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EZ5006 Total / Calcium Hardness & Total / Free Alkalinity Analyser

Method and reagent sheets

09/2020, Edition 4

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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/Calcium Hardness & Total/Free Alkalinity - All specifications			
Analysis method	Acid-base titration (alkalinity); Calmagite/HNB EDTA titration with LED dipping probe (hardness)		
Parameter	Total & calcium hardness; total & free alkalinity ($CaCO_3$)		
Cycle time	20 – 30 minutes		
Limit of detection (LOD)	≤ 10 mg/L Hardness; ≤ 10 mg/L Alkalinity		
Precision/Repeatability	Better than 2% full scale range for standard test solutions		
Cleaning	Automatic; frequency freely programmable		
Calibration	Automatic; one-point calibration		
Validation	Automatic; frequency freely programmable		
Interferences Hardness	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 colour and turbidity interferes. Fats, oil, proteins, surfactants and tar.		
Interferences Alkalinity	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.		
Measuring ranges Hardness	**% of range - Dilution**	**Low range (mg/L)**	**High range (mg/L)**
	10% of standard range	10	100
	25% of standard range	10	250
	50% of standard range	25	500
	standard range	**25**	**1000**
Measuring ranges Alkalinity	**% of range - Dilution**	**Low range (mg/L)**	**High range (mg/L)**
	10% of standard range	10	500
	25% of standard range	25	1250
	50% of standard range	50	2500
	standard range	**100**	**5000**

3. Analysis method

Summary

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

The Total Hardness concentration is determined in the ‘TH’- method. The Calcium Hardness concentration is determined in the ‘CaH’ – method. The Total Alkalinity and Free Alkalinity concentrations are 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 Calcium Hardness is determined in the ‘CaH’ – method. The calibration for Total 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 release 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 $CaCO_3$ solution (channel 10, Val TH valve) to adapt the slope factor by means of a one-point calibration.

3.2 Calcium Hardness

Summary

The determination of the calcium hardness concentration in water is based on the reaction of free calcium with hydroxynaphtol blue in an alkaline solution to form a purplish-red colour. The calcium– indicator complex is release 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 concentration in the sample is determined.

Calibration

The calibration procedure measures a REF2 $CaCO_3$ solution (channel 10, Val TH valve) to adapt the slope factor by means of a one-point calibration.

3.3 Total 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 $CaCO_3$ solution (channel 10, Val TA valve) to adapt the slope factor by means of a one-point calibration.

3.4 Free Alkalinity

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 8.3), the alkalinity concentration is calculated.

4. Reagents

⚠ CAUTION	
⚠	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.

⚠ CAUTION	
⚠	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.

Total Hardness / Calcium Hardness

Product	Consumption	Consumption/28 days A rata 1 analysis/30 min	Recommended containers
Acid solution	~ 1.25 mL	< 2.5 L	Plastic – 2.5L
Buffer Ca/Mg solution	~ 0.5 mL	< 1.0 L	Plastic – 2.5L
Colour Ca/Mg solution	~ 0.5 mL	< 1.0 L	Plastic – 2.5L
Buffer Ca solution	~ 2 mL	< 1.0 L	Plastic – 2.5L
Colour Ca solution	~ 0.75 mL	< 1.0 L	Plastic – 2.5L
EDTA solution	Depending on hardness concentration	0.5 L < Volume < 7 L	Plastic – 10L
REF2 Solution	~ 1 L / calibration	/	Plastic – 2.5 L

Total Alkalinity / Free Alkalinity

Product	Consumption	Consumption/28 days A rata 1 analysis/30 min	Recommended containers
HCl solution	Depending on alkalinity concentration	0.5 L < Volume < 7 L	Plastic – 10 L
REF2 Solution	~ 1 L / calibration	/	Plastic – 2.5 L

4.2 Storage and quality of chemicals

Quality of chemicals

All chemicals should be of ACS grade or better. We recommend the use of pro analysis chemicals.

Quality of water

Reagent grade, carbon dioxide-free de-ionized water must be used to prepare the chemical solutions and for rinse purposes.

Storage of Reagents

While operating the instrument, keep in mind the ambient temperature conditions as stated in the data sheet of the instrument.

Store the reagents cold; Store the reagents in the dark; Refresh the reagents after one month (unless stated differently in the chapters below).

4.3 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.

