DOC313.53.94229

EZ4044 Total Calcium Hardness Analyser

Method and reagent sheets

08/2020, Edition 7

Table of Contents

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 - All specifications			
Analysis method	Colorimetric titration by EDTA using hydroxynaphtol blue at 620 nm		
Parameter	Total calcium hardness (THCa) – $CaCO_3$		
Cycle time	10 - 15 minutes (dilution + 5 min.)		
Limit of detection (LOD)	≤ 10 mg/L		
Precision/Repeatability	Better than 2% full scale range for standard test solutions		
Cleaning	Automatic; frequency freely programmable		
Calibration	N.A.		
Validation	Automatic; frequency freely programmable		
Interferences	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.		
Measuring ranges	**% of range - Dilution**	**Low range (mg/L)**	**High range (mg/L)**
	10% of standard range	10	100
	25% of standard range	25	250
	50% of standard range	50	500
	standard range	**100**	**1000**
	internal dispenser dilution (max factor 50)	5000	50000

3. Analysis method

Summary

The determination of the total 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 620 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 620 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, REF2 valve) to adapt the slope factor by means of a one-point calibration.

The calibration is performed in the MAIN method.

Remark

The methods cannot be started at the same time.

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.

Product	Consumption	Consumption/28 days A rata 1 analysis/10 min	Recommended containers
Acid solution	~ 0.5 ml	< 2.5 L	Plastic – 2.5 L
Buffer solution	~ 1 ml	< 5 L	Plastic – 5.0 L
Color solution	~ 0.5 ml	< 2.5 L	Plastic – 2.5 L
EDTA solution	Depending on concentration	1 L < Volume < 30 L	Plastic – 10 L
REF2 solution	~ 0.5 L / calibration	/	Plastic – 1 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 using a volumetric flask of 1 litre. Mix and fill up to the grade mark with de-ionized water.

4.4 Buffer 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 1 litre. Dissolve completely and fill up to the grade mark with de-ionized water**.**

4.5 Colour 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 500 mL de-ionized water using a volumetric flask of 1 litre. Fill up to the grade mark with de-ionized water.

4.6 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. Dissolve accurately x g ethylenediaminetetraacetic acid disodium salt dihydrate ($C_{10}H_{14}N_2Na_2O_8.2H_2O$) in 500 mL de-ionized water and fill up to 1 litre.

Measuring range	Concentration EDTA solution	Amount to add to 1 litre
100 mg/L $CaCO_3$	0.005 M	1.861 g
250 mg/L $CaCO_3$	0.005 M	1.861 g
500 mg/L $CaCO_3$	0.01 M	3.722 g
1000 mg/L $CaCO_3$	**0.02 M**	**7.444 g**
Range > 1000 mg/L	0.02 M	7.444 g

4.7 Calibration solution

Products	Formula	MW (g/mol)	CAS No.	Range	1 litre solution
Calcium chloride dihydrate	$CaCl_2 * 2H_2O$	147.02	10035-04-8	≤ 1000 mg/L $CaCO_3$	14.702 g
				> 1000 mg/L $CaCO_3$	73.51 g

Preparation

Range ≤ 1000 mg/L $CaCO_3$:

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 1 litre. Add de-ionized water up to the mark grade.

$CaCO_3$ standard solution – REF2

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**

Range > 1000 mg/L $CaCO_3$:

50000 mg/L $CaCO_3$ stock solution

Dissolve accurately 73.51 g calcium chloride dihydrate ($CaCl_2 * 2H_2O$) in 500 mL de-ionized water, using a volumetric flask of 1000 mL. Add de-ionized water up to the mark grade.

$CaCO_3$ standard solution – REF2

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 1000 mL. Add de-ionized water up to the mark grade.

Measuring range	Concentration REF2	Amount of stock solution to add to 1 litre
a mg/L $CaCO_3$	a mg/L $CaCO_3$	$x = \frac{a}{50}$ mL

4.8 Cleaning solution (facultative)

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