



DOC313.53.94232

# **EZ5003 Total Hardness & Free Alkalinity Analyser**

Method and reagent sheets

11/2023, Edition 1.0

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## 1. Legal information

Manufacturer: AppliTek NV/SA

Distributor: Hach Lange GmbH

The translation of the manual is approved by the manufacturer.

## 2. Analytical specifications

Please refer also to the respective technical datasheet at Hach Support Online.

Total Hardness & Free Alkalinity - All specifications				
<b>Analysis method</b>	Acid-base titration (alkalinity); Calmagite EDTA titration with LED dipping probe (hardness)			
<b>Parameter</b>	Total hardness; free alkalinity (CaCO <sub>3</sub> )			
<b>Cycle time</b>	20 – 30 minutes			
<b>Limit of detection (LOD)</b>	≤ 10 mg/L Hardness; ≤ 10 mg/L Alkalinity			
<b>Precision/Repeatability</b>	Better than 2% full scale range for standard test solutions			
<b>Cleaning</b>	Automatic; frequency freely programmable			
<b>Calibration</b>	Automatic; one point calibration			
<b>Validation</b>	Automatic; frequency freely programmable			
<b>Interferences Hardness</b>	Some metal ions interfere by causing fading or indistinct end points or by stoichiometric consumption of EDTA. Suspended or colloidal organic matter also may interfere with the end point. Large amounts of color and turbidity interferes. Fats, oil, proteins, surfactants and tar.			
<b>Interferences Alkalinity</b>	Soaps, oily matter, suspended solids or precipitates may coat the glass electrode and cause a sluggish response. Allow additional time between titrant additions to let the electrode come to equilibrium or clean the electrodes occasionally.			
<b>Measuring ranges Hardness</b>	<b>% of range - Dilution</b>		<b>Low range (mg/L)</b>	<b>High range (mg/L)</b>
	A	10% of standard range	10	100
	B	25% of standard range	10	250
	C	50% of standard range	25	500
	<b>0</b>	<b>standard range</b>	<b>25</b>	<b>1000</b>
<b>Measuring ranges Alkalinity</b>	<b>% of range - Dilution</b>		<b>Low range (mg/L)</b>	<b>High range (mg/L)</b>
	A	10% of standard range	10	500
	B	25% of standard range	25	1250
	C	50% of standard range	50	2500
	<b>0</b>	<b>standard range</b>	<b>100</b>	<b>5000</b>



### 3. Analysis method

#### Summary

The determination of Total Hardness and Total Alkalinity is based on two methods, combined in one analyser.

The Total Hardness concentration is determined in the 'TH'- method. The Total Alkalinity concentration is determined in the 'TA'- method. The concentration of all parameters is determined alternately in the 'Main'-method.

The calibration for Total Hardness is determined in the 'TH'- method. The calibration for Free Alkalinity is determined in the 'TA'- method.

#### Remark

The methods cannot be started at the same time.

### 3.1 Total Hardness

#### Summary

The determination of the total hardness concentration in water is based on the reaction of free calcium and magnesium with calmagite in an alkaline solution to form a purplish-red colour. The calcium/magnesium – indicator complex is released by titration with EDTA, causing a blue colour. The change from red to blue colour is a measure for the amount of calcium and magnesium present in the sample. The colour change is measured at 610 nm

#### Analysis steps

The analysis vessel is cleaned and filled with fresh sample. After sampling, the acid solution, buffer solution and colour solution are added. The colorimetric titration with EDTA at 610 nm is performed. After the determination of the end point, the calcium and magnesium concentrations in the sample are determined.

#### Calibration

The calibration procedure measures a REF2 CaCO<sub>3</sub> solution (channel 10, Val TH valve) to adapt the slope factor by means of a one point calibration.

## 3.2 Free Alkalinity

### Summary

The determination of the alkalinity concentration in water is based on an acid-base titration using a pH electrode. The sample is titrated with hydrochloric acid (HCl). After the determination of the end points, the alkalinity concentration is calculated.


### Analysis steps


The analysis vessel is cleaned and filled with fresh sample. After sampling, the initial pH value is measured. Next, the titration with hydrochloric acid (HCl) is started. After the determination of the end point (pH 4.5), the alkalinity concentration is calculated.

### Calibration

The calibration procedure measures a REF2 CaCO<sub>3</sub> solution (channel 10, Val TA valve) to adapt the slope factor by means of a one point calibration.

## 4. Reagents

<b>⚠ CAUTION</b>	
	Chemical exposure hazard. Obey laboratory safety procedures and wear all of the personal protective equipment appropriate to the chemicals that are handled. Read the safety data sheet from the supplier before bottles are filled or reagents are prepared. For laboratory use only. Make the hazard information known in accordance with the local regulations of the user.

<b>⚠ CAUTION</b>	
	Chemical exposure hazard. Dispose of chemicals and wastes in accordance with local, regional and national regulations.

### 4.1 Reagent overview and consumption

In the tables below, the products that are needed to prepare the reagents are listed. The product name, the formula, the molecular weight, the CAS No. and the amount needed to prepare 1 liter of the reagents is given. Check the consumption of the reagents (28 days) to adapt the volumes needed.

