end of the titration. However, standard pH glass electrodes in ion deficient solutions, such as drinking water, have response times of several minutes. An additional problem, which is often underestimated, is the dependence of the measured pH value on the stirring speed. In the following, the Aquatrode Plus Metrosensor electrode is compared to a conventional pH glass electrode with ceramic pin diaphragm.



Sample:	$c(Na_2CO_3)$ = 0.14 mmol/L stock solution
Theoretical pH value of the sample:	10.2
Titration vessel:	Thermostatted under argon atmosphere
Calibration of pH electrodes:	Merck buffer solutions at pH = 4.005, pH = 6.863 and pH = 9.184

- The Aquatrode Plus is considerably closer to the pH value of 9.98 measured by a high precision electrode than the pH electrode with ceramic diaphragm.
- Whereas the Aquatrode Plus electrode is hardly influenced by the stirring rate, the ceramic pin diaphragm shows values that are significantly too low.

Aquatrode Plus

Characteristics

- Combined pH-glass electrode with fixed ground-joint diaphragm and double-junction reference system:
  - maintenance-free inner electrolyte (gel)
  - variable outer electrolyte for special applications
- special pH glass membrane:
  - short response time
  - excellent long-term stability
- diaphragm is insensitive to contamination

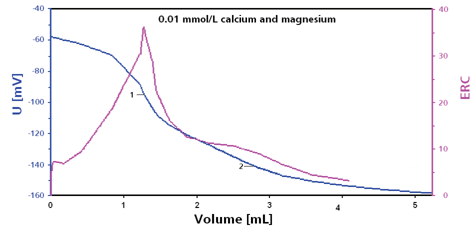
Technical specifications

Shaft material:	Glass
pH range:	0…13
Temperature range:	0…60 °C
Temperature sensor:	Pt 1000
Diaphragm:	Fixed ground joint

Total hardness

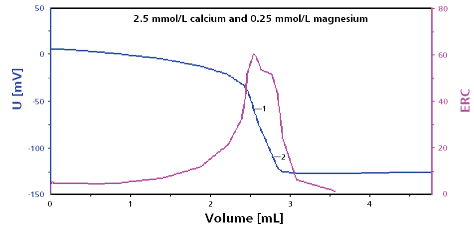
The potentiometric determination of the total hardness is best performed with a calcium ISE. A curve with two potential jumps is obtained. The first potential jump (1) corresponds to the calcium content and the second one to the sum of calcium and magnesium (2).

Calcium/magnesium ratio of 1:1



Different titrations are performed in the concentration range between 0.01…10 mmol/L. Even in the low concentration range the Ca ISE provides reliable results.

Different calcium/magnesium ratios



While the calcium concentration is held constant at 2.5 mmol/L, different calcium/magnesium ratios are analyzed. Magnesium is still detectable at a Ca/Mg ratio of 10:1. Nevertheless, at these ratios high standard deviations are observed. The precision of the magnesium determination can be significantly improved by spiking the sample with a magnesium standard.

Ca ISE

Characteristics

- Polymer-membrane electrode
- High selectivity
- No sealing problem
- Lower cost
- Dry storage

Technical specifications

Temperature range:	0…40 °C
Measuring range $c(Ca^{2+})$:	$5 \cdot 10^{-7}$…1 mol/L
pH range:	2…12
Selectivity log K_{ij} (Mg^{2+}):	−6.8
Selectivity log K_{ij} (H^{+}):	−5.8

with $K_{ij} = \frac{a_{ij}(\text{detection limit})}{a_j(\text{background})}$

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