4.4 Buffer Ca/Mg solution

Products	Formula	MW (g/mol)	CAS No.	1 litre solution
Ammonium chloride	NH_4Cl	53.49	12125-02-9	54 g
Ammonia solution 25%	NH_4OH	35.05	1336-21-6	350 mL
Mg-EDTA*	$C_{10}H_{12}MgN_2Na_2O_8 * 4H_2O$	430.56	29932-54-5	5 g

*ethylenediaminetetraacetic acid magnesium disodium salt tetrahydrate

Preparation:

Dissolve 54 g of ammonium chloride (NH_4Cl) in de-ionized water using a volumetric flask of 1000 mL. Add 350 mL of ammonium hydroxide solution (NH_4OH 25%). Add 5 g Mg-EDTA, dissolve completely and fill up to 1 litre with de-ionized water**.**

Proposal for an alternative product:

Products	Formula	MW (g/mol)	CAS No.	1 litre solution
**EDTA-K_2Mg * $2H_2O$	$C_{10}H_{12}K_2MgN_2O_8$ * $2H_2O$	426.75	CAS 15708-48-2	4.96 g
***EDTA-Na_2Mg * xH_2O	$C_{10}H_{12}N_2O_8$.Mg.2Na	358.8	CAS 14402-88-1	4.17

**ethylenediaminetetraacetic acid dipotassium magnesium salt dihydrate
*** ethylenediaminetetraacetic acid magnesium disodium hydrate

4.5 Colour Ca/Mg solution

Products	Formula	MW (g/mol)	CAS No.	1 litre solution
Calmagite	$HOC_{10}H_5[N=NC_6H_3(OH)CH_3]SO_3H$)	358.37	3147-14-6	0.2 g

Preparation*:*

Dissolve approximately 0.2 g calmagite ($HOC_{10}H_5[N=NC_6H_3(OH)CH_3]SO_3H$) in 400 mL degassed de-ionized water using a volumetric flask of 1L. Fill up to the grade mark with de-ionized water.

4.6 Buffer Ca solution

Products	Formula	MW (g/mol)	CAS No.	1 litre solution
Sodium hydroxide	NaOH	40.00	1310-73-2	20 g

Preparation:

Dissolve 20 g of sodium hydroxide (NaOH) in 500 mL de-ionized water using a volumetric flask of 1000 mL. Dissolve completely and fill up to the grade mark with de-ionized water**.**

4.7 Colour Ca solution

Products	Formula	MW (g/mol)	CAS No.	1 litre solution
Hydroxynaphtol blue (HNB)	$C_{20}H_{11}N_2Na_3O_{11}S_3$	620.47	63451-35-4	0.4 g

Preparation*:*

Dissolve approximately 0.4 g hydroxynaphtol blue (HNB) in 400 mL degassed de-ionized water using a volumetric flask of 1000 mL. Fill up to the grade mark with de-ionized water.

4.8 EDTA solution

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

*ethylenediaminetetraacetic acid disodium salt dihydrate

Preparation

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

Remark

When preparing the EDTA solution make sure that the pH of this solution stays above 8, otherwise the EDTA will not dissolve properly. To change the pH, add carefully sodium hydroxide (NaOH) pellets.

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**

4.9 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 according to the following table: 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**

4.10 Calibration solution Hardness

Products	Formula	MW (g/mol)	CAS No.	1 litre solution
Calcium chloride dihydrate	$CaCl_2 * 2H_2O$	147.02	10035-04-8	14.702 g

Preparation:

10000 mg/L $CaCO_3$ stock solution

Dissolve accurately 14.702 g calcium chloride dihydrate ($CaCl_2 * 2H_2O$) in 200 mL de-ionized water, using a volumetric flask of 1000 mL. Add de-ionized water up to the mark grade.

Calibration solution

Prepare a standard solution for calibration according to the following table: take accurately x mL of the 10000 mg/L $CaCO_3$ stock solution and transfer into a volumetric flask of 1 litre. Add de-ionized water up to the mark grade.

Measuring range	Concentration calibration solution	Amount to add to 1 litre
100 mg/L $CaCO_3$	100 mg/L $CaCO_3$	10 mL
250 mg/L $CaCO_3$	250 mg/L $CaCO_3$	25 mL
500 mg/L $CaCO_3$	500 mg/L $CaCO_3$	50 mL
1000 mg/L $CaCO_3$	**1000 mg/L $CaCO_3$**	**100 mL**

4.11 Calibration solution Alkalinity

Products	Formula	MW (g/mol)	CAS No.	1 litre solution
Sodium carbonate	Na_2CO_3	105.99	497-19-8	52.995 g

Preparation:

50000 mg/L $CaCO_3$ stock solution

Dissolve accurately 52.995 g sodium carbonate (Na_2CO_3) in 200 mL de-ionized water, using a volumetric flask of 1000 mL. Add de-ionized water up to the mark grade.

Calibration solution

Prepare a standard solution for calibration according to the following table: take accurately x mL of the 50000 mg/L $CaCO_3$ stock solution and transfer into a volumetric flask of 1 litre. Add de-ionized water up to the mark grade.

Measuring range	Concentration calibration solution	Amount to add to 1 litre
500 mg/L $CaCO_3$	500 mg/L $CaCO_3$	10 mL
1250 mg/L $CaCO_3$	1250 mg/L $CaCO_3$	25 mL
2500 mg/L $CaCO_3$	2500 mg/L $CaCO_3$	50 mL
5000 mg/L $CaCO_3$	**5000 mg/L $CaCO_3$**	**100 mL**

4.12 Cleaning solution (facultative)

The cleaning procedure should prevent any build-up of chemicals in the analyser. To obtain an effective cleaning procedure we recommend testing 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.