Product	Consumption	Consumption/28 days A rata 1 analysis/20 min	Recommended containers
Acid solution (TH)	~ 0.5 mL	< 2.5 L	Plastic – 2.5L
Buffer solution (TH)	~ 0.5 mL	< 2.5 L	Plastic – 2.5L
Colour solution (TH)	~ 0.5 mL	< 2.5 L	Plastic – 2.5L
EDTA solution (TH)	Depending on hardness concentration	1L < Volume < 13.5 L	Plastic – 10L
HCl solution (Alk)	Depending on alkalinity concentration	1L < Volume < 13.5 L	Plastic – 10 L
REF2 Solution (TH & Alk)	~ 1 L / calibration	/	Plastic – 2.5 L

## 4.2 DI-water overview and consumption

	Rinse water (mL/analysis) Type I	Dilution water (mL/analysis) Type I	Total (mL/analysis)	Consumption/28 days A rata 1 analysis / 20 min
A	100 mL	N.A.	200 mL	403 L
B	100 mL	N.A.	200 mL	403 L
C	100 mL	N.A.	200 mL	403 L
0	100 mL	N.A.	200 mL	403 L

### Remark

The indicated volumes are an estimation of the consumption for rinse and dilution water, based on a standard operating procedure, as defined in the specifications of the EZ analyser. Please be aware that, depending on the sample matrix, the rinse water volumes might increase.



## 4.3 Storage and quality of chemicals

### Quality of chemicals

All chemicals should be of Reagent grade, ACS grade or better (\*). The use of pro analysis chemicals is recommended. Poor quality of the reagents can affect the analyser performance.

(\*) Analytical Reagent (AR), Guaranteed Reagent (GR), UNIVAR, AnalaR, Premium Reagent (PR), ReagentCertified ACS reagent, ACS Plus reagent, puriss p.a. ACS reagent, ReagentPlus®, TraceCERT®, Suprapur®, Ultrapur®, or better are also possible.

### Quality of DI-water

All EZ analysers are tested with standard solutions, reagents and dilution water prepared using type I water or better as defined by ASTM D1193-91.

To achieve the specifications as stated on the data sheet, method and reagents sheet and acceptance test reports, the same water quality (or better) must be used for the preparation of the standard solutions, reagents and dilution water.

Additionally the water used for the preparation of the standard solutions for an EZ analyser must be free of the parameter or any of the interferences for the method of that EZ analyser.

### Storage of Reagents

While operating the instrument, keep in mind the reagent requirements as stated in the reagent overview, the chapters below and/or in the data sheet of the instrument.

#### CAUTION



For longer-term storage: Store the reagents cold; Store the reagents in the dark;  
If applicable: Store the reagents in a fridge during operation

#### CAUTION



Refresh the reagents after one month (unless stated differently in the chapters below).  
Do not mix old reagents with freshly prepared reagents. Remove old reagents from the container before adding freshly prepared reagents.

#### 4.4 Acid solution (0.5 M)

Products	Formula	MW (g/mol)	CAS No.	1 litre solution
Hydrochloric Acid (36%)	HCl	36.46	7647-01-0	41.5 mL

**Preparation:**

Prepare a 0.5 M hydrochloric acid (HCl) solution. Dilute 41.5 mL of hydrochloric acid (HCl) in 500 mL de-ionized water and fill up to 1 litre with demineralized water.

#### 4.5 Buffer solution

Products	Formula	MW (g/mol)	CAS No.	1 litre solution
Ammonium chloride	NH <sub>4</sub> Cl	53.49	12125-02-9	54 g
Ammonia solution 25%	NH <sub>4</sub> OH	35.05	1336-21-6	350 mL
Mg-EDTA*	C <sub>10</sub> H <sub>12</sub> MgN <sub>2</sub> Na <sub>2</sub> O <sub>8</sub> * 4H <sub>2</sub> O	430.56	29932-54-5	5 g

\*ethylenediaminetetraacetic acid magnesium disodium salt tetrahydrate

**Preparation:**

Dissolve 54 g of ammonium chloride (NH<sub>4</sub>Cl) in de-ionized water using a volumetric flask of 1000 mL. Add 350 mL of ammonium hydroxide solution (NH<sub>4</sub>OH 25%). Add 5 g Mg-EDTA, dissolve completely and fill up to 1 litre with de-ionized water.

#### 4.6 Colour solution

Products	Formula	MW (g/mol)	CAS No.	1 litre solution
Calmagite	HOC <sub>10</sub> H <sub>5</sub> [N=NC <sub>6</sub> H <sub>3</sub> (OH)CH <sub>3</sub> ]SO <sub>3</sub> H	358.37	3147-14-6	0.2 g

**Preparation:**

Dissolve approximately 0.2 g calmagite (HOC<sub>10</sub>H<sub>5</sub>[N=NC<sub>6</sub>H<sub>3</sub>(OH)CH<sub>3</sub>]SO<sub>3</sub>H) in 400 mL degassed de-ionized water using a volumetric flask of 1L. Fill up to the grade mark with de-ionized water.

## 4.7 EDTA solution

Products	Formula	MW (g/mol)	CAS No.	1 litre solution
EDTA*	$C_{10}H_{14}N_2Na_2O_8 \cdot 2H_2O$	372.2	6381-92-6	x g

\*ethylenediaminetetraacetic acid disodium salt dihydrate

### Preparation

Prepare a x M EDTA solution. Dissolve accurately x g ethylenediaminetetraacetic acid disodium salt dihydrate ( $C_{10}H_{14}N_2Na_2O_8 \cdot 2H_2O$ ) in 500 mL degassed de-ionized water and fill up to 1000 mL.

Measuring range TH	Concentration EDTA solution	Amount to add to 1 litre
100 mg/L $CaCO_3$	0.01 M	3.722 g
250 mg/L $CaCO_3$	0.01 M	3.722 g
500 mg/L $CaCO_3$	0.025 M	9.305 g
1000 mg/L $CaCO_3$	0.05 M	18.61 g

## 4.8 HCl solution

Products	Formula	MW (g/mol)	CAS No.	1 litre solution
Hydrochloric acid (1M)	HCl	36.46	7647-01-0	x mL

### Preparation

Prepare a x M hydrochloric acid (HCl) solution. Add carefully x mL hydrochloric acid (HCl 1M) to 500 mL de-ionized water and dilute to 1 litre with de-ionized water.

Measuring range	Concentration HCl solution	Amount to add to 1 litre
500 mg/L $CaCO_3$	0.05 M	50 mL
1250 mg/L $CaCO_3$	0.1 M	100 mL
2500 mg/L $CaCO_3$	0.25 M	250 mL
5000 mg/L $CaCO_3$	0.5 M	500 mL

## 4.9 Calibration solution Hardness

Products	Formula	MW (g/mol)	CAS No.	1 litre solution
Calcium chloride dihydrate	CaCl <sub>2</sub> * 2H <sub>2</sub> O	147.02	10035-04-8	14.702 g

### Preparation:

#### 10000 mg/L CaCO<sub>3</sub> stock solution

Dissolve accurately 14.702 g calcium chloride dihydrate (CaCl<sub>2</sub> \* 2H<sub>2</sub>O) in 200 mL de-ionized water, using a volumetric flask of 1000 mL. Add de-ionized water up to the mark grade.

#### CaCO<sub>3</sub> standard solution – REF2

Prepare a x mg/L CaCO<sub>3</sub> calibration solution. Add carefully x mL stock solution of 10000 mg/L CaCO<sub>3</sub> to 500 mL de-ionized water and dilute to 1 litre with de-ionized water.

Measuring range	Concentration calibration solution	Amount to add to 1 litre
100 mg/L CaCO <sub>3</sub>	100 mg/L CaCO <sub>3</sub>	10 mL
250 mg/L CaCO <sub>3</sub>	250 mg/L CaCO <sub>3</sub>	25 mL
500 mg/L CaCO <sub>3</sub>	500 mg/L CaCO <sub>3</sub>	50 mL
1000 mg/L CaCO <sub>3</sub>	1000 mg/L CaCO <sub>3</sub>	100 mL

## 4.10 Calibration solution Alkalinity

Products	Formula	MW (g/mol)	CAS No.	1 litre solution
Sodium carbonate	Na <sub>2</sub> CO <sub>3</sub>	105.99	497-19-8	52.995 g

### Preparation:

#### 50000 mg/L Na<sub>2</sub>CO<sub>3</sub> stock solution

Dissolve accurately 52.995 g sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) in 200 mL de-ionized water, using a volumetric flask of 1000 mL. Add de-ionized water up to the mark grade.

#### CaCO<sub>3</sub> standard solution – REF2

Prepare a x mg/L CaCO<sub>3</sub> calibration solution. Add carefully x mL stock solution of 50000 mg/L CaCO<sub>3</sub> to 500 mL de-ionized water and dilute to 1 litre with de-ionized water.

Measuring range	Concentration calibration solution	Amount to add to 1 litre
500 mg/L CaCO <sub>3</sub>	500 mg/L CaCO <sub>3</sub>	10 mL
1250 mg/L CaCO <sub>3</sub>	1250 mg/L CaCO <sub>3</sub>	25 mL
2500 mg/L CaCO <sub>3</sub>	2500 mg/L CaCO <sub>3</sub>	50 mL
5000 mg/L CaCO <sub>3</sub>	5000 mg/L CaCO <sub>3</sub>	100 mL

#### 4.11 Cleaning solution (facultative)

The cleaning procedure should prevent any build-up of chemicals in the analyser. To obtain an effective cleaning procedure one has to test the cleaning solution and the cleaning interval for each application. Perform the selected cleaning solution and interval for a trial period, check then the effectiveness of the procedure and change if necessary.

<b>Change Information</b>	
Date: 24/11/2023	Previous version: No previous version
<b>Reason for Change</b>	
- Method and reagent sheet not yet available	
<b>Description of Change</b>	
- Method and reagent creation	